Thermodynamic Properties of Aqueous Carbonate Species and Solid Carbonate Phases of Selected Elements

pertinent to

Drinking Water Standards

of the

U.S. Environmental Protection Agency

John A. Apps

Lawrence Berkeley National Laboratory

and

Richard T. Wilkin

U.S. Environmental Protection Agency

November 3, 2015

LBNL-190825

Abstract

This report contains a series of tables summarizing the thermodynamic properties of aqueous carbonate complexes and solid carbonate phases of the following elements: arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni) thallium (Tl), uranium (U) and zinc (Zn). Most of these elements are potentially hazardous as defined by extant primary drinking water standards of the United States Environmental Protection Agency (U.S. EPA). The remainder are not considered hazardous, but are either listed by U.S. EPA under secondary standards, or because they can adversely affect drinking water quality. Additional tables are included giving the thermodynamic properties for carbonates of the alkali metal and alkali earth elements, sodium (Na), potassium (K), magnesium (Mg), calcium (Ca), and strontium (Sr), because of their value in developing correlative models to estimate the thermodynamic properties of carbonate minerals for which no such data currently exist.

The purpose in creating the tables in this report is to provide future investigators with a convenient source for selecting and tracing the sources of thermodynamic data of the above listed elements for use in modeling their geochemical behavior in “underground sources of drinking water” (USDW). The incentive for doing so lies with a heightened concern over the potential consequences of the proposed capture and storage of carbon dioxide (CO_2) generated by fossil fuel fired power plants in deep subsurface reservoirs. If CO_2 were to leak from such reservoirs, it could migrate upward and contaminate USDWs with undesirable, but undetermined, consequences to water quality.

The U.S. EPA, Office of Research and Development, through an Interagency Agreement with the United States Department of Energy (U.S. DOE) at the Lawrence Berkeley National Laboratory (LBNL), funded the preparation of this report.

Table of Contents

Introduction

This report consists of a series of tables pertaining to the thermodynamic properties of aqueous carbonate complexes and solid carbonate phases of a selected group of elements. Most of these elements are considered potentially hazardous as defined by extant primary drinking water standards promulgated by the United States Environmental Protection Agency (U.S. EPA) Title 40, Code of Federal Regulations (40 CFR), Section 141, under Subpart B-Maximum Contaminant Levels (§141.11). Other elements, some of which are normally encountered in the environment in only trace concentrations, and which are not considered hazardous, some of which are listed by the U.S. EPA under secondary standards, are also included, because they are sometimes of environmental concern. Summary tables giving the thermodynamic properties for carbonates of the elements, sodium, potassium, magnesium, calcium, and strontium are also included, because of their value in developing models to estimate the thermodynamic properties of carbonate minerals for which no such data currently exist.

The reason for creating the tables in this report lies with a heightened concern over the consequences of the capture and deep subsurface disposal of anthropogenically generated carbon dioxide (CO_2) generated from stationary fossil fuel (especially coal) fired power plants and other stationary industrial sources. It is hoped that this anthropogenic CO_2 would be isolated indefinitely from the atmosphere through deep subsurface storage, or at least until such time when its accumulation in the atmosphere would be controlled, and no longer have the potential to modify the earth's climate. Both the integrity of deep subsurface reservoirs, and the enormous quantities of CO_2 that must be captured and stored to have a measurable effect (a single 1000 MWe coal-fired plant generates about 18,000 metric tons of CO_2 daily (Li et al., 2006)) raises serious concerns that leaking CO_2 could migrate upward into shallower aquifers containing so called "underground sources of drinking water" (USDW), defined in Title 40, Code of Federal Regulations (40 CFR), Section 144.3 as an aquifer or part of an aquifer, which "supplies any public water system, or contains a sufficient quantity of ground water to supply a public water system and currently supplies drinking water for human consumption or contains fewer than 10,000 milligrams/liter of Total Dissolved Solids (TDS)…" Waters approaching such concentrations of TDS are implausible sources of drinking water, despite the designation. However, abundant supplies of potable drinking water containing 1,000 ppm TDS or less, are major sources of drinking water in the United Sates and could be threatened by CO_2 leakage from storage reservoirs.

The consequences of CO_2 leakage into potable water aquifers are difficult to predict, because the resulting chemical reactions, the kinetics of such reactions, and the concentrations and fate of hazardous elements in the aquifer host rocks that might be mobilized as a result of CO_2 intrusion are poorly understood. Some of these issues have been articulated and discussed, and attempts made to better define their nature and scope, in an earlier report to the U.S. EPA (Birkholzer et al., 2008).

Enhanced CO_2 partial pressures in ground waters can impact in several ways the aqueous solubility of hazardous elements:

1. CO_2 reacts with the aqueous phase to produce a weak acid.
2. In the absence of acid-neutralizing minerals, the increased acidity lowers the chemical potentials of metal oxide components in solution, which enhances the solubilization of minerals containing those oxide components.

3. The distribution of aqueous hydroxyl-complexes of some metals is modified by increased acidity.
4. Dissolved aqueous carbonate species can complex with metal ions in solution, further lowering the chemical potentials of oxide, sulfide, and other components of dissolved metals.
5. Increased concentrations of dissolved carbonate and bicarbonate species would tend to displace anionic and oxy-anionic species of hazardous elements from anionic adsorption sites and exchange sites on anionic clays and oxides with high zero point of charge.
6. An increased CO_2 fugacity increases the stability of solid metal carbonate phases.

A partial understanding of the thermodynamic response of changing CO_2 partial pressures on the behavior of hazardous metals can be achieved through modeling of the geochemical properties of rock-water systems containing major and trace chemical components. During the last forty years, with the expanding use of digital computers, many software packages have been developed that facilitate the modeling of the geochemistry of such systems, especially under conditions simulating ambient temperatures at or near the earth's surface. Most use algorithms to calculate homogeneous equilibrium within the aqueous phase, assuming the presence of discrete chemical species, i.e., cations, anions and molecules, which may be simple or complex, and which possess discrete temperature and pressure dependent thermodynamic properties. The equilibrium distribution of the aqueous species is determined through solution of a non-linear series of equations either by a routine that calculates the minimum free energy of the system, based on a knowledge of the Gibbs free energies of the individual species and the excess free energies associated with their activity coefficients in solution (the Gibbs free energy minimization form), or aroutine that calculates mass action and mass balance optionally constrained by the requirement of electrical neutrality and choice of electrolyte model to describe species activity coefficients (the mass action equation form). Both methods are thermodynamically equivalent, and should lead to identical species distributions for a given problem (Van Zegeren and Storey, 1970). The former approach is generally more elegant and flexible, but the latter is more intuitive, and possesses the advantage of using thermodynamic dissociation constants of aqueous complexes derived directly from experimental measurement. The former approach is more commonly used in Russia and Eastern Europe, whereas the latter is used most extensively in Western Europe and North America.

The same software packages, used to define homogeneous equilibrium in the aqueous phase, are also used in the calculation of heterogeneous equilibrium between the aqueous phase and solid phases, or minerals. Again, the requirements for the two approaches described above, are respectively, the Gibbs free energy of the solid phase, or alternatively, the solubility product of the solid phase, defined in terms of so-called "basis" or "primary" species. More sophisticated software packages also allow calculation of the distribution of species on adsorption sites, ion exchange sites on clays and zeolites, and homogeneous solid solutions within minerals. Such packages, accounting for homogeneous equilibria in multi-component multi-phase heterogeneous systems are at present incompletely developed, because either the needed thermodynamic data are incomplete, or because not all relevant models have been incorporated. A complicating factor is the availability of competing models where their standard or reference states are inconsistent, or have not received universal acceptance.

The U.S. EPA recognizes that a review of extant thermodynamic data relating to aqueous carbonate complexation with hazardous elements, and the solubility products of carbonate minerals of hazardous elements is necessary for modeling the impact of CO_2 intrusion into potable water aquifers. An essential first step is a compilation of dissociation constants of carbonate complexes and solubility products of

hazardous carbonates reported in the published literature. The U.S. EPA also wished to examine the status of thermodynamic databases used in current software packages to establish how complete they might be in terms of the U.S. EPA's expected needs. The U.S. EPA therefore contracted with the Lawrence Berkeley National Laboratory (LBNL) under an inter-agency agreement to compile a series of databases of reported hazardous metal association constants of carbonate complexes and carbonate mineral solubility products of elements of interest. The tables were also to include, where available, the enthalpy of reaction, $\Delta H^0_{R,P,T_r}$, for both dissociation constants and solubility products and the source references for the data, the references to be appended to each set of tables for each element. The purpose of including the enthalpy of reaction data is to allow limited log-linear temperature extrapolation both above and below 25°C to permit thermodynamic calculations at temperatures between 0 and 100°C, as implemented in the MINTEQ series of codes (Allison et al., 1991; Herndon, 1998), which have received substantial support from the U.S. EPA during the past 30 years. These databases were to be supplemented with databases summarizing the corresponding dissociation constants and solubility products used in several popular distribution-of-species codes used in the United States and in Europe.

Scope of the Compilation

Elements Considered for Review

The original list of hazardous elements proposed by the U.S. EPA for inclusion in the review consists of the following: antimony (Sb), arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), thallium (Tl), selenium (Se) and uranium (U). Most of these elements are found in nature occurring in more than one oxidation state, of which some are more hazardous than others. Some, e.g., antimony, arsenic, chromium and selenium occur as hazardous oxy-anionic species, under mildly reducing sub-oxic to oxidizing conditions. These species do not complex significantly with carbonate in solution. Elevated concentrations of bicarbonate or carbonate in solution affect these species primarily through anionic replacement on adsorption or ion exchange sites, or through trace element co-precipitation in carbonate structures. Thermodynamic data relating to such adsorption, ion exchange and solid solution substitutions fall outside the scope of the evaluation and are not considered. The absence of useful data in the literature led to an agreement to drop antimony and selenium from the list of elements under consideration, but to retain arsenic.

The list of elements considered for study was expanded to include the remaining transition metals, manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni) and zinc (Zn). These elements are not considered hazardous by the U.S. EPA, although the concentrations of manganese and iron, especially, might lead to an undesirable taste and possible coloration if present at elevated concentration in drinking water. One reason for expanding the scope was to provide data on these elements that could be used subsequently in correlative studies of the thermodynamic properties of both solid carbonates and aqueous carbonate complexes of all elements of interest, thereby enhancing the ability to detect errors and inconsistencies in experimental data. Secondly, such evaluations could facilitate the interpretation of analytical data obtained from field experiments to measure the response of an aquifer to CO_2 intrusion, where extremely sensitive analytical methods such as ICP-MS now permit the quantitative determination of concentrations of most, if not all trace elements present in ground waters. The interpretation of such data depends, of course, on the availability of models permitting estimates to be made of the distribution of trace elements on adsorption and/or ion exchange sites.

A complete list of elements surveyed in this study is given in Table 1, together with applicable U.S. EPA drinking water standards.

Table 1. Hazardous Metals: U.S. EPA Drinking Water Standards (after U.S. EPA (2012))

Element	Maximum Contaminant Level Goal (MCLG) mg/L.	Maximum Contaminant Level (MCL) mg/L.	National Secondary Drinking Water Regulations (Secondary Standards) mg/L	Notes
Arsenic	zero	0.010	-	as of 01/23/06
Barium	2	2	-	
Cadmium	0.005	0.005	-	
Chromium (total)	0.1	0.1	-	
Cobalt	-	-	-	
Copper	1.3	-	1.0	
Iron	-	-	0.3	
Lead	zero	-		
Manganese		-	0.05	
Mercury (inorganic)	0.002	0.002	-	
Nickel	-	-	-	
Thallium	0.0005	0.002	-	
Uranium	zero	0.030	-	Radionuclide, as of 12/08/03
Zinc	-	-	5.0	

Definitions and Conventions

Definitions for symbols used in the report are as follows:

T Temperature, expressed in *K* (not to be confused with *K*, the equilibrium constant below), unless otherwise noted, when it is expressed in °C

P Pressure, expressed in atmospheres (*atm*), (1 *atm* = 1.01325 *bar*), *bar*, or Pascals (*Pa*), (10^5 *Pa* = 1 *bar*)

$C^o_{P_r,i}$ The standard heat capacity of a pure substance, *j*, at constant pressure, expressed in terms of *J*/gfw.*K*

$\Delta G^o_{f,T_r,P_r}$ Standard Gibbs free energy of formation (*f*) of a substance at the reference temperature (T_r) and pressure (P_r), expressed in terms of kJ/gfw (gfw = gram formula weight).

$\Delta H^o_{f,T_r,P_r}$ Standard enthalpy of formation (*f*) a substance at the reference temperature (T_r) and pressure (P_r), expressed in terms of kJ/gfw (gfw = gram formula weight).

$\Delta H^o_{R,T_r,P_r}$ Standard enthalpy of association, or dissolution reaction (R), respectively for the association of an aquous complex, or the dissolution of a pure substance a pure substance at the reference temperature (T_r) and pressure (P_r), expressed respectively in terms of kg/mol, or kJ/gfw (gfw = gram formula weight).

I The ionic strength of an aqueous solution, expressed as *mol/kg* H_2O.

K The equilibrium constant, expressed as the product of the activities of the products raised to the power of the corresponding stoichiometric coefficients, divided by the product of the activities of the reactants raised to the power of the corresponding stoichiometric coefficients. K is usually expressed as a logarithm to base 10., i.e., log K. In this report, K refers either to the association constant of an aqueous complex, or to the dissolution (solubility) constant, e.g., K_{SP} of a solid in the aqueous phase.

κ Isothermal compressibility of a phase expressed as /*atm*, /*bar* or /*Pa* x 10^5

$S^0_{P_r,T_r}$ Entropy a pure substance at the reference temperature (T_r) and pressure (P_r), expressed in terms of J/gfw.K

V^0 Standard specific volume of a substance, expressed in terms of cm^3/gfw (gfw = gram formula weight).

a, b, c Unit cell parameters of a crystalline solid phase, expressed in terms of Ångstroms ($1Å = 10^{-10}\ m$).

α, β, γ Inter-axial angles of a crystalline solid phase, expressed in degrees (°).

Z The number of formula units/unit cell of a crystalline solid.

The following conventions generally apply:

Dissociation constants of carbonate complexes are for the most part at the standard state of a hypothetical unit molal solution at infinite dilution, i.e., at zero ionic strength (I = 0), all at 25°C and one atmosphere pressure. However, not all data sources have followed this convention. For example, corrections for ionic strength may not have been made, reference temperatures may be non-standard, and more recent literature has adopted a standard pressure of one *bar*, or 10^5 *Pascals* (*Pa*). Non-standard state conditions for recorded data are noted in the tables.

Carbonate mineral solubility products of elements of interest are likewise defined in relation to the standard state of a hypothetical unit molal solution at infinite dilution, i.e., at zero ionic strength, all at 25°C and one atmosphere pressure. As with corresponding dissociation constants for complexes, corrections to standard state conditions may not have been implemented. Non-standard state conditions for recorded data are similarly noted in the tables.

In general, the correction of thermodynamic parameters for changing the standard state pressure from one atmosphere to one bar has not been made in most thermodynamic data compilations, because the correction is usually small in relation to the uncertainty of the measurement. Wolery and Jové-Colón (2015) note, however, that such corrections should be applied for precise work.

Where available, the standard enthalpy of association of a complex, or the standard enthalpy of dissolution of a solid phase carbonate, $\Delta H^0_{R,P_r,T_r}$, is included, where available, and is defined in kiloJoules (k*J*) with respect to one gram formula weight, gfw, of the given solid phase, i.e., k*J*/gfw. Usage of the term "gram formula weight" has declined in recent years in favor of the term "mole," which when applied to solid phases, can mean almost anything depending on the whim of the user. In this report, the former term is reinstated in deference to its superior rigor.

Contents of the Main Tables

Each element is represented by a set of tables, as follows:

1. Association Constants for Aqueous Carbonate Complexes
2. Solubility Constants of Carbonate Minerals and Synthetic Solid Phases

3a. Association Constants of Aqueous Carbonate Complexes extracted from Databases of Distribution-of-Species Codes

3b. Solubility Constants of Solid Carbonates extracted from Databases of Distribution-of-Species Codes

3c. Distribution-of-Species Codes: Database References

4a. Thermodynamic Properties of Carbonate Minerals and Synthetic Solid Phases: Gibbs Free Energies of Formation

4b. Thermodynamic Properties of Carbonate Minerals and Synthetic Solid Phases: Enthalpies of Formation

4c. Thermodynamic Properties of Carbonate Minerals and Synthetic Solid Phases: Entropies

5. Crystallographic Properties of Carbonate Minerals and Synthetic Solid Phases
6. Carbonate Minerals containing greater than 10 wt.% of the element

Not all elements are represented by the complete set of tables, due either to the chemical properties peculiar to that element, or the absence of data due to a lack of scientific interest. In the case of uranium, an additional table is included to account for the thermodynamic properties of uranium carbonates containing multiple components.

The primary source citations are given in chronological order in the last column of Tables 1, 2 and 4a,b and c. The respective penultimate columns list secondary sources, which are also listed chronologically with respect to each primary source. On occasion, the "primary" source is itself a secondary source to a yet earlier source, which can be searched for in preceding call outs. In this way, it is possible to trace the original source from subsequent literature compilations. It should be noted that data cited by secondary sources in reference to earlier work do not always correspond exactly to those reported in the source reference. Sometimes, the authors of the secondary source have re-worked the earlier data using state-of-the-art methods at that time. Explicit attention to such re-workings is not given, although both source and re-worked values are sometimes given in juxtaposition in the tables.

Tables 1 and 2 consist of compilations of the respective association constants of aqueous carbonate species and solubility constants of carbonate minerals and synthetic phases. The intention in compiling these tables is to present the data in a uniform format to allow for direct comparison between individual investigations. Some nominal changes were therefore made in reporting the extracted values to ensure

conformity. On occasion, other procedures were also adopted to facilitate comparison. The general rules adopted in the compilations in Tables 1 and 2 are as follows:

1. All association or dissolution constants data are given in terms of their logarithms.
2. All data are presented either as association or as dissolution reactions.
3. Both association and dissolution reactions are primarily written in terms of "basis species" involving CO_3^{2-}, H^+ and the ionic species of the hazardous element, i.e., M^+, M^{2+}, M^{3+}…, or occasionally, its oxy-anion. If the association or dissolution reactions were defined in terms of HCO_3^- and/or OH^- at 25°C, these were sometimes re-written in terms of CO_3^{2-} and/or H^+, and the respective association or dissolution constants modified using reaction constants in supplementary Table S-1. Some reactions reported in the literature were not given in terms of normally accepted basis species. They are reported as given in the source reference, as arbitrary transformations could be inconsistent with the original investigator's assumptions and derivation.
4. Where available, data corrected for zero ionic strength (I = 0) were entered, i.e., "true" equilibrium constants at infinite dilution, independent of composition. Otherwise data are usually recorded at the ionic strength employed, and should be corrected for infinite dilution (using an appropriate activity coefficient model) prior to use with typical geochemical modeling software.
5. In some earlier work, reference temperatures differed from the now standard 25°C. In these cases, the actual temperature is noted. Sometimes, measurements were undertaken only at "room temperature."
6. Some experiments were conducted over a range of temperatures and dissociation constants or solubility constants were recorded at discrete temperatures differing from the standard 25°C. $\Delta H^0_{R,P,T_r}$ derived in the source reference is included where available. Such data sets are sometimes amenable to more rigorous analysis, and a record of the data is provided in the eventuality that a future investigator should choose to conduct such an analysis.
7. Occasionally, citations are given of references containing data that could be of interest to future investigators, without reporting any data, as the data are in a form not suitable for presentation in the tables. In particular, papers reporting phase equilibria, would be amenable to the retrieval of pertinent thermodynamic data involving the participating phases. Such data retrieval is beyond the scope of the current compilation.
8. Uncertainties, where reported, are those given by the investigator(s), and may represent one or two standard deviations, or the 95% confidence level, which is normally about 2 standard deviations. Readers requiring clarification should consult the source reference. It should be noted that many secondary compilations omit uncertainties recorded in the source reference, or that the source reference does not report an uncertainty, even though the reported raw data would have permitted its determination.
9. In the measurement of solubility constants, the earlier literature commonly does not provide information characterizing the crystal structure, or degree of crystallinity, of the phase under investigation. Therefore different polymorphs might be confounded. The reported solubility products could be finely crystalline, amorphous, possess a disordered structure, have a non-equilibrium crystal habit, be a polymorph different from that assumed, or contain undesired or unrecorded contaminants, especially where control of the oxidation state is critical. Occasional comments are added to alert the reader to such issues.

In Table 2 and Tables 4a,b and c, minerals are listed in alphabetical order. The listing of minerals is followed by a listing of synthetic phases, broadly ordered in terms of increasing complexity.

Tables 3a and b give the logarithms (base 10) of the association constants and solubility constants utilized in the thermodynamic databases of several software programs commonly used to calculate aqueous species distributions and solubility quotients. The software and associated databases are listed Table 3c.

Tables 4a,b and c represent compilations retrieved from the literature, respectively of the thermodynamic parameters $\Delta G^0_{f,P_r,T_r}$, $\Delta H^0_{f,P_r,T_r}$ and $S^0_{P_r,T_r}$ for both natural and synthetic solid carbonate phases. It is common practice for $\Delta G^0_{f,P_r,T_r}$ and $\Delta H^0_{f,P_r,T_r}$ to be reported in terms of formation from the elements. Some investigators reported these parameters in terms of the phase's formation from the oxides. The latter definition is duly noted when such data are incorporated in the tables. All data are recorded in S.I. units, i.e., in terms of Joules. Where the source reference uses calories (*cal*) as the basis unit, the reported values were converted into Joules (*J*), where 1 *cal* = 4.184 *J*.

$\Delta G^0_{f,P_r,T_r}$, $\Delta H^0_{f,P_r,T_r}$ and $S^0_{P_r,T_r}$ for each solid phase are compiled in separate tables to avoid an otherwise unwieldy organization. The published thermodynamic properties of solid phases are commonly derived using several experimental procedures, the most common being calorimetry, phase equilibria (as a function of temperature and pressure) and aqueous solubility measurements (usually measured over a limited range of temperature). In principle, these independent methods should yield similar, if not identical results. However, numerous experimental artifacts limit the accuracy of all three procedures, making close agreement likely only for a limited number of well-characterized solid phases. Consistency of results between all methods would signal greater confidence in those values.

Data pertaining to the heat capacities of carbonate solid phases have not been tabulated. Heat capacity data reported in the literature are given in a variety of forms, usually as functions of absolute temperature (*K*). A standard form for presenting such data has not been implemented, which makes it difficult topresent in a consistent manner. The authors therefore decided to omit their inclusion in this report.

Table 5 is a listing of the crystallographic parameters of the solid carbonates, including the crystal class, the space group, cell constants (a, b, c, (Å); α, β, γ, (°) and Z, the number of formula units in a unit cell. The compiled information was freely drawn from mineralogical tables published in the Mineralogy Database (webmineral.com), and from Gaines et al. (1997), both of which were also used to assist in identifying the primary scientific sources for the reported data. The primary sources are independently referenced, and were consulted to verify the crystallographic parameters given in the two cited secondary sources. The primary purpose of this compilation is the calculation of the molar volume, V^0, (cm^3/gfw), which is necessary for the calculation of mineral solubilities and phase relations at elevated pressures, as discussed further below. The molar volume for each solid crystalline carbonate was calculated using the respective published cell constants, crystal class, Z, and the chemical formula. The gram formula weight, (gfw), cell volume and density were also calculated. The latter was compared with the published calculated density and measure specific gravity, where available, in oder to validate the computation of

the molar volume. Minor inconsistencies were commonly found, due mainly to idealizations of the stoichiometry. However, major discrepancies required further review and correction of errors.[1]

Table 6 summarizes information on naturally occurring mineral carbonates containing ≥ 10 wt.% of the metal of interest as an essential component, i.e., a component that is intrinsic to the mineral's identity, in contrast to accessory or trace components, which are not essential to the mineral's identity. This information was for the most part drawn from mineralogical tables published in the Mineralogy Database (webmineral.com).

Contents of the Supplementary Tables

The supplementary tables are:

S-1. Translation equations and reaction constants used for conversion of equations using HCO_3^- as a basis species to CO_3^{2-}. This table gives information regarding reactions and corresponding reaction constants needed to standardize experimental measurements of dissociation constants and solubility constants given in Tables 1 and 2, as described above.

S-2. Solubility constants and thermodynamic parameters $\Delta G^0_{f,P_r,T_r}$, $\Delta H^0_{f,P_r,T_r}$ and $S^0_{P_r,T_r}$ for both natural and synthetic solid carbonate phases in the system Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O. Most carbonate minerals containing sodium, potassium, magnesium, calcium and strontium as essential components are included, but the table is not exhaustive. With the possible exception of strontium, none of these elements are considered to be hazardous. However, in broad correlations of the thermodynamic properties of all carbonate phases, including those containing essential components of hazardous elements, their properties are very important, particularly when it is recognized that some of the former are the best characterized thermodynamically of all solid carbonate phases, and thereby provide a reliable and accurate base for correlating thermodynamic data.

Caveats regarding the Tabulated Data

Although every effort was made to identify all relevant sources of thermodynamic data, some have assuredly been missed[2]. Repeated literature searches using the Chemical Abstracts' search engine,

[1] An example of the kind of problem that can arise is demonstrated by transcriptions of cell constant data of carrboydite ($Ni_{6.50}Cu_{0.40}Al_{4.80}(SO_4)_{2.30}(CO_3)_{0.48}(OH)_{21.69}$•$3.67(H_2O)$. The type description is given by Nickel and Clarke (1975), who give the unit cell constants, identify the mineral as hexagonal, and give the calculated density as 2.692 and specific gravity as 2.51, but do not report Z. A check proved that the calculated density was consistent with Z = 1. Gaines et al. (1997) transcribed the findings in Nickel and Clarke (*loc cit*.), but generalized the chemical composition, and doubled the formula unit from one originally containing 36 oxygens to one containing 72 oxygens, thus: $(Ni,Cu)_{14}Al_9(SO_4,CO_3)_6(OH)_{43}$•$7(H_2O)$, while reporting the original cell constants, density and specific gravity. In addition, they incorrectly reported Z = 4, instead of ½. The Mineralogical Database, also gave the chemical formula based on 72 oxygens, doubled the size of the cell constants, and correctly reported Z = 4 to account for the changed cell constants and chemical formula. They also reported the original calculated density and measured specific gravity. However, their chemical formula: $Ni_{10}Cu_4Al_9(SO_4)_4(CO_3)_2(OH)_{43}$•$7(H_2O)$ is inconsistent with that reported by Nickel and Clarke and would have yielded a different calculated density of 2.714. In the respective Tables 5 for copper and nickel, the reported Z values are corrected, and the stoichiometry of the mineral composition given by Gaines et al. was refined to more accurately reflect the composition reported for the type material. As a final note, it should be pointed out that the senior author, E. H. Nickel, subsequently revised the chemical formula for carrboydite to reflect its association with the pyroaurite group of minerals: $[(Ni,AI,Cu)_8(OH)_{16}]^{3.3+}[1.65(SO_4,CO_3)^{2-}$ •$8.5(H_2O,NiSO_4)]^{3.3-}$ (Nickel and Wildman, 1981).

[2] If the reader finds additional source material, or identifies transcription errors, the authors would be grateful if such information could be brought to their attention at jaapps@lbl.gov and corrections made to the on-line manuscript. Due acknowledgement will be given.

"Scifinder," supplemented by searches using Google "Scholar," and direct retrieval of references cited in reviews and reports of original work, in which earlier work was cited, do not necessarily result in the retrieval of all data sources. It is quite likely that significant studies still wait to be unearthed. The Russian literature, in particular, is incompletely searched. Partly, this is due to difficulties in retrieving source material from libraries in the west.

Evolving trends in the publication of experimental studies also affect the usefulness of retrieved data. Scientific investigations published prior to the 2nd World War were commonly conducted with meticulous attention to precise measurements, but interpretation of the data was undertaken using models considered obsolete or incorrect by modern standards. Such studies can be re-evaluated using more recent techniques, which can lead to results that are comparable with more recent studies. As noted above, earlier studies commonly do not provide sufficient information to permit an adequate characterization of the materials under study. Such work must be scrutinized carefully for clues to help in characterizing solid phases. In contrast, more recent publications take more effort to characterize the material used. But, especially in second tier or application-oriented journals, critical experimental data may be omitted, thereby making it impossible to check the results and conclusions presented or re-analyze the data using improved methods. Although it would be prudent to ignore the findings of such papers, the data presented are sometimes available from no other source.

By reviewing different compilations, it is sometimes found that apparently independent determinations can be traced back to a common original source. An illustration of the problems that arise with repeated reworking of source material over time is given by Stipp et al. (1993) regarding the mineral otavite ($CdCO_3$). The structure of the thermodynamic tables is designed to help the reader track down original source material. However, tracing of original material is not entirely complete, and the diligent investigator may need in some instances to follow the given leads to their ultimate sources.

Finally, the reader should recognize that with a data compilation of this size, transcription errors are inevitable. The duplication of the same data by different compilers serves as a check on the accuracy of the transcription, and reference to the original source material assists with its verification. Furthermore, as noted above, not all compilations necessarily report the original data. Occasionally, these are noted. Finally, source references commonly contain additional information of value that, for reasons of space or formatting, could not be conveniently incorporated in the tables of this report. Therefore, it is incumbent on the user to use this report as a guide to original sources of information, and not to extract data without first checking the original source.

The issues of data selection for incorporation in databases of current geochemical codes, comprehensive re-evaluations of source data, and the estimation of carbonate mineral solubility constants are discussed further in the following sections.

Application of Tabulated Data to Geochemical Modeling

A comparison of the data presently incorporated in the thermodynamic databases of current geochemical modeling codes, tabulated in Tables 3a and b under each element, shows the limited extent to which available information on aqueous carbonate complexing and carbonate mineral solubility constants has been incorporated in these databases. Furthermore, much of the incorporated data are obsolescent, or have not been rigorously evaluated for some time. This deficiency can be rectified partially by consulting more

recent literature reviews, whose data are summarized in Tables 1 and 2. Systematic reviews of relevant literature have been conducted at irregular intervals with the goal of choosing recommended values for thermodynamic parameters for use in modeling studies. Some of these reviews are authoritative, particularly those undertaken during the last two decades by IUPAC, e.g., Hála, J. and Navratil, J.D. (2001) for actinide carbon compounds, Powell et al. (2005) for mercury, Powell et al. (2007) for copper, Powell et al. (2009) for lead, and Gamsjäger et al. (2011) for cadmium, or by OECD, e.g., Grenthe et al. (1992), Lemire (2001) and Guillaumont et al. (2003) for radioelement compounds. They give detailed evaluations justifying the selection of recommended values and provide parameter uncertainties. Furthermore, papers reporting recent comprehensive experimental work to better define the thermodynamic properties of the compounds of various metals, usually the products of thesis dissertations, commonly include comprehensive reviews of the earlier literature, although they do not necessarily re-evaluate earlier raw data. For those investigators wishing to modify, augment, or update the database of their chosen geochemical modeling software, without devoting time to a comprehensive analysis of past experimental work, such reviews might be the preferred route. It goes without saying, however, that any changes must be internally consistent with the rest of the data in the database, especially those data pertaining to hydroxyl complexation with the corresponding element. For this reason, the authors of this report are not in a position to select and recommend "best values" from the listed data without first making their own independent evaluation.

The preferred approach would be for the future investigator to conduct his own thorough review and analysis of the extant literature, using raw data from original sources, a labor-intensive and time-consuming task. He might well coordinate such an evaluation with recent similar recent studies to ensure consistency of reference states and basis thermodynamic parameters.

Another deficiency is evident by inspection of Table 6 under each element. Usually, research has focused almost exclusively on the most commonly occurring carbonate mineral with the simplest stoichiometry. Inspection of Tables 2 and 4a,b and c also shows that the accumulated information on that particular mineral is in some cases almost overwhelming. Other carbonate minerals for a given element, have been almost entirely neglected, which is hardly surprising, given that most are obscure. However, this does not obviate the need to consider them in geochemical modeling studies, as without accounting for their presence, there is no way of establishing whether they might or might not control hazardous element concentrations under a given set of geochemical conditions. It is therefore preferable to incorporate minerals whose thermodynamic properties have been estimated, rather than omit them and run a simulation that has the potential of having little or no basis in reality. Unfortunately, the incentive to characterize experimentally the thermodynamic properties of lesser-known carbonates is minimal, and future activity is this area is unlikely. Their properties must therefore be estimated using procedures for correlating thermodynamic data using as a reference the properties of those well-characterized carbonates given in the accompanying tables. This issue is discussed further below.

Thermodynamic Relations

Applications of geochemical modeling to problems involving the ingress of high pressure CO_2 into potable water aquifers generally involve pressures and temperatures close to ambient earth surface conditions. As such, the computation of the logarithms of carbonate mineral solubility constants, log K_{SP},

can be approximated using $\Delta G^0_{f,P_r,T_r}$, $\Delta H^0_{f,P_r,T_r}$ and $S^0_{P_r,T_r}$ summarized in Tables 4a,b and c under each element, together with the referenced thermodynamic properties of the basis aqueous species. Such is the approach adopted with the MINTEQ software (Allison et al., 1991; Herndon, 1998), where it is assumed that $\Delta H^0_{R,P_r,T_r} = \Delta H^0_{R,P,T}$. If, however, simulations of deep aquifers at pressures above 10 MPa and temperatures ≥ 100°C are to be conducted, then for precise work, corrections should be made for $\Delta C^0_{P,R}$ and $\Delta V^0_{R,P,T}$ in calculating $\log K_{SP}$. Such calculations can be facilitated using SUPCRT92 (Johnson et al., 1992). The governing thermodynamic relations are as follows:

$$G^\circ_{P,T} - G^\circ_{P_r,T_r} = -S^\circ_{P_r,T_r}(T - T_r) + \sum_{i=1}^{1+\phi_T} \int_{T_i}^{T_i+1} C^\circ_{P_r,i}\, dT - T\sum_{i=1}^{1+\phi_T} \int_{T_i}^{T_i+1} C^\circ_{P_r,i}\, d\ln T + \int_{P_r}^{P} V^\circ_{P_r,T} dP - \sum_{i=1}^{\phi P} \int_{P_{t_i},T}^{P} \Delta V^\circ_{t_i} dP - \sum_{i=1}^{\phi T} \frac{\Delta H^\circ_{t_i}}{T_{ti}}(T - T_{ti}), \quad (1)$$

Corresponding equations describing the changes in standard molar enthalpy and entropy of a solid phase are:

$$H^\circ_{P,T} - H^\circ_{P_r,T_r} = \sum_{i=1}^{1+\phi_T} \int_{T_i}^{T_{i+1}} C^\circ_{P_r,i} dT + \int_{P_r}^{P} V^\circ_{P_r,T} dP - \sum_{i=1}^{\phi P} \int_{P_{t_i},T}^{P} \Delta V^\circ_{t_i} dP + \sum_{i=1}^{\phi T} \Delta H^\circ_{t_i} \quad , \quad (2)$$

and

$$S^\circ_{P,T} - S^\circ_{P_r,T_r} = \sum_{i=1}^{1+\phi_T} \int_{T_i}^{T_i+1} C^\circ_{P_r,i} d\ln T + \sum_{i=1}^{\phi_T} \frac{\Delta H^\circ_{t_i}}{T_{t_i}}, \quad (3)$$

where $S^o_{P_r,T_r}$, $C^o_{P_r,i}$, and $V^o_{t_i}$ are the standard molar entropy, heat capacity and volume of the solid phase, and $\Delta H^o_{t_i}$ is the standard molar enthalpy of the phase transition, all terms subscripted with *i* referring to any phase transition in the solid. ϕ_T and ϕ_P stand for the number of phase transitions over the respective speciied ranges of temperature and pressure.

$C^o_{P_r,i}$ is a function of temperature, and is represented in SUPCRT92 by the Maier-Kelley equation (Maier and Kelley, 1932) describing the heat capacity as a function of temperature:

$$C^0_P = a_i + b_i T + c_i T^{-2} \quad (4)$$

where a_i, b_i and c_i are empirical coefficients. Other heat capacity functions have come into general use more recently, including that by Berman and Brown (1985):

$$C_P = k_0 + k_1 T^{-0.5} + k_2 T^{-2} + k_3 T^{-3} \quad (5)$$

This function is more accurate in extrapolations to higher temperatures.

For geochemical modeling under crustal conditions, $V^o_{t_i}$ is assumed to be independent of pressure and temperature, i.e.

$$V^o_{i,T_r,P_r} = V^o_{i,T,P} \quad (6)$$

This assumption introduces a maximum error of about 3% in the thermodynamic properties of solid phases, if the modeled pressure and temperature are less than 5 kbar and 600°C. For studies involving ground water chemistry changes in shallow aquifers, the volumetric pressure correction to $G^{\circ}_{P_r,T_r}$ and $H^{\circ}_{P_r,T_r}$ can be ignored for all but extremely precise work. In the latter case, an approximate correction to $\log K$ values for pressure can be computed as:

$$\log K_{P,T} = \log K_{P_r,T} + 2.303\left(-\Delta V\left(P - P_r\right) = 0.5\Delta\kappa P^2\right)/\,RT \qquad (7)$$

where $\Delta\kappa$ and ΔV are the average changes in the isothermal compressibility (for solids only) and volume changes for the reaction over the pressure range considered, e.g., Millero (1982) and Tanger and Helgeson (1988).

A common occurrence in compilations of thermodynamic data of solid phases is the omission of one or more of the defining parameters, $\Delta G^0_{f,P_r,T_r}$, $\Delta H^0_{f,P_r,T_r}$ or $S^0_{P_r,T_r}$. Because

$$\Delta G^0_{f,P_r,T_r} = \Delta H^o_{f,P_r,T_r} - T\Delta S_{f,P_r,T_r} \qquad (8)$$

only two of the three parameters need be specified. If only $\Delta G^0_{f,P_r,T_r}$ or $\Delta H^0_{f,P_r,T_r}$ are available, and model studies are conducted where temperatures fall within the range from 0-100°C, empirical methods of estimating $S^0_{P_r,T_r}$ (Helgeson et al., 1978, Holland, 1989) provide useful values without introducing substantial errors. Similarly, empirical heat capacity summation methods can be used to estimate the Maier-Kelley equation for a given solid phase to estimate the temperature dependence of ΔC^0_P (Helgeson et al., 1978).

SUPCRT92 also incorporates the so-called HKF "equation of state" (Shock and Helgeson, 1988), which has proven to be a useful tool for calculating aqueous phase equilibria at the hypothetical 1 *M* reference state at infinite dilution, and aqueous species thermodynamic properties at elevated temperatures.

Estimation of the Thermodynamic Properties of Carbonate Minerals

As noted above, Table 7 under each element lists naturally-occurring carbonate minerals. The purpose in identifying these minerals is primarily to provide guidance for the selection of minerals for inclusion in thermodynamic databases of simulators used in geochemical modeling. Because the thermodynamic properties of most of these minerals have not been determined experimentally, they must be estimated. The correlation techniques described below provide a means for making such estimates. The uncertainties associated with such estimates provide a measure of the degree of confidence that can be assigned to the modeling results.

During the past forty years, numerous empirical methods have been proposed to facilitate such inter-comparisons, and also to assist in estimating the thermodynamic properties of phases where some or all of the needed thermodynamic parameters are missing. In particular, where $\Delta G^0_{f,P_r,T_r}$ or $\Delta H^0_{f,P_r,T_r}$ values must be determined, several methods have been proposed, e.g., the method of polyhedral components, e.g., Hazen

(1985, 1988), Chermak and Rimstidt (1990) and La Iglesia and Félix (1994). The accuracy of such methods is commonly of the order of 1 - 3 %, which is of marginal value for precise geochemical modeling, and has no value in estimating the relative stabilities of structural polymorphs. Nevertheless, such inter-comparison studies do help identify discrepancies, which signal either model inconsistencies or errors in experimental data.

On a more comprehensive level, an inter-comparison of the thermodynamic properties between isostructural phases of a series of metals might be considered. Such an approach requires comparison of those properties with some fundamental property of the metal cation, M_i, such as its electronegativity (EN). In principle, some thermodynamic properties, such as the Gibbs free energies, or the solubility constants of an isomorphic series of phases may be correlated with EN of the substituting M_i. EN cannot be measured directly, but must be calculated from other atomic or molecular properties. Although commonly assumed to be an invariant property of the atom of an element, Li and Xue (2006) point out that the ability of an atom to attract electrons from atoms bonded to it, changes with the chemical environment, and thus the EN. These workers, expanding on earlier work by Zhang (1982), have developed an EN scale that takes into account the valence, coordination number and spin state of the cation, and can be employed in evaluating isomorphic series of phases with identical stoichiometries. Although his approach has not been attempted in this study, correlations between $\Delta G^0_{f,P_r,T_r}$ and the solubility constant of bi-valent metal hydroxides with EN using the procedure adopted by Li and Xue were examined by Apps (2013) and agreement was found to be very good. A similar approach has been used by Trolard and Bourrié (2012) in their analysis of the thermodynamic properties of layered double hydoxides, based on work by Jolivet (1994) who used the Allred and Rochow electronegativity scale (Allred and Rochow, 1958).

Issues and Limitations Concerning the Modeling of Potable Ground Waters under the Influence of Elevated CO_2 Partial Pressures

Our incomplete understanding of operative processes in shallow groundwaters complicates the modeling of chemical changes induced by the intrusion of CO_2, especially as it affects the behavior of trace elements. This deficiency can be subdivided into several categories: (1) uncertainties relating to the redox state of the groundwater and the extent to which redox reactions may not have achieved homogeneous equilibrium, (2) seasonal chemical changes introduced by dynamic recharge and drainage, especially in unconfined aquifers, (3) the extent to which heterogeneous thermodynamic equilibrium has been achieved in reactive phases that could be impacted by changing CO_2 activity, (4) the mass distribution of trace elements in reactive phases, (5) changes in the stability of secondary carbonate phases due to increased partial pressure of CO_2, (6) variations in mineral compositions, especially solid solutions, and (7) mineralogical changes of the receiving aquifer.

Birkholzer et al. (2008) and Apps et al. (2010) recognized the importance of the ambient oxidation state of the groundwater in defining the response of the aquifer to the mobilization of hazardous metals upon CO_2 intrusion. Birkholzer et al. concluded that the majority of sampled and analyzed potable ground waters from aquifers in the United States that they evaluated were reducing, and that the concentrations of many of the hazardous metals are controlled in part by saturation with respect to highly insoluble sulfides, selenides or antimonides. As pointed out in Apps et al. (2010), however, the evidence that most potable ground waters are reducing may be caused by sampling bias. Deep aquifers, isolated from the atmosphere

for a substantial length of time, and whose recharge areas are characterized by organic-rich soils, are most likely to be reducing, whereas aquifers underlying arid regions of the Southwest, or unconfined aquifers in moister temperate regions that are subject to widely fluctuating recharge rates, are more likely to be oxidizing. The sampling density is strongly biased towards those regions of greater precipitation, where population densities are also higher, and therefore sampling is biased towards those areas where surficial organic matter is likely to deplete oxygen in the underlying aquifer.

Increasing CO_2 partial pressures may have only a minor impact on the solubilization and liberation of hazardous elements from insoluble sulfides, selenides or antimonides. However, the extent to which the aquifer host rock mineral assemblage has achieved complete thermodynamic equilibrium, especially with respect to hazardous trace elements, has not been examined in any detail, and is generally unknown. For example, we do not know whether a hazardous metal sulfide has equilibrated with adsorption sites on mineral surfaces, ion exchange positions in clays, or solid solutions in more readily soluble carbonates. Recent experimental studies examining the potential impact of elevated CO_2 partial pressures in solubilizing hazardous elements, suggest that the dissolution of carbonates containing trace concentrations of these elements in solid solution may be the primary source, e.g., Wunsh et al. (2014). Other recent studies also suggest that ion exchange may dominate short-term metal release upon carbonation of ground waters, e.g., Zheng et al. (2012; 2015).

Seasonal variations in the recharge of unconfined aquifers can lead to corresponding seasonal variations in redox state, as observed during the monitoring of an unconfined aquifer in Idaho (Kharaka et al., 2010). Such conditions are favorable to the formation of metastable layered double hydroxides (LDHs). This suite of minerals belongs to a class of solid phases referred to as anionic clays. Structurally, they consist of stacked tri-octahedral sheets containing M(II) cations, similar to that found in brucite, but where limited substitution of the M(II) cations with M(III) cations, usually Al(III) or Fe(III), but occasionally Cr(III) or Mn(III) has occurred. As a result, the brucite layers are no longer electrically neutral, but carry a net positive charge. This charge is compensated for by the presence of anions in interstitial sites between the octahedral sheets. In most shallow subsurface environments where the ground waters possess relatively low TDS concentrations, the charge balancing anion is predominantly carbonate, CO_3^{2-}. About ten percent of all identified carbonate minerals belong to the LDH suite. Yet almost nothing is known regarding their thermodynamic properties.

A particular soil type referred to as a gleysol is noteworthy, as it is believed to host a Fe(II) – Fe(III) hydroxyl-carbonate LDH, known as fougerite, $[Fe^{II}_{1-x}\ Fe^{III}_{x}(OH)_2]^{x+}[x/nA^{n-}]\cdot mH_2O$, where the interlayer anion, A is CO_3^{2-}, but might be substituted by OH^- or Cl^- under some circumstances (Trolard et al., 2007; Trolard and Bourrié, 2012). This mineral is not well characterized, however, and its validity has been challenged (Christiansen et al., 2011). Fougerite is believed to form under reducing water-saturated conditions in soils during the winter months, imparting a blue-gray color, but subsequently decomposes during the following summer to amorphous rusty yellow-brown ferrihydrite as a result of de-saturation under oxic atmospheric conditions. Over time, aqueous silica species, $H_2SiO_4^{2-}$, can substitute for CO_3^{2-} (Depeges et al., 1996; Peltier et al., 2006) and polymerize, thereby leading to its transformation into a chlorite.

The extent to which hazardous elements might substitute for essential components of the LDH structure is unknown. Most, if not all, of the divalent transition elements are expected to substitute for Mg(II) or

Fe(II) in the brucite layer, whereas Cr(III), or Mn(III) could substitute for Al(III) or Fe(III), depending on oxidation state. Oxy-anions of hazardous elements, such as AsO_3^{3-}, AsO_5^{3-}, SeO_3^{2-}, SeO_4^{2-} and CrO_4^{2-} could also substitute for CO_3^{2-} in the anionic inter-layer site. It should be noted, however, that fougerite, in particular, is a reducing agent, capable of reducing most of the listed hazardous anionic species to lower, less soluble oxidation states, while concurrently oxidizing Fe(II) to Fe(III). Other, generally non-hazardous oxy-anionic species, such as NO_3^- and NO_2^- are also subject to reduction when occupying the interlayer site. See Génin et al. (2001), Ruby et al. (2006), Jönsson et al. (2008) and Génin et al. (2009). LDHs therefore constitute an important class of minerals, whose environmental significance is little understood, but which could be particularly relevant in controlling trace-element concentrations in shallow potable water aquifers, especially those subject to fluctuating, or transient elevated partial pressures of CO_2.

Finally, it should be noted in passing that Fe and Al oxy(hydroxides) with zpc higher than prevailing pH are potentially important phases for competitive sorption of oxyanions with CO_3 - surface complexes. e.g., Appelo et al. (2002).

Acknowledgements

We thank the US Environmental Protection Agency, Office of Research and Development, for funding this study under an Interagency Agreement with the United States Department of Energy (U.S. DOE) at the Lawrence Berkeley National Laboratory (LBNL), Contract No. DE-AC02-05CH11231. Among the staff of the Lawrence Berkeley National Laboratory, we are grateful to Dan Hawkes for a critical editorial review of the thermodynamic tables contained in the report, and to Helen Prieto for extensive formatting and checking for consistency. Doctors Nic Spycher and Tom Wolery graciously agreed to undertake the task of reviewing the manuscript prior to its submission to the US Environmental Protection Agency, for which, we would like to express our special thanks. Dr. Jens Birkholzer supervised the execution of the study, and we are appreciative of his patience and guidance.

References

Allison, J.D., Brown, D.S. and Kevin, J. (1991). MINTEQA2/PRODEFA2, a geochemical assessment model for environmental systems: Version 3.0 user's manual. Environmental Research Laboratory, Office of Research and Development, US Environmental Protection Agency, Athens, GA. 117 p.

Allred, A.L and Rochow, E.G. (1958). A scale of electronegativity based on electrostatic force. Journal of Inorganic and Nuclear Chemistry, 5(4), 264-268.

Appelo, C.A.J., Van der Weiden, M.J.J., Tournassat, C. and Charlet, L. (2002). Surface complexation of ferrous iron and carbonate on ferrihydrite and the mobilization of arsenic. Environmental Science and Technology, 36(14), 3096-3103.

Apps, J.A. (2013). Evaluation of titrations involving the neutralization of acidic M(II) chloride solutions with alkali metal hydroxide solution. Draft Report, September 6, 2013, Lawrence Berkeley National Laboratory, Berkeley, California. 209 p.

Apps, J., Zheng, L., Zhang, Y., Xu, T. and Birkholzer, J. (2010). Evaluation of potential changes in groundwater quality in response to CO_2 leakage from deep geologic storage. Transport in Porous Media, 82, 215-246.

Berman, R.G. and Brown, T.H. (1985). Heat capacity of minerals in the system Na_2O-K_2O-CaO-MgO-FeO-Fe_2O_3-Al_2O_3-SiO_2-TiO_2-H_2O-CO_2: representation, estimation, and high temperature extrapolation. Contributions to Mineralogy and Petrology, 89(2-3), 168-183.

Birkholzer, J., Apps, J., Zheng, L., Zhang, Y., Xu, T. and Tsang, C. (2008). Research project on CO_2 geological storage and groundwater resources: water quality effects caused by CO_2 intrusion into shallow groundwater. Lawrence Berkely National Laboratory Report LBL-1251E. 352 p.

Chermak, J.A. and Rimstidt, J.D. (1990). Estimating the free energy of formation of silicate minerals at high temperatures from the sum of polyhedral contributions. American Mineralogist, 75(11-12), 1376-1380.

Christiansen, B.C., Dideriksen, K., Skovbjerg, L.L., Nedel, S. and Stipp, S.L.S. (2011). On Fougerite. Clays and Clay Minerals, 59(1), 3-9.

Depège, C., El-Metouri, F.-Z., Forano, C., de Roy, A. and Dupuis, J. (1996) Polymerization of silicates in layered double hydroxides. Chemistry of Materials, 8, 952-960.

Gamsjäger, H., Magalhães, M.C.F., Königsberger, E., Sawada, K., Churagulov, B.R., Schmidt, P. and Zeng, D. (2011). IUPAC-NIST Solubility Data Series. 92. Metal Carbonates. Part 1. Solubility and Related Thermodynamic Quantities of Cadmium (II) Carbonate in Aqueous Systems. Journal of Physical and Chemical Reference Data, 40(4), 043104-043104.

Génin, J.M.R., Refait, P., Bourrié, G., Abdelmoula, M. and Trolard, F. (2001). Structure and stability of the Fe (II)–Fe (III) green rust “fougerite” mineral and its potential for reducing pollutants in soil solutions. Applied Geochemistry, 16(5), 559-570.

Génin, J.M., Renard, A. and Ruby, C. (2009). Fougerite FeII− III oxyhydroxycarbonate in environmental chemistry and nitrate reduction. In ICAME 2007, 913-919). Springer Berlin Heidelberg.

Grenthe, I., Fuger, J., Konings, R.J.M., Lemire, R.J., Muller, A.B., Nguyen-Trung, C., Wanner, H. and Forest, I. (1992). Chemical Thermodynamics of Uranium. Nuclear Energy Agency, Organisation for Economic Co-operation, Development, Eds., vol. 1, Chemical Thermodynamics, North Holland Elsevier Science Publishers B. V., Amsterdam, The Netherlands, 715 p.

Guillaumont, R., Fanghanel, T., Fuger, J., Grenthe, I., Neck, V., Palmer, D. and Rand, M.H. (2003). Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technecium. Elsevier: Amsterdam.

Hála, J. and Navratil, J.D. (2001). IUPAC-NIST solubility data series. 74. Actinide carbon compounds. Journal of Physical and Chemical Reference Data, 30(2), 531-698.

Hazen, R.M. (1985). Comparative crystal chemistry and the polyhedral approach. In Microscopic and macroscopic (S.W. Keiffer and A. Navrotsky, Eds.). Reviews in Mineralogy, 14, 317-345. Mineralogical Society of America.

Hazen, R.M. (1988). A useful fiction: polyhedral modeling of mineral properties. American Journal of Science, 288, 242-269.

Jönsson, J. and Sherman, D.M. (2008). Sorption of As (III) and As (V) to siderite, green rust (fougerite) and magnetite: Implications for arsenic release in anoxic groundwaters. Chemical Geology, 255(1), 173-181.

Shock, E.L. and Helgeson, H.C. (1988). Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Correlation algorithms for ionic species and equation of state predictions to 5 kb and 1000 C. Geochimica et Cosmochimica Acta, 52(8), 2009-2036.

Helgeson, H.C., Delany, J.M., Nesbitt, H.W., and Bird, D.K. (1978). Summary and critique of the thermodynamic properties of rock-forming minerals. American Journal of Science, 278A.

Herndon, V. (1998). MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: User Manual Supplement for Version 4.0. U.S. Environmental Protection Agency, National Exposure Research Laboratory, Ecosystems Research Division, Athens, Georgia. 76 p.

Holland, T.J.B. (1989). Dependence of entropy on volume for silicate and oxide minerals: A review and a predictive model. American Mineralogist, 74, 5-13. Washington, D.C.: Mineralogical Society of America. TIC: 235381.

Johnson, J.W., Oelkers, E.H. and Helgeson, H.C. (1992). SUPCRT92: A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bar and 0 to 1000°C. Computers and Geosciences, 18(7), 899-947.

Jolivet, J.P. (1994). De la solution à l'oxyde. Savoirs Actuels, Interéditions, CNRS, 387 p.

Kharaka, Y., Thordsen, J., Kakouros, E., Ambats, G., Herkelrath, W., Beers, S., Birkholzer, J., Apps, J., Spycher, N., Zheng, L., Trautz, R., Rauch, H. and Gullickson, K. (2010). Changes in the chemistry of shallow groundwater related to the 2008 injection of CO_2 at the ZERT field site, Bozeman, Montana. Environmental Earth Sciences, 60, 273-284.

La Iglesia, A. and Félix, J.F. (1994). Estimation of thermodynamic properties of mineral carbonates at high and low temperatures from the sum of polyhedral contributions. Geochimica et Cosmochimica Acta, 58(19), 3983-3991.

Lemire, R.J. (2001). Organisation for Economic Co-operation and Development (OECD)/Nuclear Energy Agency (NEA). Chemical Thermodynamics of Neptunium and Plutonium. New York, New York: Elsevier.

Li, K. and Xue, D. (2006). Estimation of electronegativity values of elements in different valence states. Journal of Physical Chemistry A, 110(39), 11332-11337.

Li, Y., Markley, B., Mohan, A.R., Rodriguez-Santiago, V., Thompson, D. and Van Niekerk, D. (2006). Utilization of carbon dioxide from coal-fired power plant for the production of value-added products. Report Submitted in partial fulfillment of the requirements for the Design Engineering of Energy and Geo-Environmental Systems Course (EGEE 580) College of Earth and Mineral Sciences, Penn Stae University, University Park, PA 16802, 109 p.

Maier, C.G. and Kelley, K.K. (1932). An equation for the representation of high-temperature heat content data. Journal of the American Chemical Society, 54(8), 3243-3246.

Millero, F.J. (1992). Stability constants for the formation of rare earth-inorganic complexes as a function of ionic strength. Geochimica et Cosmochimica Acta, 56(8), 3123-3132.

Nickel, E.H. and Clarke, R.M. (1976). Carrboydite, a hydrated sulfate of nickel and aluminum: a new mineral from Western Australia. American Mineralogist, 61, 366-372.

Nickel, E.H. and Wildman, J. E. (1981). Hydrohonessite–a new hydrated Ni-Fe hydroxy-sulphate mineral: its relationship to honessite, carrboydite, and minerals of the pyroaurite group. Mineralogical Magazine, 44, 333-337.

Peltier, E. Allada, R., Navrotsky, A. and Sparks, D.L. (2006). Nickel solubility and precipitation in soils: A thermodynamic study. Clays and Clay Minerals, 54(2), 153-164.

Powell, K.J., Brown, P.L., Byrne, R.H., Gajda, T., Hefter, G., Sjoberg, S. and Wanner, H. (2005). Chemical speciation of environmentally significant heavy metals with inorganic ligands. Part 1: The Hg^{2+} – Cl^{-}, OH^{-}, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-} aqueous systems. Pure and Applied Chemistry, 77(4), 739-800.

Powell, K.J., Brown, P.L., Byrne, R.H., Gajda, T., Hefter, G., Sjöberg, S. and Wanner, H. (2007). Chemical speciation of environmentally significant metals with inorganic ligands. Part 2: The Cu^{2+}-OH^{-}, Cl^{-}, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-} systems. Pure and Applied Chemistry, 79(5), 895-950.

Powell, K.J., Brown, P.L., Byrne, R.H., Gajda, T., Hefter, G., Leuz, A.-K., Sjöberg, S. and Wanner, H. (2009). Chemical speciation of environmentally significant metals with inorganic ligands. Part 3: The Pb^{2+} + OH^{-}, Cl^{-}, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-} systems (IUPAC Technical Report). Pure and Applied Chemistry, 81(12), 2425-2476.

Ruby, C., Upadhyay, C., Génin, A., Ona-Nguema, G. and Génin, J.M.R. (2006).In situ redox flexibility of FeII-III oxyhydroxycarbonate green rust and fougerite. Environmental Science and Technology, 40(15), 4696-4702.

Stipp, S.L., Parks, G.A., Nordstrom, D.K., Leckie, J.O. (1993). Solubility-product constant and thermodynamic properties for synthetic otavite, $CdCO_3$(s), and aqueous association constants for the Cd(II)-CO_2-H_2O system. Geochimica et Cosmochimica Acta, 57, 2699-2713.

Tanger, J.C. and Helgeson, H.C. (1988). Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures; revised equations of state for the standard partial molal properties of ions and electrolytes. American Journal of Science, 288(1), 19-98.

Trolard, F. and Bourrié, G. (2012). Fougerite a natural layered double hydroxide in gley soil: habitus, structure, and some properties. Chapter 9 in Clay minerals in nature-their characterization, modification and application (M. Valaškova and G.S. Martynkova, Eds.), 171-188. InTech, Rijeka, Croatia.

Trolard, F., Bourrié, G., Abdelmoula, M., Refait, P. and Feder, F. (2007). Fougerite, a new mineral of the pyroaurite-iowaite group: description and crystal structure. Clays and Clay minerals, 55(3), 323-334.

Van Zeggeren, F. and Storey, S.H. (1970). The computation of chemical equilibria. Cambridge University Press.

Wunsch, A., Navarre-Sitchler, A.K., Moore, J. and McCray, J.E. (2014). Metal release from limestones at high partial-pressures of CO_2. Chemical Geology, 363, 40-55.

Wolery, T.J. and Jové-Colón, C.F. (2015). Chemical thermodynamic data. I. The concept of links to the chemical elements and the historical development of key thermodynamic data. Lawrence Livermore National Laboratory Report Draft. 82 p.

Zhang, Y. (1982). Electronegativities of elements in valence states and their applications. 1. Electronegativities of elements in valence states. Inorganic Chemistry, 21, 3886.

Zheng, L., Apps, J.A., Spycher, N., Birkholzer, J.T., Kharaka, Y.K., Thordsen, J., Beers, S.R., Herkelrath, W.N., Kakouros, E. and Trautz, R.C. (2012). Geochemical modeling of changes in shallow groundwater chemistry observed during the MSU-ZERT CO_2 injection experiment. International Journal of Greenhouse Gas Control, 7, 202-217.

Zheng, L., Spycher, N., Varadharajan, C., Tinnacher, R.M., Pugh, J.D., Bianchi, M., Birkholzer, J., Nico, P.S. and Trautz, R.L. (2015). On the mobilization of metals by CO_2 leakage into shallow aquifers: exploring release mechanisms by modeling field and laboratory experiments. Greenhouse Gas Science and Technology, 5, 1-16.

Tables of the Thermodynamic Properties

of

Aqueous Carbonate Complexes

and

Solid Carbonate Phases

of

Selected Elements

Pertinent to

Drinking Water Standards

ARSENIC

Table 1. Association Constants of Aqueous Carbonate Complexes in the System As_2O_3/As_2O_5-CO_2-H_2O

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
<u>As(III)</u>					
$As^{3+} + CO_3^{2-} = AsCO_3^-$	7.0	-	Estimate based on extrapolation from corresponding lanthanide complexes.	Kim et al. (2000)	Stumm and Morgan (1996) and David (1999-2000)
$As^{III} + CO_3^{2-} = As^{III}CO_3^-$	3.79 ± 0.05	-	As^{III} corresponds to all species of free arsenite without distinguishing their protonation status.		Kim et al. (2006)
$As^{3+} + 2CO_3^{2-} = As(CO_3)_2^+$	12.5	-	Estimate based on extrapolation from corresponding lanthanide complexes.	Kim et al. (2000)	Stumm and Morgan (1996) and David (1999-2000)
$As^{III} + 2CO_3^{2-} = As^{III}(CO_3)_2$	4.08 ± 0.05	-	As^{III} corresponds to all species of free arsenite without distinguishing their protonation status.		Kim et al. (2006)
$As(OH)_3(aq) + HCO_3^- = As(OH)_2CO_3^- + H_2O$	-0.658 ± 0.08	-			Neuberger and Helz (2005)
	-	-	Direct evidence for existence of complex		Han et al. (2007)
$As(OH)_3(aq) + 2CO_3^- + 2H^+ = As(OH)_3(HCO_3)_2^{2-}$	-	-	Direct evidence for existence of complex		Han et al. (2007)
<u>As(V)</u>					
	-	-	No evidence for existence of As(V) complexes		Han et al. (2007)

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Table 2. Solubility Constants of Solid Carbonates in the System As_2O_3/As_2O_5-CO_2-H_2O

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
Minerals					
Synthetic Phases					

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Table 3a. Association Constants of Aqueous Carbonate Complexes in the System As_2O_3/As_2O_5-CO_2-H_2O extracted from Databases of Distribution-of-Species Codes

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Database	Source
As(III)				
	No data	No data		
As(V)				
	No data	No data		

(1) At standard state (25°C, 1 atm, *I* = 0), unless otherwise noted.

Table 3b. Solubility Constants of Solid Carbonates in the System As_2O_3/As_2O_5-CO_2-H_2O extracted from Databases of Distribution-of-Species Codes

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Database	Source
As(III)				
	No data	No data		
As(V)				
	No data	No data		

(1) At standard state (25°C, 1 atm, *I* = 0), unless otherwise noted.

Table 3c. Distribution-of-Species Codes: Database References

Database	Reference
Data0.com.V8.R6+	Wolery, T.J. (1994). EQ3NR, Letter report: EQ3/6 version 8.0. Differences from version 7. UCRL-ID-129749. Lawrence Livermore National Laboratory, Livermore, California. USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/LLNL.DAT
Data0.YMP.R5	BSC (Bechtel SAIC Company) (2007). Qualification of Thermodynamic Data for Geochemical Modeling of Mineral–Water Interactions in Dilute Systems. ANL-WIS-GS-000003 REV 01. Las Vegas, Nevada: Bechtel SAIC Company.DOC.20070619.0007.
MinteqA2	HydroGeoLogic, Inc. and Allison Geoscience Consultants, Inc. (1999). MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: User Manual Supplement for Version 4.0, Appendix A: thermodynamic database for MINTEQA2 V4.0, p. 44-74.
Minteq (2009)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/MINTEQ.DAT
Minteq (2006)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/minteq.v4.dat
NAGRA/PSI (2001)	Hummel, W., Berner, U., Curti, E., Pearson, F.J. and Thoenen, T. (2002). Nagra/PSI Chemical Thermodynamic Data Base 01/01. Universal Publishers/uPublish.com, Parkland, Florida. 565 p.
Phreeqc (2009)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/PHREEQC.DAT
ThermoChimie v.7.b	Duro, L., Grivém M. and Giffaut, E. (2010). ThermoChimie, the ANDRA thermodynamic database In Buckau G, Kienzler B, Duro L, Grivé M, Montoya V (eds). 2nd Annual Workshop Proceedings of the Collaborative Project “Redox Phenomena Controlling Systems” (7th EC FP CP Recosy) Larnaca (Cyprus) 16–19 March 2010. Karlsruhe: KIT Scientific Publishing, 275–283.
Thermoddem (2009)	Blanc P., Lassin A. and Piantone P. (2007) THERMODDEM a database devoted to waste minerals. BRGM (Orléans, France). For updates: http://thermoddem.brgm.fr
Wateq4f	Ball, J. W., & Nordstrom, D. K. (1991). User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters. U.S. GEOLOGICAL SURVEY, Open-File Report 91-183, Revised and reprinted - April, 2001. p. 81-94
Wateq4f (2005)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/WATEQ4F.DAT

Table 4a. Thermodynamic properties of Arsenic Carbonate Minerals and Synthetic Solid Carbonates: Gibbs Free Energies of Formation

Mineral		$\Delta G^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
As(III)				
Armangite	$Mn_{26}As^{III}_{18}O_{50}(OH)_4(CO_3)$			
As(V)				
Sailaufite	$Ca_2Mn^{III}_3O_2(AsO_4)_2(CO_3)\bullet 3(H_2O)$			
Tyrolite	$CaCu_5(AsO_4)_2(CO_3)(OH)_4\bullet 6(H_2O)$			

Table 4b. Thermodynamic properties of Arsenic Carbonate Minerals and Synthetic Solid Carbonates: Enthalpies of Formation

Mineral		$\Delta H^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
As(III)				
Armangite	$Mn_{26}As^{III}_{18}O_{50}(OH)_4(CO_3)$			
As(V)				
Sailaufite	$Ca_2Mn^{III}_3O_2(AsO_4)_2(CO_3)\bullet 3(H_2O)$			
Tyrolite	$CaCu_5(AsO_4)_2(CO_3)(OH)_4\bullet 6(H_2O)$			

Table 4c. Thermodynamic properties of Arsenic Carbonate Minerals and Synthetic Solid Carbonates: Entropies

Mineral		$S^0_{P_r,T_r}$ J K^{-1} gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
As(III)				
Armangite	$Mn_{26}As^{III}_{18}O_{50}(OH)_4(CO_3)$			
As(V)				
Sailaufite	$Ca_2Mn^{III}_3O_2(AsO_4)_2(CO_3)\bullet 3(H_2O)$			
Tyrolite	$CaCu_5(AsO_4)_2(CO_3)(OH)_4\bullet 6(H_2O)$			

Table 5. Crystallographic Properties of Arsenic Carbonate Minerals and Synthetic Solid Carbonates

	Name	Formula	Reference
	As(III)		
1	Armangite	$Mn_{26}As^{III}_{18}O_{50}(OH)_4(CO_3)$	Gaines et al. (1997), Moore and Araki (1979)
2	Armangite	$Mn_{26}As^{III}_{18}O_{50}(OH)_4(CO_3)$	Gaines et al. (1997)
	As(V)		
3	Sailaufite	$Ca_2Mn^{III}_3O_2(AsO_4)_2(CO_3)\bullet 3(H_2O)$	Gaines et al. (1997)
4	Sailaufite	$Ca_2Mn^{III}_3O_2(AsO_4)_2(CO_3)\bullet 3(H_2O)$	Wildner et al. (2003)
5	Tyrolite	$CaCu_5(AsO_4)_2(CO_3)(OH)_4\bullet 6(H_2O)$	Gaines et al. (1997)
6	Tyrolite	$CaCu_5(AsO_4)_2(CO_3)(OH)_4\bullet 6(H_2O)$	Mineralogy Database (http://webmineral.com/)
7	Clinotyrolite	$Ca_2Cu_9(AsO_4)_{3.8}(SO_4)_{0.3}(CO_3)(OH)_{9.9}\bullet 10.3(H_2O)$	Gaines et al. (1997)
8	Tyrolite-1M	$Ca_2Cu_9(AsO_4)_4(CO_3)(OH)_8\bullet 11H_2O(H_2O)_{0.5}$	Krivovchev et al. (2006)
9	Tyrolite-2M	$Ca_2Cu_9(AsO_4)_4(CO_3)(OH)_8\bullet 11H_2O(H_2O)_{0.5}$	Krivovchev et al. (2006)

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
	As(III)									
1	Armangite	13.491(2)		8.855(1)				1	P-3	840.54
2	Armangite	13.491		8.855				1	P-3	840.54
	As(V)									
3	Sailaufite	11.253	19.628	8.932		100.05		6	Cm	194.26
4	Sailaufite	11.253	19.628	8.932		100.05		6	Cm	194.26
5	Tyrolite	10.50	54.71	5.59				8	Pmma	241.73
6	Tyrolite	10.212	55.51	5.602				8	Pmma	239.05
7	Clinotyrolite	27.61	5.56	10.513		94.0		2	P2/a	484.76
8	Tyrolite-1M	27.562(3)	5.5682(7)	10.4662(15)		98.074(11)		2	P2/c	478.86
9	Tyrolite-2M	54.520(6)	5.5638(6)	10.4647(18)		96.432(9)		4	C2/c	474.90

[#]Calculated from cell constants, this work

Table 6. Carbonate Minerals containing greater than 10 wt.% Arsenic*

Name	Formula	Arsenic, wt.%	gfw	Thermodynamic Data	
As(III)					
Armangite	$Mn_{26}As^{III}_{18}O_{50}(OH)_4(CO_3)$	36.40	3704.99	no	no
Sailaufite	$Ca_2Mn^{III}_3O_2(AsO_4)_2(CO_3)\bullet 3(H_2O)$	24.19	650.52	no	no
As(V)					
Gartrellite	$Pb(Cu,Fe^{II})_2(As^{V}O_4,SO_4)_2(CO_3,H_2O)_{0.7}$	18.11	620.46	no	no
Tyrolite	$CaCu_5(As^{V}O_4)_2(CO_3)(OH)_4\bullet 6(H_2O)$	17.19	871.78	no	no

*Data taken primarily from a compilation given by the Mineralogy Database (http://webmineral.com).

References

David, R.L. (1999-2000). C.R.C. Handbook of Chemistry and Physics, 80th ed. CRC Press Inc., p. 12-14. (Cited by Kim et al., 2000.)

Gaines, R.V., Skinner, H.C.W., Foord, E.E., Mason, B., Rosenzweig, A. King, V.T. and Dowty, E. (1997). Dana's New Mineralogy (Eighth edition). John Wiley and Sons, Inc., New York. 1819 p.

Han, M-J., Jumin Hao, J., Christodoulatos, C., Korfiatis, G.P., Wan, L-J. and Meng, X. (2007). Direct evidence of arsenic(III)-carbonate complexes obtained using electrochemical scanning tunneling microscopy. Analytical Chemistry, 79, 3615-3622.

Kim, M-J., Nriagu, J. and Haack, S. (2000). Carbonate ions and arsenic dissolution by groundwater. Environmental Science and Technology, 34**(15)**, 3094-3100.

Kim, J., Korshin, G.V., Frenkel, A.I. and Velichenko, A.B. (2006). Electrochemical and XAFS Studies of Effects of Carbonate on the Oxidation of Arsenite. Environmental Science and Technology, 40, 228-234**.**

Krivovichev, S.V., Chernyshov, D.Y., Dobelin, N., Armbruster, T., Kahlenberg, V., Kaindl, R., Tessadri, R. and Kaltenhauser, G. (2006). Crystal chemistry and polytypism of tyrolite. American Mineralogist, 91, 1378-1384.

Moore, P.B. and Araki, T. (1979). Armangite, $Mn_{26}[As_6(OH)_4O1_4][As_6O_{18}]_2[CO_3]$, a fluorite derivative structure. American Mineralogist, 64, 748-757.

Neuberger, C.S. and Helz, G.R. (2005). Arsenic(III) carbonate complexing. Applied Geochemistry, 20, 1218-1225.

Stumm, W. and Morgan, J.J. (1996). Aquatic Chemistry. John Wiley & Sons Inc., New York, p. 986-987. (Cited by Kim et al., 2000.)

Wildner M., Tillmanns, E, Andrut, M. and Lorenz, J. (2003). Sailaufite, $(Ca,Na,)_2Mn_3O_2(AsO_4)_2(CO_3).3H_2O$, a new mineral from Hartkoppe hill, Ober-Sailauf (Spessart mountains, Germany), and its relationship to mitridatite-group minerals and pararobertsite. European Journal of Mineralogy, 15, 555-564.

BARIUM

Table 1. Association Constants for Aqueous Carbonate Complexes in the System $BaO-CO_2-H_2O$

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
$Ba^{2+} + CO_3^{2-} = BaCO_3(aq)$	3.78		I = 0.01		Benes and Selecka (1973)
	3.78			Palmer and Van Eldik (1983)	Benes and Selecka (1973)
	2.78		I = 0	Palmer and Van Eldik (1983)	Smith and Martell (1976)
	3.20	-		Millero and Hawke (1992)	Millero and Schreiber (1982)
	2.71	14.84	Sol.		Busenberg and Plummer (1986)
	2.71	14.85		Nordstrom et al. (1990)	Busenberg and Plummer (1986)
$Ba^{2+} + CO_3^{2-} + H^+ = BaHCO_3^+$	11.85 ± 0.03*	-	EMF		Nakayama and Rasnick (1969)
	11.31*	8.36*	Cond.		Busenberg and Plummer (1986)
	11.31*	8.36*		Nordstrom et al. (1990)	Busenberg and Plummer (1986)
$Ba^{2+} + HCO_3^- = BaHCO_3^+$	0.982	23.26	Cond.		Busenberg and Plummer (1986)

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

* Equation recast using bicarbonate dissociation equation from PHREEQC.

Table 2. Solubility Constants of Solid Carbonates in the System $BaO-CO_2-H_2O$

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
Minerals					
Alstonite					
$BaCaCO_3)_2(cr) = Ba^{2+} + Ca^{2+} + 2CO_3^{2}$	-17.37	-	From Fig. 3 of ref. Sol./pH		Garrels et al. (1960)
	-18.00		Estimated		Yoder and Rowand (2006)
Barytocalcte					
$BaCa(CO_3)_2(cr) = Ba^{2+} + Ca^{2+} + 2CO_3^{2}$	-17.25	-	From Fig. 3 of ref. Sol./pH		Garrels et al. (1960)
Norsethite					
$BaMg(CO_3)_2(cr) = Ba^{2+} + Mg^{2+} + 2CO_3^{2}$	-19.56 ± 0.08	-			Konigsberger et al. (1998)
Witherite					
$BaCO_3(cr) = Ba^{2+} + CO_3^{2-}$	-8.565		In pure water. T not specified. Recalc. by Näsänen (1946b)	Näsänen (1946b)	Bineau (1857)
	-8.71	-	16°C	Weissenberger (1914)	Schloesing (1872a,b)
	-8.15	-	16°C	Johnston (1915)	Schloesing (1872a,b)
	-8.647		16°C. In pure water. Recalc. by Näsänen (1946b)	Näsänen (1946b)	Schloesing (1872a,b)
	-8.379		16°C, I = 0. H_2CO_3 soln. Recalc. by Näsänen (1946b)	Näsänen (1946b)	Schloesing (1872a,b)
		-	8.8 and 24.2°C. Solubility		Holleman (1893)
	-8.052	-			Bodländer (1900)
			Solubility in NH_4Cl solution		Kernot et al. (1908)
	-8.09	-			McCoy and Smith (1911)
	-8.31			Latimer (1952)	McCoy and Smith (1911)
	-8.28		25°C, I = 0. Higher $P(CO_2)$. Recalc. by Näsänen (1946b)	Näsänen (1946b)	McCoy and Smith (1911)
	-8.31			Naumov et al. (1974)	McCoy and Smith (1911)
	-8.805		13°C, in pure water. Recalc. by Näsänen (1946b)	Näsänen (1946b)	Weissenberger (1914)

Table 2. Solubility Constants of Solid Carbonates in the System BaO-CO_2-H_2O (continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	-8.706		18°C, in pure water. Recalc. by Näsänen (1946b)	Näsänen (1946b)	Weissenberger (1914)
	-8.675		22°C, in pure water. Recalc. by Näsänen (1946b)	Näsänen (1946b)	Weissenberger (1914)
	-8.583		27°C, in pure water. Recalc. by Näsänen (1946b)	Näsänen (1946b)	Weissenberger (1914)
	-8.485		33°C, in pure water. Recalc. by Näsänen (1946b)	Näsänen (1946b)	Weissenberger (1914)
	-8.419		37°C, in pure water. Recalc. by Näsänen (1946b)	Näsänen (1946b)	Weissenberger (1914)
			Solubility = 0.27% and 0.59% at $P(CO_2)$ = 1 and 25 atm., respectively		Haehnel (1924)
	-7.70	-			Hahn and Brunngässer (1926)
	-8.307	-	Review. No correction for activity coefficients		Kelley and Anderson (1935)
	-9.265	-	Calc. from solubility		Townley et al. (1937)
	-8.681		In pure water. 25°C. Recalc. by Näsänen (1946b)	Näsänen (1946b)	Townley et al. (1937)
	-8.02, -7.95, -7.84		25°C, *I* = 0. Titration of 0.2 *N* $BaCl_2$ with Na_2CO_3 soln		Näsänen (1946a)
	-8.286		25°C, *I* = 0. In NaCl solution.		Näsänen (1946b)
	-8.286		25°C, *I* = 0. In KCl solution.		Näsänen (1946b)
	-8.31	-		Zhuk (1954)	Goskhimizdat (1952)
	-8.80		calculated		Latimer (1952)
	-8.78	-		Millero et al. (1984)	Rossini et al. (1952)
			Soly of witherite in H_2O at 100-225°C and $P(CO_2)$ ≤100 kg./cm^2		Malinin (1963)
	-8.68	-	From Fig. 3 of ref. Sol./pH		Garrels et al. (1960)
	-8.57	-		Millero et al. (1984)	Garrels et al. (1960)
	-8.29			Naumov et al. (1974)	Sillen and Martell (1964)
			Activity product at elevated temperatures		Malinin (1970)

Table 2. Solubility Constants of Solid Carbonates in the System BaO-CO_2-H_2O (continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	-8.30 ± 0.01	-		Palmer and Van Eldik (1983)	Smith and Martell (1976)
	-8.30	-		Millero et al. (1984)	Smith and Martell (1976)
	-8.56 ± 0.05	-			Millero et al. (1984)
	-8.562	2.94	Sol.		Busenberg and Plummer (1986)
	-8.562	2.941		Nordstrom et al. (1990)	Busenberg and Plummer (1986)
	-8.46 ± 0.05	-			Konigsberger et al. (1998)
		3.16 ± 0.7			Parker (1995)
	-8.10		Estimated		Yoder et al. (2010)
$BaCO_3(cr) = BaCO_3(aq)$	-5.48 ± 0.04		I = 0.01		Benes and Selecka (1973)
	-5.48	-	I = 0.01	Palmer and Van Eldik (1983)	Benes and Selecka (1973)
Synthetic Phases					
$Na_2Ba(CO_3)_2$					
$Na_2Ba(CO_3)_2 = Ba^{2+} + 2Na^{+} + 2CO_3^{2}$	-7.22		Estimated		Yoder and Rowand (2006)
$K_2Ba(CO_3)_2$					
$K_2Ba(CO_3)_2 = Ba^{2+} + 2K^{+} + 2CO_3^{2}$	-0.30		Estimated		Yoder and Rowand (2006)
$Ba_2CO_3(OH)_2$					
$Ba_2CO_3(OH)_2 + 2H^{+} = 2Ba^{2+} + CO_3^{2} + 2H_2O$	19.90		Estimated		Yoder et al. (2010)
$Ba_3CO_3(OH)_4$					

Table 2. Solubility Constants of Solid Carbonates in the System BaO-CO_2-H_2O (continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
$Ba_3CO_3(OH)_4 + 4H^+ = 3Ba^{2+} + CO_3^{2} + 4H_2O$	47.90		Estimated		Yoder et al. (2010)
$\underline{Ba_4CO_3(OH)_6}$					
$Ba_4CO_3(OH)_6 + 6H^+ = 4Ba^{2+} + CO_3^{2} + 6H_2O$	75.85		Estimated		Yoder et al. (2010)
$\underline{Ba_5CO_3(OH)_8}$					
$Ba_5CO_3(OH)_8 + 8H^+ = 5Ba^{2+} + CO_3^{2} + 82H_2O$	103.85		Estimated		Yoder et al. (2010)
$\underline{Ba_3(CO_3)_2(OH)_2}$					
$Ba_3(CO_3)_2(OH)_2 + 2H^+ = 3Ba^{2+} + 2CO_3^{2} + 2H_2O$	11.85		Estimated		Yoder et al. (2010)
$\underline{Ba_5(CO_3)_2(OH)_6}$					
$Ba_5(CO_3)_2(OH)_6 + 6^+ = 5Ba^{2+} + 2CO_3^{2} + 6H_2O$	67.78		Estimated		Yoder et al. (2010)

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Table 3a. Association Constants of Aqueous Carbonate Complexes in the System BaO-CO_2-H_2O extracted from Databases of Distribution-of-Species Codes

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Database	Source
$Ba^{2+} + CO_3^{2-} = BaCO_3(aq)$	2.71		MinteqA2	
	2.60		Wateq4f	
	2.65		Data0.com.V8.R6+	
	-	-	Minteq (2009)	
	2.71	16.	Minteq (2006)	NIST46.4
	2.71	14.85	Phreeqc (2009)	
	2.71	14.85	Wateq4f (2005)	
	2.71	14.841	ThermoChimie v.7.b	#86BUS/PLU
	2.713	14.842	NAGRA/PSI (2001)	
	2.6454	-	Data0.YMP.R5	Sverjensky et al. (1997)
	2.6600	-	Thermoddem (2009)	Sverjensky et al. (1997)
$Ba^{2+} + 2CO_3^{2-} = Ba(CO_3)_2^{2-}$			MinteqA2	
			Wateq4f	
			Data0.com.V8.R6+	
	-	-	Minteq (2009)	
	-	-	Minteq (2006)	
	-	-	Phreeqc (2009)	
	-	-	Wateq4f (2005)	
	-	-	ThermoChimie v.7.b	
	-	-	NAGRA/PSI (2001)	
	-	-	Data0.YMP.R5	Stipp et al. (1993)
			Thermoddem (2009)	
$Ba^{2+} + CO_3^{2-} + H^+ = BaHCO_3^+$	11.31		MinteqA2	
	11.27		Wateq4f	
	-		Data0.com.V8.R6+	
	-	-	Minteq (2009)	
	11.309	10.4	Minteq (2006)	NIST46.4
	11.311	8.364	Phreeqc (2009)	
	11.311	8.364	Wateq4f (2005)	
	11.31	8.56	ThermoChimie v.7.b	#86BUS/PLU
	11.311	8.362	NAGRA/PSI (2001)	
	11.3462	-	Data0.YMP.R5	Shock and Koretsky (1995)
	11.3608	-	Thermoddem (2009)	Shock and Koretsky (1995)

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Table 3b. Solubility Constants of Solid Carbonates in the System BaO-CO_2-H_2O extracted from Databases of Distribution-of-Species Codes

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Database	Source
Alstonite				
$BaCa(CO_3)_2(s) = Ba^{2+} + Ca^{2+} + CO_3^{2-}$	-18.0733		Data0.YMP.R5	Wagman et al. (1982)
Barytocalcite				
$BaCa(CO_3)_2(s) = Ba^{2+} + Ca^{2+} + CO_3^{2-}$	-17.9156		Data0.YMP.R5	Wagman et al. (1982)
Witherite				
$BaCO_3(s) = Ba^{2+} + CO_3^{2-}$	-8.57		MinteqA2	
	-8.61		Wateq4f	
From Johnson and Oelkers 1992	-13.33		Data0.com.V8.R6+	
	-	-	Minteq (2009)	
	-8.57	4.	Minteq (2006)	
	-8.562	2.941	Phreeqc (2009)	
	-8.562	2.941	Wateq4f (2005)	
	-8.56	2.941	ThermoChimie v.7.b	#86BUS/PLU
	-8.562	2.940	NAGRA/PSI (2001)	
	-8.5649	-	Data0.YMP.R5	Barin and Platzki (1995); Binnewies and Milke (1999)
	-	-	Thermoddem (2009)	

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Table 3c. Distribution-of-Species Codes: Database References

Database	Reference
Data0.com.V8.R6+	Wolery, T.J. (1994). EQ3NR, Letter report: EQ3/6 version 8.0. Differences from version 7. UCRL-ID-129749. Lawrence Livermore National Laboratory, Livermore, California. USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/LLNL.DAT
Data0.YMP.R5	BSC (Bechtel SAIC Company) (2007). Qualification of Thermodynamic Data for Geochemical Modeling of Mineral–Water Interactions in Dilute Systems. ANL-WIS-GS-000003 REV 01. Las Vegas, Nevada: Bechtel SAIC Company.DOC.20070619.0007.
MinteqA2	HydroGeoLogic, Inc. and Allison Geoscience Consultants, Inc. (1999). MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: User Manual Supplement for Version 4.0, Appendix A: thermodynamic database for MINTEQA2 V4.0, p. 44-74.
Minteq (2009)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/MINTEQ.DAT
Minteq (2006)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/minteq.v4.dat
NAGRA/PSI (2001)	Hummel, W., Berner, U., Curti, E., Pearson, F.J. and Thoenen, T. (2002). Nagra/PSI Chemical Thermodynamic Data Base 01/01. Universal Publishers/uPublish.com, Parkland, Florida. 565 p.
Phreeqc (2009)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/PHREEQC.DAT
ThermoChimie v.7.b	Duro, L., Grivém M. and Giffaut, E. (2010). ThermoChimie, the ANDRA thermodynamic database In Buckau G, Kienzler B, Duro L, Grivé M, Montoya V (eds). 2nd Annual Workshop Proceedings of the Collaborative Project “Redox Phenomena Controlling Systems” (7th EC FP CP Recosy) Larnaca (Cyprus) 16–19 March 2010. Karlsruhe: KIT Scientific Publishing, 275–283.
Thermoddem (2009)	Blanc P., Lassin A. and Piantone P. (2007) THERMODDEM a database devoted to waste minerals. BRGM (Orléans, France). For updates: http://thermoddem.brgm.fr
Wateq4f	Ball, J. W., & Nordstrom, D. K. (1991). User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters. U.S. GEOLOGICAL SURVEY, Open-File Report 91-183, Revised and reprinted - April, 2001. p. 81-94
Wateq4f (2005)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/WATEQ4F.DAT

Table 4a. Thermodynamic properties of Barium Carbonate Minerals and Synthetic Solid Carbonates: Gibbs Free Energies of Formation

Mineral		$\Delta G^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
Minerals				
Alstonite	$BaCa(CO_3)_2$	-2272.2		Garrels et al. (1960)
		-2272.16	Karpov et al. (1968)	Garrels et al. (1960)
		-2271.9	La Iglesia and Felix (1994)	Garrels et al. (1960)
		-2272.75		Parker et al. (1971)
Predicted		-2285.3 ± 3.2		La Iglesia and Felix (1994)
Barytocalcite	$BaCa(CO_3)_2$	-2271.54		Garrels et al. (1960)
		-2271.54	Karpov et al. (1968)	Garrels et al. (1960)
		-2271.5	La Iglesia and Felix (1994)	Garrels et al. (1960)
		-2271.91		Parker et al. (1971)
Predicted		-2283.3 ± 3.2		La Iglesia and Felix (1994)
Kampfite	$Ba_{12}(Si_{11}Al_5)O_{31}(CO_3)_8Cl_5$			
Norsethite	$BaMg(CO_3)_2$			
Witherite	$BaCO_3$	-1112.23		Kelley and Anderson (1935)
		-1138.88	Latimer (1952)	Rossini et al. (1952)?
		-1138.88	Zhuk (1954)	Rossini et al. (1952), Karapet'yants (1953)
		-1138.86 ± 6.28	Robie (1962, 1966)	Rossini et al. (1952)
		-1138.9	Woods and Garrels (1987)	Rossini et al. (1952)
calculated		-1136.17		Zhuk (1954)
		-1136.17	Karpov et al. (1968)	Zhuk (1954)
		-1136.17	Karapet'yants and Karapet'yants (1970)	Zhuk (1954)
		-1138.0		Garrels et al. (1960)
		-1138.22		Garrels et al. (1960)
		-1138.22	Karpov et al. (1968)	Garrels et al. (1960)

Table 4a. Thermodynamic properties of Barium Carbonate Minerals and Synthetic Solid Carbonates: Gibbs Free Energies of Formation (Continued)

Mineral		$\Delta G^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
		-1123.0 ± 1.3	Naumov et al. (1974)	McCoy and Smith (1911), Sillen and Martell (1964)
		-1132.2		Adami and Conway (1966)
		-1132.210 ± 2.240	Robie et al. (1979)	Adami and Conway (1966)
		-1132.2 ± 2.2	Robie and Hemingway (1995)	Adami and Conway (1966)
		-1138.88	Karpov et al. (1968)	Ermolaev (1966)
		-1137.63		Parker et al. (1971)
		-1123.0	Woods and Garrels (1987)	Naumov et al. (1974)
		-1138.4	Dobrydiev et al. (2005)	Ryabin et al. (1977)
		-1132.2	Woods and Garrels (1987)	Robie et al. (1978)
		-1164.8	Woods and Garrels (1987)	Helgeson et al. (1978)
		-1337.6	Woods and Garrels (1987)	Wagman et al. (1982)
		-1132.21		Busenberg and Plummer (1986)
		-1249.72	Stern (2000)	Barin (1993)
		-1134.37		Parker (1995)
		-1132.2		Robie and Hemingway (1995)
Synthetic Phases				

Table 4b. Thermodynamic properties of Barium Carbonate Minerals and Synthetic Solid Carbonates: Enthalpies of Formation

Mineral		$\Delta H^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
Minerals				
Alstonite	$BaCa(CO_3)_2$			
Barytocalcite	$BaCa(CO_3)_2$			
Kampfite	$Ba_{12}(Si_{11}Al_5)O_{31}(CO_3)_8Cl_5$			
Norsethite	$BaMg(CO_3)_2$			
Witherite	$BaCO_3$	-1192.19		Kelley and Anderson (1935)
		-1218.80	Latimer (1952)	Rossini et al. (1952)?
		-1218.80	Zhuk (1954)	Rossini et al. (1952), Karapet'yants (1953)
		1218.80 ± 4.60	Robie (1962, 1966)	Rossini et al. (1952)
		-1218.80	Karpov et al. (1968)	Rossini et al. (1952)
		-1218.8	Woods and Garrels (1987)	Rossini et al. (1952)
		-1190.56 ± 1.26*	Naumov et al. (1974)	Kapustinskii and Staxanova (1954)
		-1201.06 ± 2.09	Naumov et al. (1974)	McCoy and Smith (1911), Sillen and Martell (1964)
		-1210.9 ± 2.2		Adami and Conway (1966)
		-1210.850 ± 2.230	Robie et al. (1978)	Adami and Conway (1966)
		-1210.9 ± 2.2	Robie and Hemingway (1995)	Adami and Conway (1966)
		-1234.28	Karapet'yants and Karapet'yants (1970)	Maksimova (1962)
		-1216.29		Parker et al. (1971)
		-1201.0	Woods and Garrels (1987)	Naumov et al. (1974)
		-1217.1	Dobrydiev et al. (2005)	Ryabin et al. (1977)
		-1210.8	Woods and Garrels (1987)	Robie et al. (1978)
		-1244.7	Woods and Garrels (1987)	Helgeson et al. (1978)
		-1216.3	Woods and Garrels (1987)	Wagman et al. (1982)
		-1210.85		Busenberg and Plummer (1986)
		-1216.29	Stern (2000)	Barin (1993)

Table 4b. Thermodynamic properties of Barium Carbonate Minerals and Synthetic Solid Carbonates: Enthalpies of Formation (Continued)

Mineral		$\Delta H^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
		-1213.03 ± 2.0		Parker (1995)
		-1210.9		Robie and Hemingway (1995)
Synthetic Phases				
$Ba(HCO_3)_2$	$Ba(HCO_3)_2$	-1974.85	Karapet'yants and Karapet'yants (1970)	Yatsimirskii (1956)
		-1970.66 ± 62.76	Estimated value of fictive compound	Wilcox and Bromley (1963)
		-1970.66	Karapet'yants and Karapet'yants (1970)	Wilcox and Bromley (1963)

*Not recommended by Naumov et al. (1974)

Table 4c. Thermodynamic properties of Barium Carbonate Minerals and Synthetic Solid Carbonates: Entropies

Mineral		$S^0_{P_r,T_r}$ J K^{-1} gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
Minerals				
Alstonite	$BaCa(CO_3)_2$			
Barytocalcite	$BaCa(CO_3)_2$			
Kampfite	$Ba_{12}(Si_{11}Al_5)O_{31}(CO_3)_8Cl_5$			
Norsethite	$BaMg(CO_3)_2$			
Witherite	$BaCO_3$	111.92 ± 2.09		Anderson (1934)
		111.92 ± 2.09	Kelley and King (1961)	Anderson (1934)
		112.13 ± 2.1	Naumov et al. (1974)	Anderson (1934)
		112.13	Latimer (1952)	Rossini et al. (1952)
		112.13	Zhuk (1954)	Rossini et al. (1952), Karapet'yants (1953)
		112.13	Karpov et al. (1968)	Rossini et al. (1952)
		112.1	Woods and Garrels (1987)	Rossini et al. (1952)
calculated		102.93		Zhuk (1954)
		102.93	Karpov et al. (1968)	Zhuk (1954)
		102.93	Karapet'yants and Karapet'yants (1970)	Zhuk (1954)
		109.20	Karpov et al. (1968)	Yatsimirskii and Krestov (1960)
		112.13 ± 2.09	Robie (1962; 1966)	Kelley and King (1961)
		112.13 ± 2.09	Karpov et al. (1968)	Kelley and King (1961)
		112.13	Karapet'yants and Karapet'yants (1970)	Kelley and King (1961)
		112.13 ± 2.09	Robie et al. (1979)	Kelley and King (1961)
		109.20	Karapet'yants and Karapet'yants (1970)	Yatsimirskii and Krestov (1960)
		112.13		Parker et al. (1971)
		112.1	Woods and Garrels (1987)	Naumov et al. (1974)
		112.1	Woods and Garrels (1987)	Robie et al. (1978)
		112.1	Woods and Garrels (1987)	Helgeson et al. (1978)
		112.1	Woods and Garrels (1987)	Wagman et al. (1982)

Table 4c. Thermodynamic properties of Barium Carbonate Minerals and Synthetic Solid Carbonates: Entropies (Continued)

Mineral		$S^0_{P_r,T_r}$ J K^{-1} gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
		112.1 ± 2.1		Busenberg and Plummer (1986)
		112.1 ± 2.1	Robie and Hemingway (1995)	Busenberg and Plummer (1986)
		112.13	Stern (2000)	Barin (1993)
		112.10 ± 2.0	Parker (1995)	Gurvich et al. (1981)
		112.13		Robie and Hemingway (1995)
Synthetic Phases				

Table 5. Crystallographic Properties of Barium Carbonate Minerals and Synthetic Solid Carbonates

	Name	Formula	Reference
	Minerals		
1	Alstonite	$BaCa(CO_3)_2$	Gaines et al. (1997)
2	Alstonite	$BaCa(CO_3)_2$	Sartori (1975)
3	Alstonite	$BaCa(CO_3)_2$	Roberts (1976)
4	Barytocalcite	$BaCa(CO_3)_2$	Alm (1960)
5	Barytocalcite	$BaCa(CO_3)_2$	Gaines et al. (1997)
6	Barytocalcite	$BaCa(CO_3)_2$	Dickens and Bowen (1971)
7	Paralstonite	$CaBa(CO_3)_2$	Gaines et al. (1997), Effenberger (1980)
8	Benstonite	$Ca_7Ba_6(CO_3)_{13}$	Gaines et al. (1997), Lippmann (1962)
9	Dresserite	$BaAl_2(CO_3)_2(OH)_4•(H_2O)$	Gaines et al. (1997), Jambor et al. (1969)
10	Hydrodresserite	$BaAl_2(CO_3)_2(OH)_4•3(H_2O)$	Szymanski (1982)
11	Fencooperite	$Ba_6Fe^{III}_3Si_8O_{23}(CO_3)_2Cl_3•(H_2O)$	Gaines et al. (1997)
12	Fencooperite	$Ba_6Fe^{III}_3Si_8O_{23}(CO_3)_2Cl_3•(H_2O)$	Grice (2001)

	Name	Cell Constants							Space Group	$V^{o\#}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		$cm^3\ gfw^{-1}$
	Minerals									
1	Alstonite	17.38	14.40	6.123	90.35	90.12	120.08	12	PI or P-1	66.546*
2	Alstonite	30.14	17.40	6.12	90.	90.	90.	24	C1 or C-1	80.535
3	Alstonite	17.38	14.40	6.123	90.	90.	120.	12	PI or P-1	66.602*
4	Barytocalcite	8.15	5.22	6.58		106.13		2	$P2_1$	80.972
5	Barytocalcite	8.134	5.229	6.547		73.867		2	$P2_1$	80.544
6	Barytocalcite	8.092	5.2344	6.544		106.05		2	$P2_1/m$	80.209
7	Paralstonite	8.692		6.148				3	$P3_21$	80.748
8	Benstonite	8.28(1)		8.67(2)				3	R_3 or R3	103.33
9	Dresserite	9.27	16.83	5.63				4	Pbmm	132.24
10	Hydrodresserite	9.7545	10.4069	5.6322	95.695	92.273	115.643	2	P-1	153.78
11	Fencooperite	10.727		7.085				1	P3m1	425.19
12	Fencooperite	10.7409		7.0955				1	P3m1	426.92

	Name	Formula	Reference
13	Kampfite	$Ba_{12}(Si_{11}Al_5)O_{31}(CO_3)_8Cl_5$	Basciano and Groat (2007)
14	Norsethite	$BaMg(CO_3)_2$	Lippmann (1967)
15	Norsethite	$BaMg(CO_3)_2$	Effenberger and Zemann (1985)
16	Norsethite	$BaMg(CO_3)_2$	Gaines et al. (1997)
17	Podlesnoite	$BaCa_2(CO_3)_2F_2$	Zubkova et al. (2007)
18	Witherite	$BaCO_3$	Antao and Hassan (2009), syn neutron
19	Witherite *syn HRPXRD*	$BaCO_3$	Antao and Hassan (2009),
20	Witherite	$BaCO_3$	Gaines et al. (1997), De Villiers (1971)
21	Witherite	$BaCO_3$	Mineralogy Database (http://webmineral.com/)
	Synthetic Phases		
22			

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
	Minerals									
13	Kampfite	31.2329	5.2398	9.0966		106.933		1	Cc	857.66
14	Norsethite	5.017		16.77				3	R32	73.381
15	Norsethite	5.022		16.770				3	R-3m	73.527
16	Norsethite	5.02		16.75				3	R32	73.381
17	Podlesnoite	12.501	5.846	9.443				4	Cmcm	103.90
18	Witherite	5.31640(8)	8.9056(1)	6.43383(7)				4	Pmcn	45.861
19	Witherite *syn HRPXRD*	5.31459(1)	8.90428(2)	6.43409(2)				4	Pmcn	45.840
20	Witherite	5.3126	8.8958	6.4286				4	Pmcn	45.740
21	Witherite	5.313	8.904	6.43				4	Pmcn	45.796
	Synthetic Phases									
22										

*Reported cell constants appear to be erroneous.

#Calculated from cell constants, this work

Table 6. Carbonate Minerals containing greater than 10 wt.% Barium*

Name	Formula	Barium, wt.%	gfw	Thermodynamic Data	
				Est.	Meas.
Alstonite	$BaCa(CO_3)_2$	46.17	297.42	no	yes
Barytocalcite	$BaCa(CO_3)_2$	46.17	297.42	no	yes
Benstonite	$(Ba,Sr)_6(Ca,Mn)_6Mg(CO_3)_{13}$	34.02	1816.58	no	no
Bussenite	$Na_2(Ba,Sr)_2(Fe,Mn)TiSi_2O_7(CO_3)(OH)_3F$	26.13	657.06	no	no
Cebaite-(Ce)	$Ba_3Ce_2(CO_3)5F_2$	39.76	1030.25	no	no
Cebaite-(Nd)	$Ba_3(Nd,Ce)_2(CO_3)_5F_2$	39.75	1036.44	no	no
Cordylite-(Ce)	$Ba(Ce,La)_2(CO_3)_3F_2$	21.63	634.98	no	no
Dresserite	$BaAl_2(CO_3)_2(OH)_4•(H_2O)$	34.56	397.35	no	no
Ewaldite	$(Ba,Sr)(Ca,Na,Y,Ce)(CO_3)_2$	34.94	294.76	no	no
Fencooperite	$Ba_6Fe(III)_3Si_8O_{23}(CO_3)_2Cl_3•(H_2O)$	44.99	1800.97	no	no
Huanghoite-(Ce)	$BaCe(CO_3)_2F$	32.97	416.46	no	no
Hydrodresserite	$BaAl_2(CO_3)_2(OH)_4•3(H_2O)$	31.69	433.38	no	no
IMA2009-010	$[Ba_6(PO4)_2(CO_3)][Fe(II)7(OH)_4Fe(III)_2O_2(SiO_3)_8]$	36.06	2285.23	no	no
Kampfite	$Ba_{12}(Si_{11}Al_5)O_{31}(CO_3)_8Cl_5$	50.96	3266.13	no	no
Khanneshite	$(NaCa)_3(Ba,Sr,Ce,Ca)_3(CO_3)_5$	22.40	613.02	no	no
Krasnovite	$Ba(Al,Mg)(PO_4,CO_3)(OH)_2•(H_2O)$	45.49	301.90	no	no
Kukharenkoite-(Ce)	$Ba_2Ce(CO_3)_3F$	44.75	613.80	no	no
Mackelveyite-(Y)	$NaBa_3CaY(CO_3)_3(OH)_6•3(H_2O)$	45.77	900.07	no	no
Mckelveyite-(Nd)	$(Ba,Sr)(Ca,Na,Nd,REE)(CO_3)_2•3\text{-}10(H_2O)$	22.54	456.93	no	no
Mckelveyite-(Y)	$NaCa(Ba,Sr)_3(Y,REE)(CO_3)_6•3(H_2O)$	39.43	971.59	no	no
Niksergievite	$[Ba,Ca)_2(Al,Si)7O_10(CO_3)(OH)_6•n(H_2O)$	24.13	722.73	no	no
Norsethite	$BaMg(CO_3)_2$	48.76	281.65	no	yes
Paralstonite	$BaCa(CO_3)_2$	46.17	297.42	no	no
Podlesnoite	$BaCa_2(CO_3)_2F_2$	36.95	379.11	no	no
Qaqarssukite-(Ce)	$Ba(Ce,REE)(CO_3)_2F$	24.60	379.62	no	no
Stenonite	$(Sr,Ba,Na)_2Al(CO_3)F_5$	22.02	374.12	no	no
Tuliokite	$BaNa_6Th(CO_3)_6•6(H_2O)$	14.08	975.45	no	no
Witherite	$BaCO_3$	69.59	197.34	no	yes
Zhonghuacerite-(Ce)	$Ba_2Ce(CO_3)_3F$	44.74	613.84	no	no

*Data taken primarily from a compilation given by the Mineralogy Database (http://webmineral.com).

References

Adami, L.H. and Conway, K.C. (1966). Heats and free energies of formation of anhydrous carbonates of barium, strontium and lead. U.S. Bureau of Mines Report of Investigations 6822, 7 p.

Alm, K F. (1960). The crystal structure of barytocalcite $BaCa(CO_3)_2$. Arkiv for Mineralogi och Geologi, 2, 399-410.

Anderson, C.T. (1934). The heat capacities at low temperatures of the alkaline earth carbonates 1. Journal of the American Chemical Society, 56(2), 340-342.

Antao, S.M. and Hassan, I. (2009). The orthorhombic structure of $CaCO_3$, $SrCO_3$, $PbCO_3$ and $BaCO_3$: Linear structural trends. Canadian Mineralogist, 47, 1245-1255.

Barin, I. (1993). Thermochemical Data of Pure Substances VCH Velagsgesellschaft, Weinheim, Germany

Barin, I. and Platzki, G. 1995. Thermochemical Data of Pure Substances. (3rd Edition). VCH., Weinheim, Germany; New York, NY.

Basciano, L.C. and Groat, L A. (2007). The crystal structure of kampfite. Canadian Mineralogist, 45, 935-943.

Benes, P. and Selecka, H. (1973). Ion pair formation and solubility of barium carbonate in aqueous solutions. Radiochemical and Radioanalytical Letters, 13, 339-348.

Bineau, A. (1857). Remarques sur les dissolutions de quelques carbonates et notablement du carbonate de chaux. Annales de Chimie et de Physique, Ser. 3, vol. 51, p. 290.

Binnewies, M. and Milke, E. (1999). Thermochemical Data of Elements and Compounds. Wiley-VCH. New York, New York.

Bodländer, G. (1900). Über die Loslichkeit der Erdkalikarbonate in kohlensäurehaltigem Wasser. Zeitschrift für Physikalische Chemie, Stoechiometrie und Verwandtschaftslehre, 35, 23-32.

Busenberg, E. Plummer, L.N. (1986). The solubility of $BaCO_3$(cr) (witherite) in CO_2-H_2O solutions between 0 and 90°C, evaluation of the association constants of $BaHCO_3^+$(aq) and $BaCO_3$°(aq) between 5 and 80°C, and a preliminary evaluation of the thermodynamic properties of Ba^{2+}(aq). Geochimica et Cosmochimica Acta, 50, 2225-2233.

De Villiers, J.P.R. (1971). Crystal structures of aragonite, strontianite, and witherite. American Mineralogist, 56, 758-767.

Dickens, B. and Bowen, J S. (1971). The crystal structure of $BaCa(CO_3)_2$ (barytocalcite). Journal of Research of the National Bureau of Standards - Physics and Chemistry, 75A, 1-97-203.

Dobrydiev, S.V., Nilova, E.V. and Beskov, V.S. (2005). Calculation of $\Delta_f G^0(298)$ and $\Delta_f H^0(298)$ for sparingly soluble metal carbonates and oxalates in the solid state. Zhurnal Neorganicheskoi Khimii, 50(12), 2015-2018. [In Russian].

Effenberger, H. (1980). Die kristallstruktur des minerals paralstonite, $BaCa(CO_3)_2$. Neues Jahrbuch fur Mineralogie, Monatshefte 1980, 353-363.

Effenberger, H, and Zemann, J. (1985). Single crystal X-Ray investigation of norsethite, $BaMg(CO_3)_2$: one more mineral with an aplanar carbonate group. Zeitschrift für Kristallographie 171, 275-280.

Ermolaev, M.M. (1966). Calculation of the free energy values of some supergene minerals based on the hypothesis of fixed chemical potentials and major element concentrations in the Pacific Ocean. Kora Vyvetrivaniya (1966), No. 7, 13-45. [In Russian].

Gaines, R.V., Skinner, H.C.W., Foord, E.E., Mason, B., Rosenzweig, A. King, V.T. and Dowty, E. (1997). Dana's New Mineralogy (Eighth edition). John Wiley and Sons, Inc., New York. 1819 p.

Garrels R.M., Thompson M.E. and Siever R. (1960). Stability of some carbonates at 25°C and one atmosphere total pressure. American Journal of Science, 258, 402-418.

Glushko V.P. et al. (1979). Thermal Constants of Substances. Vol. 9. Viniti, Moscow (in Russian). *[not cited in text]*

Goskhimizdat. (1952). Chemical Reference, vol. 3. [In Russian]. (As cited in Zhuk, 1954).

Grice, J D. (2001). The crystal structure of fencooperite: Unique [Fe_3O_{13}] pinwheels cross-connected by [Si_8O_{22}] islands. The Canadian Mineralogist, 39, 1065-1071.

Gurvich, L.V., Bergman, G.A. et al. (1982). Thermodynamic data on metal carbonates and related oxides, (V.P. Glushko, General Ed.), vol. 3.

Haehnel, O. (1924). Über die Löslichkeit der Carbonate des Strontiums, des Bariums und der Schwermetalle in Wasser unter hohen Kohlendioxyddrucken sowie über die Eigenschaften solcher Lösungen. Journal für Praktische Chemie (Leipzig), 108, 187-193

Hahn, F.L. and Brunngässer, K. (1926). Die Übersättigung bei Trübungstitrationen und ein Verfahren zur Löslichkeitsbestimmung. Zeitschrift für anorganische und allgemeine Chemie, 153, 88-96.

Helgeson, H.C., Delany, J.M., Nesbitt, H.W. and Bird, D.K. (1978). Summary and critique of the thermodynamic properties of rock-forming minerals. American Journal of Science, 278A. New Haven, Connecticut: Kline Geology Laboratory, Yale University.

Holleman, A.F. (1893). Bestimmungen der Löslichkeit sogetnannter unlöslicher Salze. Zeitschrift für Physikalische Chemie, 12, 125-139.

Jambor, J.L., Fong, D.G. and Sabina, A.P. (1969). Dresserite, the new barium analogue of dundasite, Canadian Mineralogist, 10, 84-89.

Johnston, J. (1915). The solubility-product constant of calcium and magnesium carbonates. Journal of the American Chemical Society, 37, 2001-2020.

Kapustinskii, A.F. and Stakhanova, M.S. (1954). Termokhimiya I Stroenie Atomov. VII. Issledovanie Karbonatov Elementov Vtoroi (Osnovnoi) Gruppy Sistemy Mendeleeva. (Thermochemistry and atomic structure. VII. The study of the Group II (alkaline earth) carbonates). Izvestiya Akademii Nauk Sssr-Seriya Khimicheskaya, (4), 587-597.

Karapet'yants, M. Kh. (1953). Khimicheskaya Termodinamika (Chemical Thermodynamics). 2nd Edition. Goshkhimizdat. 611 p. [In Russian].

Karapet'yants, M.Kh. and Karapet'yants, M.L. (1970). Thermodynamic constants of Inorganic and Organic Compounds (translated by J. Schmorak). Humphrey Science Publishers, Ann Arbor, Michigan. 461 p.

Karpov, I.K., Kashik, S.A. and Pampura, V.D. (1968). Thermodynamic Constants for Calculations in Geochemistry and Petrology. [In Russian] Izdva, Nauka, 143 p.

Kelley, K.K. and Anderson, C.T. (1935). Theoretical metallurgy. IV. Metal carbonates-correlations and applications of thermodynamic properties. U.S. Bureau of Mines Bulletin No. 384, 73 p.

Kelley, K.K. and King. E.G. (1961). Contribution to the Data on Theoretical Metallurgy. XIV. Entropies of the Elements and Inorganic Compounds. U.S. Bureau of Mines Bulletin No. 592, 149 p.

Kernot, G., D'Agositno, A. and Pellegrino, M. (1908). Sulle influenze di solubilita. Gazzetta Chimica Italiana Ser. I, 38(1), 532-554.

Konigsberger, E. Tran-Ho, L.-C. and Heinz Gamsjager, H. (1998). Solid-solute phase equilibria in aqueous solutions X. Solubility constant and stability of norsethite, Monatshefte für Chemie, 129, 1061-1066.

La Iglesia, A. and Félix, J.F. (1994). Estimation of thermodynamic properties of mineral carbonates at high and low temperatures from the sum of polyhedral contributions. Geochimica et Cosmochimica Acta, 58(19), 3983-3991.

Latimer, W.M. (1952). The Oxidation States of the Elements and their Potentials in Aqueous Solutions. Second edition. Prentice Hall, New York, 392 p.

Lippmann, F. (1962). Benstonite, $Ca_7Ba_6(CO_3)_{13}$, a new mineral from the barite deposit in Hot Spring county. Arkansas. American Mineralogist, 47, 585-598.

Lippmann, F. (1967). Die kristallstruktur des norsethit, $BaMg(CO_3)_2$, im vergleich zum dolomit, $CaMg(CO_3)_2$. Naturwissenschaften, 54, 514-514.

Maksimova, I.N. (1962). Ionization potentials and heats of formation of compounds. Zhurnal Strukturnoi Khimii, 3(2), 208-10. [In Russian].

Malinin S.D. (1963). An experimental investigation of the solubility of calcite and witherite under hydrothermal conditions. Geokhimiya, (7), 631-46. [In Russian]. Also in Geochemistry (English trans.), p. 650-667.

Malinin S.D. (1970). Application of the strong electrolyte theory to the solubility of carbonates (calcite and witherite) at high temperatures. Geokhimiya, 5, 540-551. [In Russian].

McCoy, H.N. and Smith, H.J. (1911). Equilibrium between alkali-earth carbonates, carbon dioxide and water. Journal of the American Chemical Society, 33, 468-473.

Millero, F.J. and Hawke, D.J. (1992). Ionic interactions of divalent metals in natural waters. Marine Chemistry, 40, 19-48.

Millero, F.J., Milne, P.J. and Thurmond, V.L. (1984). The solubility of calcite, strontianite and witherite in NaCl solutions at 25°C. The solubility of calcite, strontianite and witherite in NaCl solutions at 25°C. Geochimica et Cosmochimica Acta, 48(5), 1141-1143.

Millero, F.J. and Schreiber, D.R. (1982). Use of the ion pairing model to estimate activity coefficients of the ionic components of natural waters. American Journal of Science, 282, 1508-1540.

Nakayama, F.S. and Rasnick, B.A. (1969). Bicarbonate complexes of barium and strontium. Journal of Inorganic and Nuclear Chemistry, 31, 3491-3494.

Näsänen, R. (1946b). Potentiometric studies on hydrolytic precipitation reactions. I. Barium carbonate. Annales Academiae Scientiarum Fennicae, Series A2: Chemica, No. 17, 18 p.

Näsänen, R. (1946a). Zur Einwirkung der Säure- und Basenzusätze auf die Fällungskurve von Bariumcarbonat. Suomen Kemistilehti B, 19B, 24-6.

Naumov, G.B., Ryzhenko, B.N. and Khodakovskiy, I.L. (1971). Handbook of Thermodynamic Data. Atomizdat, Moscow. [In Russian].

Naumov, G.B., Ryzhenko, B.N. and Khodakovsky, 1.L. (1974). Handbook of Thermodynamic Data. Natl. Tech. Inf. Service, 722176A, U.S. Dept. Commerce. 328 p.

Nordstrom, D.K., Plummer, L.N., Langmuir, D., Busenberg, E., May, H.M., Jones, B.F. and Parkhurst, D.L. (1990). Revised chemical equilibrium data for major water-mineral reactions and their limitations, Chapter 31 in: Chemical Modelling of Aqueous Systems II, (Melchoir D.C., Basset R.L., eds.) p. 398-413, ACS Symp. Ser. 146, American Chemical Society, Washington, DC

Palmer, D.A. and van Eldik, R. (1983). The chemistry of metal carbonate and carbon dioxide complexes. Chemical Reviews, 83, 651-731.

Parker, V.B. (1969). The status of the thermochemical data on some Ba compounds, Chap. 9. U.S. Nat. Bur. Standards NBSIR 10074. *[not cited in text]*

Parker, V.B. (1995). Thermodynamic properties of the aqueous Ba^{2+} ion and the key compounds of barium. Journal of Physical and Chemical Reference Data, 24(2), 1023-1036.

Parker V.B., Wagman D.D. and Evans W.H. (1971). Selected Values of Chemical Thermodynamic Properties. Tables for alkaline earth elements (elements 92 through 97 in the standard order of arrangement. Tech. Note 270-6, U.S. Department of Commerce, National Bureau of Standards, 106 p.

Radha, A.V. and Navrotsky, A. (2013). Thermodynamics of carbonates. Reviews in Mineralogy and Geochemistry, 77(1), 73-121.

Roberts, A.C. (1976). A mineralogical investigation of alstonite, $BaCa(CO_3)_2$. Unpubl. M.Sc. thesis, Queen's University, Kingston, Ontario, Canada.

Robie, R.A. (1962). Thermodynamic properties of minerals. U.S. Geological Survey Open File Report TEI-816. 31 p.

Robie, R.A. (1966). Section 20: Thermodynamic properties of minerals. Handbook of Physical Constants, Geological Society of America Memoirs, 97, 437-458.

Robie, R.A. and Hemingway, B.S. (1995), Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 Pascals) pressure and at higher temperatures. U.S. Geolical Survey Bulletin No. 2131, 461 p.

Robie, R.A., Hemingway, B.S. and Fisher, J.R. (1978). Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 Pa) pressure and at higher temperatures. U.S. Geological Survey Bulletin No. 1452. U.S. Government Printing Office, Washington, DC. 456 p.

Rossini, F.D., Wagman D.D., Evans W.H., Levine S. and Jaffe I. (1952). Selected values of chemical tbermodynamical properties. NBS Circular 500. 1268 p, Washington, D.C.

Ryabin, V.A., Ostroumov, M.A. and Svit, T.F. (1977). Thermodynamic Properties of Substances. Handbook (Termodinamicheskie Svoistva Veshchestv: Spravochnik). Khimiya, Leningr. Otd. Leningrad, USSR 389 p. [In Russian].

Sartori, F. (1975). New data on alstonite. Lithos, 8, 199-207.

Schloesing, T. (1872a). Sur la dissolution du carbonate de chaux par I'acide carbonique. Comptes Rendus de l'Academie des Sciences de Paris, 74, 1552-1556.

Schloesing, T. (1872b). Sur la dissolution du carbonate de chaux par I'acide carbonique. Deuxieme note. Comptes Rendus de l'Academie des Sciences de Paris, 75, 70-73.

Shock, E.L. and Koretsky, C.M. (1995). Metal-organic complexes in geochemical processes: estimation of standard partial molal thermodynamic properties of aqueous complexes between metal cations and monovalent organic acid ligands at high pressures and temperatures. Geochimica et Cosmochimica Acta. 59(8). 1497-1532.

Sillen, L.G. and Martell, A.E. (1964). Stability constants of metal-ions complexes. The Chemical Society, Burlington House, London, 356 p.

Smith, R.M. and Martell, A.E. (1976). Critical Stability Constants, Volume 4 Inorganic Complexes. Plenum Press, New York.

Stern, K.H. (2000). High Temperature Properties and Thermal Decomposition of Inorganic Salts with Oxyanions. 256 p. CRC Press LLC, 2000 N.W. Corporate Blvd., Boca Raton Florida 33431.

Stipp, S.L.S., Parks, G.A., Nordstrom, D.K. and Leckie, J.O. (1993). Solubility-product constant and thermodynamic properties for synthetic otavite, $CdCO_3$(s), and Aqueous Association Constants for the Cd(II)-CO_2-H_2O System. Geochimica et Cosmochimica Acta, 57(12), 2699-2713.

Sverjensky, D.A., Shock, E.L. and Helgeson, H.C. (1997). Prediction of the thermodynamic properties of aqueous metal complexes to 1000°C and 5 kb. Geochimica et Cosmochimica Acta, 61(7), 1359-1412. [New York, New York]: Elsevier Science.

Szymanski, J T. (1982). The crystal structure of hydrodresserite $BaAl_2(CO_3)_2(OH)_4.3H_2O$. Canadian Mineralogist, 20, 253-262.

Townley, R.W., Whitney, W.B. and Felsing, W.A. (1937). The solubilities of barium and strontium carbonates in aqueous solutions of some alkali chlorides. Journal of the American Chemical Society, 59, 631-633.

Wagman, D.D., Evans, W.H., Parker, V.B., Schumm, R.H., Halow, I., Bailey, S.M., Churney, K.L. and Nuttall, R.L. (1982). The NBS Tables of Chemical Thermodynamic Properties: Selected Values for Inorganic and C1 and C2 Organic Substances in SI Units: American Chemical Society and the American Institute of Physics for the National Bureau of Standards (Journal of Physical Chemical Reference Data, 11, supp. 2, 392 p.).

Weissenberger, G. (1914). Uber das Gleichgewicht $BaCO_3$-H_2O. Zeitschrift für Physikalische Chemie, 88, 257-270.

Wilcox, D.E. and Bromley, L.A. (1963). Computer Estimation of heat and free energy for simple inorganic compounds. Industrial and Engineering Chemistry, 55(7), 32-39.

Woods, T.L. and Garrels, R.M. (1987). Thermodynamic Values at Low Temperature for Natural Inorganic Materials. An Uncritical Summary. Oxford University Press. 242 p. plus references.

Yatsimirskii, K.B. (1956). The lattice energy of salts with polyatomic ions. Zhurnal Obshchei Khimii, 26, 2376-2380. [In Russian].

Yatsimirskii, K.B. and Krestov, G.A. (1960). Entropy of the lattice of compounds with multiatomic ions. Zhurnal Fizicheskoi Khimii, 34, 2448-2453. [In Russian].

Yoder, C.H. and Rowand, J.P. (2006). Application of the simple salt lattice energy approximation to the solubility of minerals. American Mineralogist, 91(5-6), 747-752.

Yoder, C.H., Gotlieb, N.R. and Rowand, A.L. (2010). The relative stability of stoichiometrically related natural and synthetic double salts. American Mineralogist, 95(1), 47-51.

Zhuk, N.P. (1954). Thermodynamic constants of sulfates, carbonates, chromates, bromates, iodates, oxalates, and other salts slightly soluble in water. Zhurnal Fizicheskoi Khimii, 28, 1690-1697. [In Russian].

Zubkova. N V., Pushcharovsky, D.Y, Pekov, I.V. and Rabadanov, M K. (2007). The crystal structure of podlesnoite, $BaCa_2(CO_3)_2F_2$. Zeitschrift für Kristallographie, 222, 474-476.

CADMIUM

Table 1. Association Constants for Aqueous Carbonate Complexes in the System $CdO-CO_2-H_2O$

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
$Cd^{2+} + CO_3^{2-} = CdCO_3(aq)$	5.4	-	Estimate		Zirino and Yamamoto (1972)
	5.1	-	$I = 0$	Bilinski et al. (1976)	Zirino and Yamamoto (1972)
	5.4	-	$I = 0$	Palmer and Van Eldik (1983)	Zirino and Yamamoto (1972)
	4.02 ± 0.04	-	20ºC, ISE, 0.001 *M* KNO_3,		Gardiner (1974)
	4.02	-	DPP, 0.001 *M* KNO_3	Bilinski et al. (1976)	Gardiner (1974)
	4.1	-		Long and Angino (1977)	Gardner (1974)
	3.1	-	Equilibration of at 25 ± 1ºC, with various concentrations of complexing ligand, L^{n-}.		Santillan-Medrano and Jurinak (1975)
	≈ 3.5	-	DPP, 0.1 *M* KNO_3		Bilinski et al. (1976)
	3.48	-	I = seawater, estimate		Sipos et al. (1980)
	4.35	-		Millero and Hawke (1992)	Turner et al. (1981)
	4.35	0.54	Estimate		Fouillac and Criaud (1984)
	3.55 ± 0.05	-	20ºC, ISE, graphic, 0.05 *M* $NaClO_4$		Stella et al. (1984)
	3.49 ± 0.04	-	20ºC, ISE, computer, 0.05 *M* $NaClO_4$		Stella et al. (1984)
	3.86 ± 0.04	-	20ºC, ASV, 0.05 *M* $NaClO_4$		Stella et al. (1984)
	4.02	-	3 mol/kg $NaClO_4^+$ (?)		Königsberger et al. (1991)
	4.71				Rai et al. (1991a)
	3.0 ± 0.4				Stipp et al. (1993)
$Cd^{2+} + 2CO_3^{2-} = Cd(CO_3)_2^{2-}$	6.25	-	I = seawater, estimate		Sipos et al. (1980)
	6.28 ± 0.10	-	20ºC, ISE, graphic, 0.05 *M* $NaClO_4$		Stella et al. (1984)
	6.37 ± 0.10	-	20ºC, ISE, computer, 0.05 *M* $NaClO_4$		Stella et al. (1984)
	6.50± 0.09	-	20ºC, ASV, 0.05 *M* $NaClO_4$		Stella et al. (1984)
	6.49	-			Rai et al. (1991a)
	6.4 ± 0.1	-	Estimate†		Stipp et al. (1993)

Table 1. Association Constants for Aqueous Carbonate Complexes in the System $CdO-CO_2-H_2O$ (Continued)

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
$Cd^{2+} + 3CO_3^{2-} = Cd(CO_3)_3^{4-}$	-6.24	-	Pol. 7 N (K_2CO_3-KOH)		Lake and Goodings (1958)
	6.24	-	Sol.	Krishnamurty et al. (1970)	Lake and Goodings (1958)
$Cd^{2+} + CO_3^{2-} + H^+ = CdHCO_3^+$	12.4		Estimate		Zirino and Yamamoto (1972)
	12.4	-	Estimate		Zirino and Yamamoto (1972)
	12.33*	-10.69*	Estimate		Fouillac and Criaud (1984)
	12.26 ± 0.01	-	20ºC, ISE, graphic, 0.05 *M* ClO_4		Stella et al. (1984)
	12.35 ± 0.01	-	20ºC, ISE, computer, 0.05 *M* ClO_4		Stella et al. (1984)
	11.70*	-			Millero and Hawke (1992)
	11.46 ± 0.1*	-	EMF, *I* = 0		Neher-Neuman (1992)
	11.83		Estimate †		Stipp et al. (1993)
$Cd^{2+} + H_2O + CO_2(g) = CdHCO_3^+ + H^+$	-7.11 ± 0.1	-	EMF, 3 *M* $NaClO_4$		Neher-Neuman (1992)
$Cd^{2+} + HCO_3^- = CdHCO_3^+$	2.1	-		Long and Angino (1977)	Zirino and Yamamoto (1972)
	2.1	-	*I* = 3	Palmer and Van Eldik (1983)	Sillen and Martell (1967)
	0.26	-	*I* = seawater, estimate		Sipos et al. (1980)
$Cd^{2+} + 2HCO_3^- = Cd(HCO_3)_2(aq)$	1.54	-	*I* = seawater, estimate		Sipos et al. (1980)

(1) At standard state (25°C, 1 atm, *I* = 0), unless otherwise noted.

† Based on a review of data in Stella et al. (1984)

* Corrected using bicarbonate dissociation equation from PHREEQC

Table 2. Solubility Constants of Solid Carbonates in the System $CdO-CO_2-H_2O$

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
Minerals					
Otavite					
$CdCO_3(s) = Cd^{2+} + CO_3^{2-}$	-13.740	-	Review. No correction for activity coefficients		Kelley and Anderson (1935)
	-13.740	-	25°C, thermodynamic calculations	Clever et al. (1992)	Kelley and Anderson (1935)
	-11.60	-	Based on electrochemical cell measurements		Saegusa (1950)
	-11.602	-	25°C, thermodynamic calculations	Clever et al. (1992)	Saegusa (1950)
	-13.60	-		Zhuk (1954)	Goskhimizdat (1952)
	-11.28	-	25°C, thermodynamic calculations	Latimer (1952)	Rossini et al. (1952)?
	-11.284	-	25°C, thermodynamic calculations	Clever et al. (1992)	Latimer (1952)
	-11.209	-	25°C, thermodynamic calculations	Clever et al. (1992)	Wagman et al. (1982)
	-11.292	-	25°C, thermodynamic calculations	Clever et al. (1992)	Egorov and Titova (1962)
	-12.00 ± 0.15	-			Gamsjäger et al. (1965)
	-12.00 ± 0.15	-		Naumov et al. (1974)	Gamsjäger et al. (1965)
	-12.000	-	25°C, thermodynamic calculations	Clever et al. (1992)	Gamsjäger et al. (1965)
	-11.180	-	25°C, I = 3.0 ($NaClO_4$)	Clever et al. (1992)	Gamsjäger et al. (1965)
	-11.2	-		Santillan-Medrano and Jurinak (1975)	Wagman et al. (1968)
	-11.215	-	16°C, I = 0.1 ($KClO_4$)	Clever et al. (1992)	Kaunaukov et al. (1973)
	-11.6	-			Santillan-Medrano and Jurinak (1975)
	-13.74	-	I = 0	Palmer and Van Eldik (1983)	Smith and Martell (1976)
	-12.060	-	25°C, thermodynamic calculations	Clever et al. (1992)	Krestov et al. (1977)
	-12.14	-			Miller et al. (1984)
	-12.14	-			Miller et al. (1984)
	-12.24	-	25°C, I = 0		Davis et al. (1987)
	-11.31 ± 0.03	-			Rai et al. (1991a)
	-12.1 ± 0.1	-			Stipp et al. (1993)

Table 2. Solubility Constants of Solid Carbonates in the System CdO-CO_2-H_2O (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	-12.398	-	5°C, I = 0.1 ($KClO_4$)	Clever et al. (1992)	Stipp et al. (1993)
	-12.102	-	25°C, I = 0.1 ($KClO_4$)	Clever et al. (1992)	Stipp et al. (1993)
	-12.201	-	50°C, I = 0.1 ($KClO_4$)	Clever et al. (1992)	Stipp et al. (1993)
	-12.00 ± 0.10	-			Gamsjäger et al. (1999)
	-12.1 ± 0.2	-	Review		Grauer (1999)
	-12.03 ± 0.13	-			Gamsjäger et al. (2011)
$CdCO_3(s) + 2H+ = Cd^{2+} + CO_2 + H_2O$	6.47 ± 0.15	-	3 *M* $NaClO_4$		Gamsjäger et al. (1965)
	6.41 ± 0.02	-	3 mol/kg $NaClO_4$		Königsberger et al. (1991)
	6.11 ± 0.10	-	25°C, I = 0		Gamsjäger et al. (2011)
$CdCO_3(cr) = CdCO_3(aq)$	-7.59 ± 0.30		25°C, I = 0		Gamsjäger et al. (2011)
$CdCO_3(cr) + CO_3^{2-} = Cd(CO_3)_2^{2-}$	-5.50 ± 0.10		25°C, I = 0		Gamsjäger et al. (2011)
Synthetic Phases					

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Table 3a. Association Constants of Aqueous Carbonate Complexes in the System $CdO-CO_2-H_2O$ extracted from Databases of Distribution-of-Species Codes

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Reference	Comments
$Cd^{2+} + CO_3^{2-} = CdCO_3(aq)$	4.37		MinteqA2	
	2.90		Wateq4f	
	3.00		V8.R6+	
	-	-	Minteq (2009)	
	4.3578	0.	Minteq (2006)	NIST46.4, MTQ3.11
	2.9	-	Phreeqc (2009)	
	2.9	-	Wateq4f (2005)	
	4.7	4.299	ThermoChimie v.7.b	#91RAI/FEL
			NAGRA/PSI (2001)	
	3.0000	-	Data0.YMP.R5	Stipp et al. (1993)
	4.6998	-	Thermoddem (2009)	Rai et al. (1991b)
$Cd^{2+} + 2CO_3^{2-} = Cd(CO_3)_2^{2-}$	7.23		MinteqA2	
	6.40		Wateq4f	
	6.40		V8.R6+	
	-	-	Minteq (2009)	
	7.2278	0.	Minteq (2006)	NIST46.4, MTQ3.11
	6.4	-	Phreeqc (2009)	
	6.4	-	Wateq4f (2005)	
	6.5	-	ThermoChimie v.7.b	#91RAI/FEL
	-	-	NAGRA/PSI (2001)	
	6.4000	-	Data0.YMP.R5	Stipp et al. (1993)
	6.4996	-	Thermoddem (2009)	Rai et al. (1991b)
$Cd^{2+} + CO_3^{2-} + H^+ = CdHCO_3^+$	11.83		MinteqA2	
	11.96		Wateq4f	
	11.83		V8.R6+	
	-	-	Minteq (2009)	
	10.6868	0.	Minteq (2006)	NIST46.4, MTQ3.11
	11.829	-	Phreeqc (2009)	
	11.829	-	Wateq4f (2005)	
	11.83	-	ThermoChimie v.7.b	Stipp et al. (1993)
	-	-	NAGRA/PSI (2001)	
	11.8288	-	Data0.YMP.R5	Stipp et al. (1993)
	11.8298	-	Thermoddem (2009)	92sti/par

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Table 3b. Solubility Constants of Solid Carbonates in the System $CdO-CO_2-H_2O$ extracted from Databases of Distribution-of-Species Codes

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Reference	Comments
Otavite				
$CdCO_3(s) = Cd^{2+} + CO_3^{2-}$	-12.06		MinteqA2	
	-12.10		Wateq4f	
	-12.10		V8.R6+	
	-	-	Minteq (2009)	
	-12.	-0.55	Minteq (2006)	
	-12.1	-0.079	Phreeqc (2009)	
	-12.1	-0.079	Wateq4f (2005)	
	-12.1	1.482	ThermoChimie v.7.b	#91RAI/FEL
	-	-	NAGRA/PSI (2001)	
	-12.1000	-	Data0.YMP.R5	Stipp et al. (1993)
	-12.0998	-	Thermoddem (2009)	91rai/fel

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Table 3c. Distribution-of-Species Codes: Database References

Database	Reference
Data0.com.VR.R6+	Wolery, T.J. (1994). EQ3NR, Letter report: EQ3/6 version 8.0. Differences from version 7. UCRL-ID-129749. Lawrence Livermore National Laboratory, Livermore, California. USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/LLNL.DAT
Data0.YMP.R5	BSC (Bechtel SAIC Company) (2007). Qualification of Thermodynamic Data for Geochemical Modeling of Mineral–Water Interactions in Dilute Systems. ANL-WIS-GS-000003 REV 01. Las Vegas, Nevada: Bechtel SAIC Company.DOC.20070619.0007.
MinteqA2	HydroGeoLogic, Inc. and Allison Geoscience Consultants, Inc. (1999). MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: User Manual Supplement for Version 4.0, Appendix A: thermodynamic database for MINTEQA2 V4.0, p. 44-74.
Minteq (2009)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/MINTEQ.DAT
Minteq (2006)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/minteq.v4.dat
NAGRA/PSI (2001)	Hummel, W., Berner, U., Curti, E., Pearson, F.J. and Thoenen, T. (2002). Nagra/PSI Chemical Thermodynamic Data Base 01/01. Universal Publishers/uPublish.com, Parkland, Florida. 565 p.
Phreeqc (2009)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/PHREEQC.DAT
ThermoChimie v.7.b	Duro, L., Grivém M. and Giffaut, E. (2010). ThermoChimie, the ANDRA thermodynamic database In Buckau G, Kienzler B, Duro L, Grivé M, Montoya V (eds). 2nd Annual Workshop Proceedings of the Collaborative Project “Redox Phenomena Controlling Systems” (7th EC FP CP Recosy) Larnaca (Cyprus) 16–19 March 2010. Karlsruhe: KIT Scientific Publishing, 275–283.
Thermoddem (2009)	Blanc P., Lassin A. and Piantone P. (2007) THERMODDEM a database devoted to waste minerals. BRGM (Orléans, France). For updates: http://thermoddem.brgm.fr
Wateq4f	Ball, J. W., & Nordstrom, D. K. (1991). User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters. U.S. GEOLOGICAL SURVEY, Open-File Report 91-183, Revised and reprinted - April, 2001. p. 81-94
Wateq4f (2005)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/WATEQ4F.DAT

Table 4a. Thermodynamic Properties of Cadmium Carbonate Minerals and Synthetic Solid Carbonates: Gibbs Free Energies of Formation

Mineral		$\Delta G^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
Minerals				
Otavite	$CdCO_3$	-683.75		Kelley and Anderson (1935)
		-683.67	Latimer (1952)	Kelley and Anderson (1935)
		-669.13		Saegusa (1950)
		-669.13	Karpov et al. (1968)	Saegusa (1950)
		-669.126	Karapet'yants and Karapet'yants (1970)	Saegusa (1950a)
		-672.79	Karapet'yants and Karapet'yants (1970)	Latimer (1952)
		-624.36 ± 4.18	Robie (1962, 1966)	Rossini et al. (1952)
		-670.28	Latimer (1952)	Rossini et al. (1952)?
		-670.28	Zhuk (1954)	Rossini et al. (1952), Karapet'yants (1953)
		-670.3	Woods and Garrels (1987)	Rossini et al. (1952)
		-670.3	Gamsjäger et al. (1965)	Rossini et al. (1952)
		-670.28	Karpov et al. (1968)	Rossini et al. (1952)
		-670.3	La Iglesia and Felix (1994)	Rossini et al. (1952)
calculated		-683.46		Zhuk (1954)
		-683.46	Karpov et al. (1968)	Zhuk (1954)
		-683.46	Karapet'yants and Karapet'yants (1970)	Zhuk (1954)
		-666.51	Karapet'yants and Karapet'yants (1970)	Karapet'yants (1955)
		-672.79	Karpov et al. (1968)	Karapet'yants (1957)
		-595.07 ± 4.18	Karpov et al. (1968)	Robie (1962)
		-51.04	Karpov et al. (1968)	Kireev (1964)
		-674.34 ± 0.84		Gamsjäger et al. (1965)
		-674.34	Karapet'yants and Karapet'yants (1970)	Gamsjäger et al. (1965)
		-674.25	Naumov et al. (1974)	Gamsjäger et al. (1965)
		-669.440 ± 2.636	Robie et al. (1979)	Wagman et al. (1968)
		-669.44 ± 2.64	Radha and Navrotsky (2013)	Wagman et al. (1968), Robie et al. (1978)
		-674.2	Woods and Garrels (1987)	Naumov et al. (1974)

Table 4a. Thermodynamic Properties of Cadmium Carbonate Minerals and Synthetic Solid Carbonates: Gibbs Free Energies of Formation (Continued)

Mineral		$\Delta G^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
		-674.2	La Iglesia and Felix (1994)	Naumov et al. (1974)
		-779.43	Stern (2000)	Barin et al. (1977)
		-669.4	Woods and Garrels (1987)	Robie et al. (1978)
		-669.4	Woods and Garrels (1987)	Wagman et al. (1982)
		-669.4 ± 2.6	Robie and Hemingway (1995)	Wagman et al. (1982), Chang and Ahmad (1982)
		-669.4	La Iglesia and Felix (1994)	Wagman et al. (1982), Robie et al. (1979), Sangameshwar and Barnes (1983)
		-669.4	Woods and Garrels (1987)	Sangameshwar and Barnes (1983)
		-662.7		Sverjensky (1984)
		-670.3 ± 2.1		La Iglesia and Felix (1994)
		-674.2 ± 0.6		Gamsjäger et al. (1999)
		-674.3 ± 0.6		Gamsjäger et al. (2011)
Synthetic Phases				
$CdZn(CO_3)_2$ *disordered*	$CdZn(CO_3)_2$	-1406.7 ± 1.1		Tareen et al. (1995)
$CdMg(CO_3)_2$ *disordered*	$CdMg(CO_3)_2$	-1701.5 ± 2.4		Tareen et al. (1995)
$CdMn(CO_3)_2$ *disordered*	$CdMn(CO_3)_2$	-1490.0 ± 3.0		Tareen et al. (1995)

(1) Formation from the oxides

Table 4b. Thermodynamic Properties of Cadmium Carbonate Minerals and Synthetic Solid Carbonates: Enthalpies of Formation

Mineral		$\Delta H^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
Minerals				
Otavite	$CdCO_3$	-761.03		Kelley and Anderson (1935)
		-749.05		Saegusa (1950)
		-749.05	Karpov et al. (1968)	Saegusa (1950)
		-749.049	Karapet'yants and Karapet'yants (1970)	Saegusa (1950a)
		-747.68	Latimer (1952)	Rossini et al. (1952)?
amorphous		-142.66	Latimer (1952)	Rossini et al. (1952)?
		-749.10 ± 2.49	Robie (1962, 1966)	Rossini et al. (1952)
		-747.68	Zhuk (1954)	Rossini et al. (1952), Karapet'yants (1953)
		-747.68	Karpov et al. (1968)	Rossini et al. (1952)
		-747.7	Woods and Garrels (1987)	Rossini et al. (1952)
		-747.7	La Iglesia and Felix (1994)	Rossini et al. (1952)
		-748.94 ± 8.37	Karpov et al. (1968)	Kubachewski and Evans (1956)
		-749.10 ± 2.51	Karpov et al. (1968)	Robie (1962)
		-99.58	Karpov et al. (1968)	Kireev (1964)
		-754.04	Naumov et al. (1974)	Gamsjäger et al. (1965)
		-747.85	Karpov et al. (1968)	Gerasimov (1966)
		-750.610 ± 2.510	Robie et al. (1979)	Wagman et al. (1968)
		-750.61 ± 2.51	Radha and Navrotsky (2013)	Wagman et al. (1968), Robie et al. (1979)
		-754.0	Woods and Garrels (1987)	Naumov et al. (1974)
		-751.87	Stern (2000)	Barin et al. (1977)
		-754.7	La Iglesia and Felix (1994)	Helgeson et al. (1978)
		-750.6	Woods and Garrels (1987)	Robie et al. (1978)
		-750.6	Woods and Garrels (1987)	Wagman et al. (1982)
		-750.6 ± 2.5	Robie and Hemingway (1995)	Wagman et al. (1982), Chang and Ahmad (1982)
		-150.6	La Iglesia and Felix (1994)	Wagman et al. (1982), Robie et al. (1979), Sangameshwar and Barnes (1983)
		-750.6	Woods and Garrels (1987)	Sangameshwar and Barnes (1983)
predicted		-750.6 ± 2.6		La Iglesia and Felix (1994)

Table 4b. Thermodynamic Properties of Cadmium Carbonate Minerals and Synthetic Solid Carbonates: Enthalpies of Formation (Continued)

Mineral		$\Delta H^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
		-746.63		Archer (1996)
		-752.1 ± 0.6		Gamsjäger et al. (1999)
		-752.2 ± 0.8		Gamsjäger et al. (2011)
amorphous		-742.66	Karpov et al. (1968)	Rossini et al. (1952)
Synthetic Phases				
$Cd(HCO_3)_2$	$Cd(HCO_3)_2$	-1497.87 ± 62.76	Estimated value of fictive compound	Wilcox and Bromley (1963)
		-1497.87	Karapet'yants and Karapet'yants (1970)	Wilcox and Bromley (1963)
$CdZn(CO_3)_2$, *disordered*	$CdZn(CO_3)_2$	-1566.3 ± 1.1		Tareen et al. (1995)
$CdMg(CO_3)_2$ *disordered*	$CdMg(CO_3)_2$	-1863.5 ± 2.4		Tareen et al. (1995)
$CdMn(CO_3)_2$ *disordered*	$CdMn(CO_3)_2$	-1641.5 ± 3.0		Tareen et al. (1995)

(1) Formation from the oxides

Table 4c. Thermodynamic Properties of Cadmium Carbonate Minerals and Synthetic Solid Carbonates: Entropies

Mineral		$S^0_{P_r,T_r}$	Secondary Reference	Primary Reference
Name	Formula	J K^{-1} gfw^{-1}		
Minerals				
Otavite	$CdCO_3$	105.44		Kelley and Anderson (1935)
		96.65		Saegusa (1950)
		96.65	Karpov et al. (1968)	Saegusa (1950)
		96.65	Karapet'yants and Karapet'yants (1970)	Saegusa (1950a)
		105.44	Latimer (1952)	Rossini et al. (1952)?
		105.44	Zhuk (1954)	Rossini et al. (1952), Karapet'yants (1953)
		105.44	Karpov et al. (1968)	Rossini et al. (1952)
		105.4	Woods and Garrels (1987)	Rossini et al. (1952)
calculated		149.37		Zhuk (1954)
		100.42	Karpov et al. (1968)	Kubachewski and Evans (1958)
		100.42	Karapet'yants and Karapet'yants (1970)	Kubaschewski and Evans (1958)
estimate		97.49 ± 2.51		Kelley and King (1961)
		97.49 ± 2.51	Robie (1962, 1966)	Kelley and King (1961)
		97.49 ± 2.51	Karpov et al. (1968)	Kelley and King (1961)
		97.49	Karapet'yants and Karapet'yants (1970)	Kelley and King (1961)
		97.49 ± 2.51	Naumov et al. (1974)	Kelley and King (1961)
		92.47 ± 2.51	Robie et al. (1979)	Kelley and King (1961)
		97.5	Woods and Garrels (1987)	Naumov et al. (1974)
		92.47	Stern (2000)	Barin et al. (1977)
		92.5	Woods and Garrels (1987)	Robie et al. (1978)
		92.5 ± 5.5	Robie and Hemingway (1995)	Chang and Ahmad (1982)
		92.5	Woods and Garrels (1987)	Wagman et al. (1982)
			Woods and Garrels (1987)	Sangameshwar and Barnes (1983)
		106.3		Sverjensky (1984)
		103.88		Archer (1996)
		103.9 ± 0.2		Gamsjäger et al. (1999)
		103.9 ± 0.2		Gamsjäger et al. (2011)

Table 4c

Thermodynamic Properties of Cadmium Carbonate Minerals and Synthetic Solid Carbonates: Entropies (Continued)

Mineral		$S^0_{P_r,T_r}$ J K^{-1} gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
Synthetic Phases				

Table 5. Crystallographic Properties of Cadmium Carbonate Minerals and Synthetic Solid Carbonates

	Name	Formula	Reference
	Minerals		
1	Otavite	$CdCO_3$	Gaines et al. (1997)
2	Otavite	$CdCO_3$	Mineralogy Database (http://webmineral.com/)
3	Otavite*	$CdCO_3$	Bromily et al. (2007)
4	Otavite	$CdCO_3$	Graf (1961)
5	Otavite	$CdCO_3$	Graf (1961)
6	Otavite	$CdCO_3$	Graf (1961)
	Synthetic Phases		
7	$CdMg(CO_3)_2$ *ordered*	$CdMg(CO_3)_2$	Graf (1961)
8	$CdMg(CO_3)_2$ *disordered*	$CdMg(CO_3)_2$	Graf (1961)

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
	Minerals									
1	Otavite	4.923		16.287				6	R3c	34.311
2	Otavite	4.912		16.199				6	R3c	33.973
3	Otavite*	4.9207		16.2968				6	R3c	34.299
4	Otavite	4.936		16.29				6		34.372
5	Otavite	4.9207		16.295				6		34.296
6	Otavite	4.9204		16.298				6		34.298
	Synthetic Phases									
7	$CdMg(CO_3)_2$ *ordered*	4.7770(9)		15.641(3)				3		62.049
8	$CdMg(CO_3)_2$ *disordered*	4.7746(9)		15.678(3)				3		62.133

* Synthesized at 600°C, 1GPa, 3 hr.

#Calculated from cell constants, this work

Table 6. Carbonate Minerals containing greater than 10 wt.% Cadmium*

Name	Formula	Cadmium, wt.%	gfw	Thermodynamic Data	
				Est.	Meas.
Otavite	$CdCO_3$	65.20	172.42	no	yes

*Data taken primarily from a compilation given by the Mineralogy Database (http://webmineral.com).

References

Archer, D.G. (1996). Thermodynamic properties of synthetic otavite, $CdCO_3$(cr): Enthalpy increment measurements from 4.5 K to 350 K. Journal of Chemical and Engineering Data, 41, 852-858

Barin, I., Knacke, O. and Kubaschewski, O. (1977). Thermodynamic properties of inorganic substances. Supplement. Springer Verlag, Berlin.

Bilinski, H., Huston, R. and Stumm, W. (1976). Determination of the stability constants of some hydroxo and carbonato complexes of Pb(II), Cu(II), Cd(II), and Zn(II) in dilute solutions by anodic stripping voltammetry and differential pulse polarography. Analytica Chimica Acta, 84, 157-164.

Bromiley, F A, Boffa, Ballaran, T. Langenhorst, F. and Seifert F. (2007). Order and miscibility in the otavite - magnesite solid solution. American Mineralogist, 92, 829-836.

Chang, Y.A. and Ahmad, H. (1982). Thermodynamic data on metal carbonates and related oxides. Metallurgical Society of AIME Publication, 235 p.

Clever, H.L., Derrick, M.E. and Johnson, S.A. (1992). The solubility of some sparingly soluble salts of zinc and cadmium in water and in aqueous electrolyte solutions. Journal of Physical and Chemical Reference Data, 21(5), 941-1004.

Davis, J.A., Fuller, C.C. and Cook, A.S. (1987). A model for trace metal sorption processes at the calcite surface: Adsorption of Cd^{2+} and subsequent solid solution formation. Geochimica et Cosmochimica Acta, 51, 1477-1490.

Egorov, A.M. and Titova, Z.P. (1962). Solubility products of salts with polyatomic ions as a function of the temperature. Zhurnal Neorganicheskoi Khimii, 7, 275-8 [In Russian]. Russian Journal of Inorganic Chemistry. (English Translation) 7, 141. (cited by Clever et al., 1992).

Fouillac, A. and Criaud, A. (1984). Carbonate and bicarbonate trace metal complexes: Critical reevaluation of stability constants. Geochemical Journal, 18, 297-303.

Gaines, R.V., Skinner, H.C.W., Foord, E.E., Mason, B., Rosenzweig, A. King, V.T. and Dowty, E. (1997). Dana's New Mineralogy (Eighth edition). John Wiley and Sons, Inc., New York. 1819 p.

Gamsjäger, H., Stuber, H.U. and Schindler, P. (1965). Zur Thermodynamik der Metallcarbonate 1. Löslichkeitskonstanten und Freie Bildungsenthalpien von Cadmiumcarbonat, ein Beitrag zur Thermodynamik des ternaren Systems Cd_{aq}^{2+}-$H_2O_{(l)}$-$CO_{2(g)}$. Helvetica Chimica Acta, 48, 723-729.

Gamsjäger, H., Preis, W., Konigsberger, E., Magalhaes, M.C. and Brandao, P. (1999). Solid-solute phase equilibria in aqueous solution. XI. Aqueous solubility and standard Gibbs energy of cadmium carbonate. Journal of Solution Chemistry, 28(6), 711-720.

Gamsjäger, H., Magalhães, M.C.F., Königsberger, E., Sawada, K., Churagulov, B.R., Schmidt, P. and Zeng, D. (2011). IUPAC-NIST Solubility Data Series. 92. Metal Carbonates. Part 1. Solubility and Related Thermodynamic Quantities of Cadmium (II) Carbonate in Aqueous Systems. Journal of Physical and Chemical Reference Data, 40(4), 043104-043104.

Gardiner, J. (1974). The chemistry of cadmium in natural water: I. A study of cadmium complex formation using the cadmium specific-ion electrode. Water Research, 8, 23-30.

Gardner, L.R. (1974). Organic vs inorganic trace metal complexes in sulfidic waters-some speculative calculations based on available stability constants. Geochimica et Cosmochimica Acta, 38, 1297-1302.

Gerasimov, Ya.I., Krestovnikov, A.N. and Shakhov, A.S. (1966). Khimicheskaya Termodinamika v Tsvetnoi Metallurgii, Tom IV (Chemical Thermodynamics in Nonferrous Metallurgy, Volume 4). 427 p. [In Russian].

Goskhimizdat. (1952). Chemical Reference, vol. 3. [In Russian]. (As cited in Zhuk, 1954).

Graf, D.L. (1961). Crystallographic tables for the rhombohedral carbonates. American Mineralogist, 46, 1283-1316.

Grauer, R. (1999). Solubility products of M(II) carbonates (edited and translated by U. Berner). Waste Management laboratory, PSI Bericht Nr. 99-04 January 1999 ISSN 1019-0643.

Helgeson, H.C., Delany, J.M., Nesbitt, H.W. and Bird, D.K. (1978). Summary and critique of the thermodynamic properties of rock-forming minerals. American Journal of Science, 278A.

Karapet'yants, M.Kh. (1953). Khimicheskaya Termodinamika (Chemical Thermodynamics). 2nd Edition. Goshkhimizdat. 611 p. [In Russian].

Karapet'yants, M.Kh. (1954b). Approximate method of calculation of entropy. Trudy Instituta - Moskovskii Khimiko-Tekhnologicheskii Institut imeni D. I. Mendeleeva, (No. 18), 27-34.

Karapet'yants, M.Kh. (1955). Approximate method for the calculation of the isobaric potential and heat of formation of different substances. Trudy Instituta - Moskovskii Khimiko-Tekhnologicheskii Institut imeni D. I. Mendeleeva, No. 20, p. 10-28. [In Russian].

Karapet'yants, M. Kh. (1957). Investigation of specific methods for the comparative calculation of physico-chmical properties of different substances. Author's dissertation for a degree in chemical sciences, MKhTI im D.I. Mendeleeva. [In Russian].

Karapet'yants, M.Kh. and Karapet'yants, M.L. (1970). Thermodynamic constants of Inorganic and Organic Compounds (trans. By J. Schmorak). Humphrey Science Publishers, Ann Arbor, Michigan. 461 p.

Karnaukhov, A.I., Grinevich, V.V. and Skobets, E.M. (1973). Determination of the solubility of slightly soluble compounds by inverse chronopotentiometry. Zhurnal Analiticheskoi Khimii, 28(12), 2298-301. [In Russian]. English translation: Journal of Analytical Chemistry (USSR), 18, 2042 (1973), (cited by Clever et al., 1992).

Karpov, I.K., Kashik, S.A. and Pampura, V.D. (1968). Thermodynamic Constants for Calculations in Geochemistry and Petrology. Izdva, Nauka, 143 p. [In Russian].

Kelley, K.K. and Anderson, C.T. (1935). Theoretical metallurgy. IV. Metal carbonates-correlations and applications of thermodynamic properties. U.S Bureau of Mines Bulletin No. 384, 73 p.

Kelley, K.K. and King. E.G. (1961). Contribution to the Data on Theoretical Metallurgy. XIV. Entropies of the Elements and Inorganic Compounds. U.S Bureau of Mines Bulletin No. 592, 149 p.

Kireev, V.A. (1964). Acid-base properties of oxides. Zhurnal Fizicheskoi Khimii, 38(8), 1881-1894. [In Russian].

Königsberger, E., Hausner, R. and Gamsjäger, H. (1991). Solid-solute phase equilibria in aqueous solution: V. The system $CdCO_3$-$CaCO_3$-CO_2-H_2O. Geochimica et Cosmochimica Acta, 55, 3505-3514.

Krestov, G.A., Kobenin, V.A. and Sokolov, V.N. (1977). Method for calculating the solubility product at 273-373°K. Zhurnal Neorganicheskoi Khimii, 22(10), 2864-7 [In Russian]. Russian Journal of Inorganic Chemistry (English Translation), 22, 1556 (cited by Clever et al., 1992).

Krishnamurty, K.V. Harris, G.M. and Sastri, V.S. (1970). The chemistry of the metal carbonato complexes. Chemical Reviews, 70(2), 171-197.

Kubachewski, O. and Evans, E.M. (1956). [In Russian],

Kubaschewski, O. and Evans, E.L. (1958). Metallurgical Thermochemistry, 3rd Edition, Pergamon Press, New York.

La Iglesia, A. and Félix, J.F. (1994). Estimation of thermodynamic properties of mineral carbonates at high and low temperatures from the sum of polyhedral contributions. Geochimica et Cosmochimica Acta, 58(19), 3983-3991.

Lake, P.E. and Goodings, J.M. (1958). The nature of the cadmium ions in hydroxide and carbonate solutions. Canadian Journal of Chemistry, 36, 1089-1096.

Latimer, W.M. (1952). The Oxidation States of the Elements and their Potentials in Aqueous Solutions. Second edition. Prentice Hall, New York, 392 p.

Long, D.T. and Angino, E.E. (1977). Chemical speciation of Cd, Cu, Pb, and Zn in mixed freshwater, seawater, and brine solutions. Geochimica et Cosmochimica Acta, 41(9), 1183-1191.

Miller, R.L., Grove, D.B., and Stollenwerk, K.G. (1984). A solution-chemistry model of the interference of cadmium-carbonate precipitation in the determination of cation-exchange separation factors. USGS Water Supply Paper 2262, p. 33-41.

Millero, F.J. and Hawke, D.J. (1992). Ionic interactions of divalent metals in natural waters. Marine Chemistry, 40, 19-48.

Naumov, G.B., Ryzhenko, B.N. and Khodakovsky, I.L. (1974). Handbook of Thermodynamic Data. National Technical Information Service, 722176A, U.S. Dept. Commerce. 328 p.

Neher-Neumann, E. (1992). Studies on metal carbonate equilibria 24. The hydrogen carbonate and carbonate complexes of lead(II) and cadmium ions in acid solutions and a 3 M (Na)ClO_4 ionic medium at 25ºC. Acta Chemica Scandinavica, 46, 231-239.

Palmer, D.A. and van Eldik, R. (1983). The chemistry of metal carbonato and carbon dioxide complexes. Chemical Reviews, 83, 651–731.

Radha, A.V. and Navrotsky, A. (2013). Thermodynamics of carbonates. Reviews in Mineralogy and Geochemistry, 77(1), 73-121.

Rai, D., Felmy, A. R. and Moore, D.A. (1991a). Thermodynamic model for aqueous Cd^{2+}-CO_3^{2-} ionic interactions in high-ionic-strength carbonate solutions, and the solubility product of crystalline $CdCO_3$. Journal of Solution Chemistry, 20, 1169-1187.

Rai D., Felmy A.R. and Szelmeczka R.W. (1991b). Hydrolysis constants and ion interaction parameters for Cd(II) in zero to high concentrations of NaOH, KOH, and the solubility product of crystalline $Cd(OH)_2$. Journal of Solution Chemistry, 20, p. 375 390.

Robie, R.A. (1962). Thermodynamic properties of minerals. U.S. Geological Survey Open File Report TEI-816. 31 p.

Robie, R.A. (1966). Section 20: Thermodynamic properties of minerals. Handbook of Physical Constants, Geological Society of America Memoirs, 97, 437-458.

Robie, R.A. and Hemingway, B.S. (1995). Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 Pascals) pressure and at higher temperatures. U.S. Geological Survey Bulletin No. 2131, 461 p.

Robie R.A., Hemingway B.S. and Fisher J.R. (1978). Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 Pa) pressure and at higher temperatures. U.S. Geological Survey Bulletin No. 1452. U.S. Government Printing Office, Washington, DC. 456 p.

Robie, R.A., Hemingway, B.S. and Fisher, J.R. (1979). Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 Pa) pressure and at higher temperatures. U.S. Geological Survey Bulletin 1452. (Reprinted with corrections). U.S. Government Printing Office, Washington, DC. 456 p.

Rossini F.D., Wagman D.D., Evans W.H., Levine S. and Jaffe I. (1952). Selected values of chemical thermodynamical properties. NBS Circular 500. 1268 p., Washington, D.C.

Saegusa, F. (1950). Thermodynamic studies on carbonates. Part I. Thermodynamic studies of cadmium, zinc, lead, mercurous, and thallous carbonates. Science Reports. Tohoku University, First Series, 34(1), 55-65.

Sangameshwar, S.R. and Barnes, H.L. (1983). Supergene processes in zinc-lead-silver sulfide ores in carbonates. Economic Geology, 78, 1379-1397.

Santillan-Medrano, J. and Jurinak, J.J. (1975). The chemistry of lead and cadmium in soil: Solid phase formation. Soil Science Society of America Proceedings, 39, 85l-856.

Sillen, L.G. and Martell, A.E. (1967). Stability Constants of Metal Ion Complexes, 2nd ed.; Chemical Society, London, Special Publication 17, 754 p.

Sipos, L., Raspor, B., Nurnberg, H.W. and Pytkowicz, R.M. (1980). Interaction of metal complexes with coulombic ion-pairs in aqueous media of high salinity. Marine Chemistry, 9(1), 37-47.

Smith, R.M. and Martell, A.E. (1976). Critical Stability Constants, Volume 4, Inorganic Complexes. Plenum Press: New York.

Stella, R., Valentini, M.T.G. and Borroni, P.A. (1984). The use of cadmium ion-selective electrode and voltammetric techniques in the study of cadmium complexes with inorganic ligands. 4th Symposium on Ion-Selective Electrodes, Matrafured, p. 633-645.

Stern, K.H. (2000). High Temperature Properties and Thermal Decomposition of Inorganic Salts with Oxyanions. 256 p. CRC Press LLC, 2000 N.W. Corporate Blvd., Boca Raton Florida 33431.

Stipp, S.L., Parks, G.A., Nordstrom, D.K. and Leckie, J.O. (1993). Solubility-product constant and thermodynamic properties for synthetic otavite, $CdCO_3$(s), and aqueous association constants for the Cd(II)-CO_2-H_2O system. Geochimica et Cosmochimica Acta, 57, 2699-2713.

Sverjensky, D.A. (1984). Prediction of Gibbs free energies of calcite type carbonates and the equilibrium distribution of trace elements between carbonates and aqueous solutions. Geochimica et Cosmochimica Acta, 48, 1127-1134.

Tareen, J.A.K., A.R. Fazeli, B. Basavalingu and G.T. Bhandige (1995). Decarbonation curves and associated thermodynamic data for synthetic Cd-dolomites $CdMg(CO_3)_2$, $CdMn(CO_3)_2$ and $CdZn(CO_3)_2$. Journal of Thermal Analysis and Calorimetry, 44 (4), 937-954.

Turner, D.R., Whitfield, M. and Dickson, A.G. (1981). The equilibrium speciation of dissolved components in freshwater and seawater at 25°C and 1 atm pressure. Geochimica et Cosmochimica Acta, 45, 855-881.

Wagman, D.D., Evans, W.H., Parker, V.B., Halow, I., Bailey, S.M. and Schumm, R.H. (1968). Selected Values of Chemical Thermodynamic Properties. NBS Technical Note 270-3.

Wagman, D.D., Evans, W.H., Parker, V.B., Schumm, R.H., Halow, I., Bailey, S.M., Churney, K.L. and Nuttall, R.L. (1982). The NBS Tables of Chemical Thermodynamic Properties: Selected Values for Inorganic and C1 and C2 Organic Substances in SI Units: American Chemical Society and the American Institute of Physics for the National Bureau of Standards (Journal of Physical Chemical Reference Data, 11, supp. 2, 392 p.).

Wllcox. D.E. and Bromley, L.A. (1963). Computer Estimation of heat and free energy for simple inorganic compounds. Industrial and Engineering Chemistry, 55(7), 32-39.

Woods, T.L. and Garrels, R.M. (1987). Thermodynamic Values at Low Temperature for Natural Inorganic Materials. An Uncritical Summary. Oxford University Press. 242 p. plus references.

Zhuk, N.P. (1954). Thermodynamic constants of sulfates, carbonates, chromates, bromates, iodates, oxalates, and other salts slightly soluble in water. Zhurnal Fizicheskoi Khimii, 28, 1690-1697. [In Russian].

Zirino, A. and Yamamoto, S. (1972). A pH-dependent model for the chemical speciation of copper, zinc, cadmium, and lead in seawater. Limnology and Oceanography, 17, 661-671.

CHROMIUM

Table 1. Association Constants for Aqueous Carbonate Complexes in the System $CrO/Cr_2O_3/CrO_2$-CO_2-H_2O

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
Cr(II)					
$2Cr^{2+} + yCO_3^{2-} = Cr_2(CO_3)_y^{(4-2y)+}$	-	-	Evidence for binuclear complex		Cannon and Tsay (1967)
$2Cr^{2+} + 4CO_3^{2-} + H_2O = [Cr_2(CO_3)_4(H_2O)_2]^{2-}$	-	-			Ouahes and Suquet (1968)
Cr(III)					
$Cr(OH)_3(am) + CO_2(g) = Cr(OH)(CO_3)_2^{2-} + 2H^+$	-19.07 ± 0.41	-	22 ± 2ºC		Rai et al. (2007)
$Cr(OH)_3(am) + OH^- + CO_3^{2-} = Cr(OH)_4CO_3^{3-}$	-4.19 ± 0.19	-	22 ± 2ºC		
Cr(IV)					

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Table 2. Solubility Constants of Solid Carbonates in the System $CrO/Cr_2O_3/CrO_2$-CO_2-H_2O

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
Minerals					
Cr(II)					
$\underline{CrCO_3(cr)}$					
$CrCO_3(cr) = Cr^{2+} + CO_3^{2-}$					
Cr(III)					
Synthetic Phases					

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Table 3a. Association Constants of Aqueous Carbonate Complexes in the System CrO/Cr_2O_3/CrO_2-CO_2-H_2O extracted from Databases of Distribution-of-Species Codes

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Database	Source
Cr(II)				
No entries	No data	No data		
Cr(III)				
No entries				
	No data	No data		

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Table 3b. Solubility Constants of Solid Carbonates in the System CrO/Cr_2O_3/CrO_3-CO_2-H_2O extracted from Databases of Distribution-of-Species Codes

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Database	Source
Cr(II)				
	No data	No data		
Cr(III)				
	No data	No data		

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Table 3c. Distribution-of-Species Codes: Database References

Database	Reference
Data0.com.VR.R6+	Wolery, T.J. (1994). EQ3NR, Letter report: EQ3/6 version 8.0. Differences from version 7. UCRL-ID-129749. Lawrence Livermore National Laboratory, Livermore, California. USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/LLNL.DAT
Data0.YMP.R5	BSC (Bechtel SAIC Company) (2007). Qualification of Thermodynamic Data for Geochemical Modeling of Mineral–Water Interactions in Dilute Systems. ANL-WIS-GS-000003 REV 01. Las Vegas, Nevada: Bechtel SAIC Company.DOC.20070619.0007.
MinteqA2	HydroGeoLogic, Inc. and Allison Geoscience Consultants, Inc. (1999). MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: User Manual Supplement for Version 4.0, Appendix A: thermodynamic database for MINTEQA2 V4.0, p. 44-74.
Minteq (2009)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/MINTEQ.DAT
Minteq (2006)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/minteq.v4.dat
NAGRA/PSI (2001)	Hummel, W., Berner, U., Curti, E., Pearson, F.J. and Thoenen, T. (2002). Nagra/PSI Chemical Thermodynamic Data Base 01/01. Universal Publishers/uPublish.com, Parkland, Florida. 565 p.
Phreeqc (2009)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/PHREEQC.DAT
ThermoChimie v.7.b	Duro, L., Grivém M. and Giffaut, E. (2010). ThermoChimie, the ANDRA thermodynamic database In Buckau G, Kienzler B, Duro L, Grivé M, Montoya V (eds). 2nd Annual Workshop Proceedings of the Collaborative Project “Redox Phenomena Controlling Systems” (7th EC FP CP Recosy) Larnaca (Cyprus) 16–19 March 2010. Karlsruhe: KIT Scientific Publishing, 275–283.
Thermoddem (2009)	Blanc P., Lassin A. and Piantone P. (2007) THERMODDEM a database devoted to waste minerals. BRGM (Orléans, France). For updates: http://thermoddem.brgm.fr
Wateq4f	Ball, J. W., & Nordstrom, D. K. (1991). User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters. U.S. GEOLOGICAL SURVEY, Open-File Report 91-183, Revised and reprinted - April, 2001. p. 81-94
Wateq4f (2005)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/WATEQ4F.DAT

Table 4a. Thermodynamic Properties of Chromium Carbonate Minerals and Synthetic Solid Carbonates: Gibbs Free Energies of Formation

Mineral		$\Delta G^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
Minerals				
Cr(II)				
Cr(III)				
Barbertonite	$Mg_6Cr^{III}_2(CO_3)(OH)_{16}•4(H_2O)$	No data		
Stichtite	$Mg_6Cr^{III}_2(CO_3)(OH)_{16}•4(H_2O)$	No data		
Petterdite	$PbCr^{III}_2(CO_3)_2(OH)_4•(H_2O)$	No data		
Putnisite,	$SrCa_4Cr^{3+}_8(CO_3)_8SO_4(OH)_{16}•25(H_2O)$	No data		
Cr(IV)				
Synthetic Phases				
Cr(II)				
$CrCO_3$[1]	$CrCO_3$	No data		Erhardt et al. (1980)
$Li_2Cr(CO_3)_2•x(H_2O)$	$Li_2Cr(CO_3)_2•x(H_2O)$	No data		Ouahes et al. (1970a,b)
$Na_2Cr(CO_3)_2•10(H_2O)$	$Na_2Cr(CO_3)_2•10(H_2O)$	No data	Cannon and Tsay (1967)	Bauge (1900)
$Na_2Cr(CO_3)_2•(H_2O)$	$Na_2Cr(CO_3)_2•(H_2O)$	No data	Cannon and Tsay (1967)	Bauge (1900)
$Na_2Cr(CO_3)_2•0.5(H_2O)$	$Na_2Cr(CO_3)_2•0.5(H_2O)$	No data		Suquet and Malard (1968), Ouahes and Suquet (1968), Ouahes et al. (1970a,b)
$K_2Cr(CO_3)_2•1.5(H_2O)$	$K_2Cr(CO_3)_2•1.5(H_2O)$	No data	Cannon and Tsay (1967)	Bauge (1900)
$K_2Cr(CO_3)_2•2(H_2O)$	$K_2Cr(CO_3)_2•2(H_2O)$	No data		Suquet and Malard (1968), Ouahes and Suquet (1968), Ouahes et al. (1970a,b)
$(NH_4)_2Cr(CO_3)_2•(H_2O)$	$(NH_4)_2Cr(CO_3)_2•(H_2O)$	No data	Cannon and Tsay (1967)	Bauge (1900)
$(NH_4)_2Cr(CO_3)_2•2(H_2O)$	$(NH_4)_2Cr(CO_3)_2•2(H_2O)$	No data		Suquet and Malard (1968), Ouahes and Suquet (1968), Ouahes et al. (1970a,b)
$Cs_2Cr(CO_3)_2•2(H_2O)$	$Cs_2Cr(CO_3)_2•2(H_2O)$	No data		Suquet and Malard (1968), Ouahes and Suquet (1968), Ouahes et al. (1970a,b)

Table 4a. Thermodynamic Properties of Chromium Carbonate Minerals and Synthetic Solid Carbonates: Gibbs Free Energies of Formation (Continued)

Mineral		$\Delta G^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
$Rb_2Cr(CO_3)_2$•2(H_2O)	$Rb_2Cr(CO_3)_2$•2(H_2O)	No data		Suquet and Malard (1968), Ouahes and Suquet (1968), Ouahes et al. (1970a,b)
$MgCr(CO_3)_2$•x(H_2O)	$MgCr(CO_3)_2$•x(H_2O)	No data		Ouahes et al. (1970a,b)
Cr(III)				
$NH_4Cr(CO_3)(OH)_2$[2]	$NH_4Cr(CO_3)(OH)_2$	No data		Ali et al. (2005)
$(NH_4)_2[Cr_2(OH)_4(CO_3)_2]$•($H_2O$)	$(NH_4)_2[Cr_2(OH)_4(CO_3)_2]$•($H_2O$)	No data		Sengupta et al. (2004)
$K_7[Cr_4(OH)_9(CO_3)_5]$•6(H_2O)	$K_7[Cr_4(OH)_9(CO_3)_5]$•6(H_2O)	No data		Sengupta et al. (2004)
$Na_3[Cr_2(OH)_5(CO_3)_2]$•4(H_2O)	$Na_3[Cr_2(OH)_5(CO_3)_2]$•4(H_2O)	No data		Sengupta et al. (2004)
$NH_4[Co(NH_3)_6]$ $[Cr_3(OH)_7(CO_3)_3]$•4(H_2O)	$NH_4[Co(NH_3)_6]$ $[Cr_3(OH)_7(CO_3)_3]$•4(H_2O)	No data		Sengupta et al. (2004)
$K_6[Co(NH_3)_6]_2[Cr_2(OH)_4(CO_3)_3]$ 3	$K_6[Co(NH_3)_6]_2[Cr_2(OH)_4(CO_3)_3]$ 3	No data		Sengupta et al. (2004)
$Mg_xZn_{6-x}Cr^{III}_2(OH)_{16}(CO_3)$•4($H_2O$)	$Mg_xZn_{6-x}Cr^{III}_2(OH)_{16}(CO_3)$ •4(H_2O)	No data		Frost et al. (2003)
$Ni_xCo_{6-x}Cr_2(OH)_{16}(CO_3)$ •4(H_2O)	$Ni_xCo_{6-x}Cr_2(OH)_{16}(CO_3)$ •4(H_2O)	No data		Frost et al. (2003)
$Ni_{1-x}Cr_x(OH)_2(CO_3)_{x/2}$•n($H_2O$) (x ≈ 0.32-0.36)[3]	$Ni_{1-x}Cr_x(OH)_2(CO_3)_{x/2}$•n($H_2O$) (x ≈ 0.32-0.36)	No data		Jobbagy et al. (2007)
Cr(IV)				
Synthetic[4]	$Cr^{IV}O_{10}(CO_3)_2$ (?)	No data		Ali et al. (2005)

Notes 1. Synthesis from $Cr(CO)_6$ at 280°C and 3,000 bar $P(CO_2)$; 2. Dawsonite structure synthesized from a gel at pH = 11 and 100°C; 3. Homogeneous nucleation involving decomposition of urea at 180ºC; 4. Decomposition product of $NH_4Cr(CO_3)(OH)_2$ at 153-350°C,

Table 4b. Thermodynamic Properties of Chromium Carbonate Minerals and Synthetic Solid Carbonates: Enthalpies of Formation

Mineral		$\Delta H^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
Minerals				
Cr(II)				
		No data		
Cr(III)				
		No data		
Cr(IV)				
		No data		
Synthetic Phases				
		No data		

Table 4c. Thermodynamic Properties of Chromium Carbonate Minerals and Synthetic Solid Carbonates: Entropies

Mineral		$S^0_{P_r,T_r}$ J K^{-1} gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
Minerals				
Cr(II)				
		No data		
Cr(III)				
		No data		
Cr(IV)				
		No data		
Synthetic Phases				
		No data		

Table 5. Crystallographic Properties of Chromium Carbonate -Minerals and -Synthetic Solid Carbonates

	Name	Formula	Reference
	Minerals		
	Cr(II)		
1			
	Cr(III)		
2	Barbertonite	$Mg_6Cr^{III}_2(CO_3)(OH)_{16}•4(H_2O)$	Frondel (1941)
3	Barbertonite	$Mg_6Cr^{III}_2(CO_3)(OH)_{16}•4(H_2O)$	Gaines et al. (1997)
4	Barbertonite	$Mg_6Cr^{III}_2(CO_3)(OH)_{16}•4(H_2O)$	Mineralogy Database (http://webmineral.com/)
5	Mountkeithite	$Mg_{21.52}Ni_{2.24}Cu_{0.04}Cr_{2.21}Fe_{2.85}Al_{1.42}(OH)_{52.14}(CO_3)_{2.42}(SO4)_{5.04}•20.40(H_2O))$	Hudson and Bussell (1981)
6	Mountkeithite	$Ni_{1.12}Cu_{0.02}Fe^{3+}_{1.42}Cr_{1.1}Al_{0.71}(SO_4)_{2.52}(CO_3)_{1.21}Mg_{10.76}(OH)_{26.07}•10.2(H_2O)$	Gaines et al. (1997)
7	Petterdite	$PbSr_{0.1}Cr_{1.5}Al_{0.4}(CO_3)_{2.1}(OH)_{3.6}•(H_2O)$	Gaines et al. (1997)
8	Petterdite	$PbCr^{III}_2(CO_3)_2(OH)_4•(H_2O)$	Birch et al. (2000)

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
	Minerals									
	Cr(II)									
1										
	Cr(III)									
2	Barbertonite	6.17		15.52				1	P63/mmc	308.14
3	Barbertonite	6.20		15.6				1	P63/mmc	312.74
4	Barbertonite	6.17		15.52				1	P63/mmc	308.14
5	Mountkeithite	10.698		22.545				1	hex	1345.7
6	Mountkeithite	10.698		22.545				2	hex	672.83
7	Petterdite	9.079	16.321	5.786				4	Pbnm	129.08
8	Petterdite	9.079(3)	16.321(9)	5.786(7)				4	Pbnm	129.08

	Name	Formula	Reference
9	Putnisite	$SrCa_4Cr^{3+}_8(CO_3)_8SO_4(OH)_{16}•25(H_2O)$	Elliot et al. (2014)
10	Stichtite	$Mg_6Cr^{III}_2(CO_3)(OH)_{16}•4(H_2O)$	Gaines et al. (1997)
11	Stichtite	$Mg_6Cr^{III}_2(CO_3)(OH)_{16}•4(H_2O)$	Mineralogy Database (http://webmineral.com/)
12	Stichtite	$Mg_6Cr^{III}_2(CO_3)(OH)_{16}•4(H_2O)$ (3R1)	Mills et al. (2011)
13	Stichtite[1]	$Mg_6Cr^{III}_2(CO_3)(OH)_{16}•4(H_2O)$ (2H1)	Mills et al. (2011)
14	Stichtite[1]	$Mg_6Cr^{III}_2(CO_3)(OH)_{16}•4(H_2O)$ (2H1)	Mills et al. (2011)
15	Stichtite[1]	$Mg_6Cr^{III}_2(CO_3)(OH)_{16}•4(H_2O)$	RRUFF ID: R050328.1 Mineralogy Database (http://webmineral.com/)
16	Stichtite[1]	$Mg_6Cr^{III}_2(CO_3)(OH)_{16}•4(H_2O)$	RRUFF ID: R050475.1 Mineralogy Database (http://webmineral.com/)
	Cr(IV)		
17			

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
9	Putnisite	15.351(3)	20.421(4)	18.270(4)				4	Pnma	862.27
10	Stichtite	6.19		46.47				3	R-3m	309.54
11	Stichtite	6.18		46.38				3	R-3m	307.94
12	Stichtite	3.09575(3)		23.5069(6)				3/8	R-3m	313.31
13	Stichtite[1]	3.09689(6)		15.6193(8)				1/4	P6-3/mmc	312.50
14	Stichtite[1]	3.09646(6)		15.627(1)				1/4	P6-3/mmc	312.57
15	Stichtite[1]	3.0868(4)		23.517(6				3/8	hex	311.64
16	Stichtite[1]	3.146(2)		24.53(9)				3/8	hex	337.65
	Cr(IV)									
17										

	Name	Formula	Reference
	Synthetic Phases		
	Cr(II)		
18	$CrCO_3$[1]	$CrCO_3$	Erhardt et al. (1980)
19	$Li_2Cr(CO_3)_2•x(H_2O)$	$Li_2Cr(CO_3)_2•x(H_2O)$	Ouahes et al. (1970a,b)
20	$Na_2Cr(CO_3)_2•10(H_2O)$	$Na_2Cr(CO_3)_2•10(H_2O)$	Bauge (1900)
21	$Na_2Cr(CO_3)_2•(H_2O)$	$Na_2Cr(CO_3)_2•(H_2O)$	Bauge (1900)
22	$Na_2Cr(CO_3)_2•0.5(H_2O)$	$Na_2Cr(CO_3)_2•0.5(H_2O)$	Ouahes et al. (1970a,b)
23	$K_2Cr(CO_3)_2•1.5(H_2O)$	$K_2Cr(CO_3)_2•1.5(H_2O)$	Bauge (1900)
24	$K_2Cr(CO_3)_2•2(H_2O)$	$K_2Cr(CO_3)_2•2(H_2O)$	Ouahes et al. (1970a,b)
25	$(NH_4)_2Cr(CO_3)_2•(H_2O)$	$(NH_4)_2Cr(CO_3)_2•(H_2O)$	Bauge (1900)
26	$(NH_4)_2Cr(CO_3)_2•2(H_2O)$	$(NH_4)_2Cr(CO_3)_2•2(H_2O)$	Ouahes et al. (1970a,b)
27	$Cs_2Cr(CO_3)_2•2(H_2O)$	$Cs_2Cr(CO_3)_2•2(H_2O)$	Ouahes et al. (1970a,b)
28	$Rb_2Cr(CO_3)_2•2(H_2O)$	$Rb_2Cr(CO_3)_2•2(H_2O)$	Ouahes et al. (1970a,b)
29	$MgCr(CO_3)_2•x(H_2O)$	$MgCr(CO_3)_2•x(H_2O)$	Ouahes et al. (1970a,b)

	Name	Cell Constants							Space Group	$V^{o\#}$ cm^3 gfw^{-1}
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
	Synthetic Phases									
	Cr(II)									
18	$CrCO_3$[1]									
19	$Li_2Cr(CO_3)_2•x(H_2O)$	6.83	7.04	9.77	85.15	117.23	108.83	?	tricl	?
20	$Na_2Cr(CO_3)_2•10(H_2O)$									
21	$Na_2Cr(CO_3)_2•(H_2O)$									
22	$Na_2Cr(CO_3)_2.0.5(H_2O)$	13.94	9.843	8.886					orthorh	
23	$K_2Cr(CO_3)_2•1.5(H_2O)$									
24	$K_2Cr(CO_3)_2.2(H_2O)$	6.913	15.57	7.590		108.08		4?	P2/c	116.92
25	$(NH_4)_2Cr(CO_3)_2•(H_2O)$								P2/c	
26	$(NH_4)_2Cr(CO_3)_2•2(H_2O)$	6.918	16.18	7.800		108.92			P2/c	124.35
27	$Cs_2Cr(CO_3)_2•2(H_2O)$	-	-	-	-				P2/c	
28	$Rb_2Cr(CO_3)_2•2(H_2O)$	-	-	-	-				P2/c	
29	$MgCr(CO_3)_2•x(H_2O)$	6.83	7.04	9.77	85.15	117.23	108.83	?	tricl	?

	Name	Formula	Reference
	Synthetic Phases, cont.		
	Cr(III)		
30	$(NH_4)_2[Cr_2(OH)_4(CO_3)_2]\bullet(H_2O)$	$(NH_4)_2[Cr_2(OH)_4(CO_3)_2]\bullet(H_2O)$	Sengupta et al. (2004)
31	$K_7[Cr_4(OH)_9(CO_3)_5]\bullet6(H_2O)$	$K_7[Cr_4(OH)_9(CO_3)_5]\bullet6(H_2O)$	Sengupta et al. (2004)
32	$Na_3[Cr_2(OH)_5(CO_3)_2]\bullet4(H_2O)$	$Na_3[Cr_2(OH)_5(CO_3)_2]\bullet4(H_2O)$	Sengupta et al. (2004)
33	$NH_4[Co(NH_3)_6]$ $[Cr_3(OH)_7(CO_3)_3]$ $\bullet4(H_2O)$	$NH_4[Co(NH_3)_6]$ $[Cr_3(OH)_7(CO_3)_3]\bullet4(H_2O)$	Sengupta et al. (2004)
34	$K_6[Co(NH_3)_6]_2[Cr_2(OH)_4(CO_3)_3]_3$	$K_6[Co(NH_3)_6]_2[Cr_2(OH)_4(CO_3)_3]_3$	Sengupta et al. (2004)
35	$Mg_xZn_{6-x}Cr^{III}{}_2(OH)_{16}(CO_3)\bullet4(H_2O)$	$Mg_xZn_{6-x}Cr^{III}{}_2(OH)_{16}(CO_3)\bullet4(H_2O)$	Frost et al. (2003)
36	$TlCr^{III}(CO_3)_2$	$TlCr^{III}(CO_3)_2$	Ehrhardt et al. (1981)
	Cr(IV)		
37	$Cr^{IV}O_{10}(CO_3)_2$ (?)	$Cr^{IV}O_{10}(CO_3)_2$ (?)	Ali et al. (2005)

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
	Synthetic Phases, cont.									
	Cr(III)									
30	$(NH_4)_2[Cr_2(OH)_4(CO_3)_2]\bullet(H_2O)$									
31	$K_7[Cr_4(OH)_9(CO_3)_5]\bullet6(H_2O)$									
32	$Na_3[Cr_2(OH)_5(CO_3)_2]\bullet4(H_2O)$									
33	$NH_4[Co(NH_3)_6]$ $[Cr_3(OH)_7(CO_3)_3]$ $\bullet4(H_2O)$									
34	$K_6[Co(NH_3)_6]_2[Cr_2(OH)_4(CO_3)_3]_3$									
35	$Mg_xZn_{6-x}Cr^{III}{}_2(OH)_{16}(CO_3)\bullet4(H_2O)$									
36	$TlCr^{III}(CO_3)_2$	19.917(7)	8.605(3)	19.138(5)		104.79(3)		24	$P2_1/c$	79.576
	Cr(IV)									
37	$Cr^{IV}O_{10}(CO_3)_2$ (?)									

Note. 1. Stichtite (2H1) = Barbertonite. See Mills et al. (2011)

#Calculated from cell constants, this work

Table 6. Carbonate Minerals containing greater than 10 wt.% Chromium*

Name	Formula	Chromium, wt.%	gfw	Thermodynamic Data	
				Est.	Meas.
Cr(II)					
Cr(III)					
Barbertonite	$Mg_6Cr^{III}_2(CO_3)(OH)_{16}•4(H_2O)$	15.90	654.01	no	no
Mountkeithite	$(Mg,Ni)_{11}(Fe^{III},Cr^{III})_3(SO_4,CO_3)_{3.5}(OH)_{24}•11(H_2O)$	4.01	1426.01	no	no
Petterdite	$PbCr^{III}_2(CO_3)_2(OH)_4•(H_2O)$	15.29	510.01	no	no
Stichtite	$Mg_6Cr^{III}_2(CO_3)(OH)_{16}•4(H_2O)$	15.90	654.01	no	no
Cr(IV)					

*Data taken primarily from a compilation given by the Mineralogy Database (http://webmineral.com).

References

Ali, A.A., Hasan, M.A. and Zaki, M.I. (2005). Dawsonite-type precursors for catalytic Al, Cr, and Fe oxides: Synthesis and characterization. Chemistry of Materials, 17(26), 6797-6804.

Bauge, G. (1900). Sur quelques carbonates doubles du protoxyde de chrome. Oxyde salin de chrome. Annales de Chimie et de Physique, 19(7), 158-184.

Birch, W.D., U. Kolitsch, T. Witzke, L. Nasdala, and R.S. Bottrill (2000). Petterdite, the Cr-dominant analogue of dundasite, a new mineral species from Dundas, Tasmania, Australia and Callenberg, Saxony, Germany. Canadian Mineralogist, 38, 1467-1476.

Cannon, R.D. and Tsay, J.L. (1967). Binuclear carbanato-complex of chromium (II). Nature, 216, 681-682.

Ehrhardt, H.; Schober, H. C.; Seidel, H. (1980). Hochdrucksynthesen von Carbonaten. III. Darstellung von Carbonaten zweiwertiger Metalle durch Zersetzung ihrer Oxalate unter hohem CO_2-Druck. Zeitschrift für anorganische und allgemeine Chemie, 465, 83-91.

Ehrhardt, H., Lemor, R. and Seidel, H. (1981). Hochdrucksynthesen von Carbonaten. V [l]. Carbonatdarstellungen durch Schmelzreaktionen unter hohen CO_2-Drucken. Zeitschrift für anorganische und allgemeine Chemie, 477, 183-195.

Elliott, P., Giester, G., Rowe, R. and Pring, A. (2014). Putnisite, $SrCa_4Cr^{3+}_8(CO_3)_8SO_4(OH)_{16}\cdot 25H_2O$, a new mineral from Western Australia: description and crystal structure. Mineralogical Magazine, 78(1), 131-144.

Frondel, C. (1941). Constitution and polymorphism of the pyroaurite and sjögrenite groups, American Mineralogist, 26, 295-315.

Frost, R.L., Martens, W., Ding, Z., Kloprogge, J.T. and Johnson, T.E. (2003). The role of water in synthesized hydrotalcites of formula $Mg_xZn_{6-x}Cr_2(OH)_{16}(CO_3)\cdot 4H_2O$ and $Ni_xCo_{6-x}Cr_2(OH)_{16}(CO_3)\cdot 4H_2O$-an infrared spectroscopic study. Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy, 59A(2), 291-302.

Hudson, D.R. and M. Bussell (1981). Mountkeithite, a new pyroaurite-related mineral with an expanded interlayer containing exchangeable $MgSO_4$. Mineralogical Magazine, 44, 345-350.

Jobbagy, M., Blesa, M.A. and Regazzoni, A. E. (2007). Homogeneous precipitation of layered Ni(II)-Cr(III) double hydroxides. Journal of Colloid and Interface Science, 309(1), 72-77.

Mills S.J., Whitfield P.S., Wilson S.A., Woodhouse J.N., Dipple G.M., Raudsepp M. and Francis C.A. (2011). The crystal structure of stichtite, re-examination of barbertonite, and the nature of polytypism in MgCr hydrotalcites. American Mineralogist. 96, 179-187.

Ouahes, R. and Suquet, H. (1968). Étude du spectre infrarouge des complexes cabonato de chrome-II et d'alcalins. Comptes Rendus des Séances de l'Academie des Sciences, Serie C: Sciences Chimiques, 267(20), 1325-1328.

Ouahes, R., Devallez, B. and Amiel, J. (1970a). Contribution à l'étude des complexes carbonato Chrome (II). III. Étude par spectroscopie Infrarouge des sels d'alcalins, d'ammonium et de magnésium. Revue de Chimie Minérale, 7(5), 855-874.

Ouahes, R., Pezerat, H. and Gayoso, J. (1970b). Contribution à l'étude des complexes carbonato Chrome (II). II. Étude radiocristallographique des sels d'alcalins, d'ammonium et de magnésium. Revue de Chimie Minérale. 7(5), 849-854.

Rai, D., Moore, D.A., Hess, N.J., Rosso, K.M., Rao, L. and Heald, S.M. (2007). Chromium(III) hydroxide solubility in the aqueous K^+-H^+-OH^--CO_2-HCO_3^--CO_3^{2-}-H_2O System: A thermodynamic model. Journal of Solution Chemistry, 36, 1261-1285.

Sengupta, A. K. and Nandi, A. K. (2004). Complex Carbonates of Chromium(III). Zeitschrift für anorganische und allgemeine Chemie, 404(1), 81-86.

Suquet, H. and Malard, C. (1968). Sur la structure de quelques complexes cabonato de chrome-II et d'alcalins. Comptes Rendus des Seances de l'Academie des Sciences, Serie C: Sciences Chimiques, 267(13), 770-772

COBALT

Table 1. Association Constants for Aqueous Carbonate Complexes in the System CoO/Co_2O_3-CO_2-H_2O

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary reference
Co(II)					
$Co^{2+} + CO_3^{2-} = CoCO_3(aq)$	3.17	-	Estimated. *I* = 0.7	Cosovic et al. (1982)	Zhorov et al. (1976)
	3.15 ± 0.10	-	20 ± 1ºC, Pol., 0.56 *M* $NaClO_4$		Cosovic et al. (1982)
	4 – 5	-	Estimate at *I* = 0 from Cosovic et al. (1982)	Hummel and Curti (2003)	Cosovic et al. (1982)
$Co^{2+} + 2CO_3^{2-} = Co(CO_3)_2^{2-}$					
$Co^{2+} + CO_3^{2-} + H^+ = CoHCO_3^+$					
$Co^{2+} + HCO_3^- = CoHCO_3^+$	1.39	-	Estimated	Cosovic et al. (1982)	Zhorov et al. (1976)
Co(III)					
$Co^{3+} + 3CO_3^{2-} = Co(CO_3)_3^{3-}$	-	-	Synthesis		McCutcheon and Schuele (1953)
	29	-	1 *M* KCl? Approximate value, Hydrolysis of CO_3^{2-} and HCO_3^- neglected.		Al-Obadie (1980)
	29	-	*I* = 1	Palmer and Van Eldik (1983)	Al-Obadie (1980)

(1) At standard state (25°C, 1 atm, *I* = 0), unless otherwise noted.

* Corrected using bicarbonate dissociation equation from PHREEQC

Table 2. Solubility Constants of Solid Carbonates in the System CoO/Co_2O_3-CO_2-H_2O

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary reference
Minerals					
Co(II)					
Sphaerocobaltite					
$CoCO_3(s) = Co^{2+} + CO_3^{2-}$					
	-12.84	-	Estimated value		Kelley and Anderson (1935)
	-12.10	-	Estimated from primary reference with revized value of DGf for Co^{2+}	Latimer (1952)	Kelley and Anderson (1935)
	-12.0	-		Zhuk (1954)	Goskhimizdat (1952)
	-9.82			Naumov et al. (1974)	Butkevitsch (1967)
	-9.98	-		Cosovic et al. (1982)	Butkevitsch (1967)
	-9.98	-	I = 0	Palmer and Van Eldik (1983)	Smith and Martell (1976)
	-9.52	-	Estimated. I = 0.7	Cosovic et al. (1982)	Zhorov et al. (1976)
	-11.2 ± 0.2	-	Recommended value		Grauer (1999)
$CoCO_3(cr) + 2H+ = Co^{2+} + CO_2(g) + H_2O$	10.35	-		Cosovic et al. (1982)	Kelley and Anderson (1935)
	8.17		25°C, I = 0	Gamsjäger (1974)	Butkevitsch (1967)
	7.19 ± 0.04		50°C, 1 M $NaClO_4$,	Gamsjäger (1985)	Reiterer (1980)
Co(III)					
Synthetic Phases					
Co(II)					
$K_2Co(CO_3)_2$					
$K_2Co(CO_3)_2 = Co^{2+} + 2K^+ + CO_3^{2-}$	-6.00	-	Estimated		Yoder and Rowand (2006)
$Co_2Al^{III}(CO_3)_{0.5}(OH)_6 \bullet (H_2O)$					

Table 2. Solubility Constants of Solid Carbonates in the System CoO/Co_2O_3-CO_2-H_2O (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary reference
$Co_2Al^{III}(CO_3)_{0.5}(OH)_6 \bullet (H_2O) + 6H^+ = 2Mg^{2+} + Al^{3+} + 0.5CO_3^{2-} + 7H_2O$	23.89 ± 0.38 20.92 ± 1.03 23.04 ± 0.44 23.09 ± 0.70	- - - -	*I* = 0, corrected using the Davies equation. *I* = 6.5 m*M* and 12.8 m*M*. Equilibration up to 147 days		Johnson and Glasser (2003)
$Co_{0.76}Al_{0.24}(OH)_2(CO_3)_{0.12} \bullet 0.81(H_2O) + 2H^+ = 0.76Co^{2+} + 0.24Al^{3+} + 0.12CO_3^{2-} + 2.81H_2O$	7.12	-	Calculated from thermochemical data.		Allada et al. (2006)
Co(III)					

(1) At standard state (25°C, 1 atm, *I* = 0), unless otherwise noted.

Table 3a. Association Constants of Aqueous Carbonate Complexes in the System CoO/Co_2O_3-CO_2-H_2O extracted from Databases of Distribution-of-Species Codes

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Database	Source
Co(II)				
$Co^{2+} + CO_3^{2-} = CoCO_3(aq)$	-	-	Minteq (2009)	
	4.228	0	Minteq (2006)	NIST46.4; MTQ3.11
	-	-	Phreeqc (2009)	
	-	-	Wateq4f (2005)	
	4.23	-	ThermoChimie v.9	
	-	-	NAGRA/PSI (2001)	
	-	-	Data0.com.V8.R6+	
	-	-	Data0.YMP.R5	
$Co^{2+} + HCO_3^- = CoCO_3(aq) + H^+$	6.0970	-	Thermoddem (2009)	97Smi/Mar
$Co^{2+} + 2CO_3^{2-} = Co(CO_3)_2^{2-}$	-	-	Minteq (2009)	
	-	-	Minteq (2006)	
	-	-	Phreeqc (2009)	
	-	-	Wateq4f (2005)	
		-	ThermoChimie v.9	
	-	-	Data0.com.V8.R6+	
	-	-	NAGRA/PSI (2001)	
	-	-	Data0.YMP.R5	
	-	-	Thermoddem (2009)	
$Co^{2+} + CO_3^{2-} + H^+ = CoHCO_3^+$	-	-	Minteq (2009)	
	12.2199	0	Minteq (2006)	NIST46.4; MTQ3.11
	-	-	Phreeqc (2009)	
	-	-	Wateq4f (2005)	
	12.22	-	ThermoChimie v.9	
	-	-	Data0.com.V8.R6+	
	-	-	NAGRA/PSI (2001)	
	-	-	Data0.YMP.R5	
$Co^{2+} + HCO_3^- + H^+ = CoHCO_3^+$	-1.8930	0	Thermoddem (2009)	97Smi/Mar
Co(III)				
No entries				

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Table 3b. Solubility Constants of Solid Carbonates in the System CoO/Co_2O_3-CO_2-H_2O extracted from Databases of Distribution-of-Species Codes

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Database	Source
Sphaerocobaltite				
$CoCO_3(s) = Co^{2+} + CO_3^{2-}$	-	-	Minteq (2009)	
	-9.98	-12.7612	Minteq (2006)	
	-	-	Phreeqc (2009)	
	-	-	Wateq4f (2005)	
	-11.2	-	ThermoChimie v.9	
	-	-	NAGRA/PSI (2001)	
$CoCO_3(s) + H^+ = Co^{2+} + HCO_3^-$	-0.2331	-	Data0.com.V8.R6+	
	0.7971	-	Data0.YMP.R5	
	-0.8730	-	Thermoddem (2009)	

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Table 3c. Distribution-of-Species Codes: Database References

Database	Reference
Data0.com.V8.R6+	Wolery, T.J. (1994). EQ3NR, Letter report: EQ3/6 version 8.0. Differences from version 7. UCRL-ID-129749. Lawrence Livermore National Laboratory, Livermore, California. USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/LLNL.DAT
Data0.YMP.R5	BSC (Bechtel SAIC Company) (2007). Qualification of Thermodynamic Data for Geochemical Modeling of Mineral–Water Interactions in Dilute Systems. ANL-WIS-GS-000003 REV 01. Las Vegas, Nevada: Bechtel SAIC Company.DOC.20070619.0007.
MinteqA2	HydroGeoLogic, Inc. and Allison Geoscience Consultants, Inc. (1999). MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: User Manual Supplement for Version 4.0, Appendix A: thermodynamic database for MINTEQA2 V4.0, p. 44-74.
Minteq (2009)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/MINTEQ.DAT
Minteq (2006)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/minteq.v4.dat
NAGRA/PSI (2001)	Hummel, W., Berner, U., Curti, E., Pearson, F.J. and Thoenen, T. (2002). Nagra/PSI Chemical Thermodynamic Data Base 01/01. Universal Publishers/uPublish.com, Parkland, Florida. 565 p.
Phreeqc (2009)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/PHREEQC.DAT
ThermoChimie v.9	Duro, L., Grivém M. and Giffaut, E. (2010). ThermoChimie, the ANDRA thermodynamic database In Buckau G, Kienzler B, Duro L, Grivé M, Montoya V (eds). 2nd Annual Workshop Proceedings of the Collaborative Project “Redox Phenomena Controlling Systems” (7th EC FP CP Recosy) Larnaca (Cyprus) 16–19 March 2010. Karlsruhe: KIT Scientific Publishing, 275–283.
Thermoddem (2009)	Blanc P., Lassin A. and Piantone P. (2007) THERMODDEM a database devoted to waste minerals. BRGM (Orléans, France). For updates: http://thermoddem.brgm.fr
Wateq4f	Ball, J. W., & Nordstrom, D. K. (1991). User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters. U.S. GEOLOGICAL SURVEY, Open-File Report 91-183, Revised and reprinted - April, 2001. p. 81-94
Wateq4f (2005)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/WATEQ4F.DAT

Table 4a. Thermodynamic Properties of Cobalt Carbonate Minerals and Synthetic Solid Carbonates: Gibbs Free Energies of Formation

Mineral Name	Formula	$\Delta G^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Minerals				
Co(II)				
Sphaerocobaltite *estimated*	$CoCO_3$	-650.90		Kelley and Anderson (1935)
		-650.90	Latimer (1952)	Kelley and Anderson (1935)
		-650.90	Karpov et al. (1968)	Latimer (1952)
		-650.90	Karapet'yants and Karapet'yants (1970)	Latimer (1952)
		-650.9	Woods and Garrels (1987)	Latimer (1952)
		-647.26	Karapet'yants and Karapet'yants (1970)	Karapet'yants (1953)
calculated		-648.06		Zhuk (1954)
		-648.06	Karpov et al. (1968)	Zhuk (1954)
		-648.06	Karapet'yants and Karapet'yants (1970)	Zhuk (1954)
		-647.26	Karpov et al. (1968)	Karapet'yantz (1954b)
		-650.9	Woods and Garrels (1987)	Pourbaix (1960)
		-36.40	Karpov et al. (1968)	Kireev (1964)
		-640.15	Naumov et al. (1974)	Butkevitsch (1967)
		-640.2	Woods and Garrels (1987)	Naumov et al. (1974)
		-739.20	Stern (2000)	Barin et al. (1977)
		-657.27 ± 3.10		Tareen et al. (1991)
Co(III)				
Synthetic Phases				
Co(II)				
$CoCO_3.K_2CO_3$	$CoCO_3.K_2CO_3$	-1726.74	Karapet'yants and Karapet'yants (1970)	Karapet'yants (1953)
Co(III)				

(1) Formation from the oxides

Table 4b. Thermodynamic Properties of Cobalt Carbonate Minerals and Synthetic Solid Carbonates: Enthalpies of Formation

Mineral Name	Formula	$\Delta H^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Minerals				
Co(II)				
Sphaerocobaltite	$CoCO_3$	-725.129	Kelley and Anderson (1935)	De Carli (1931)
		-722.58	Zhuk (1954)	Rossini et al. (1952), Karapet'yantz (1953)
		-89.54	Karpov et al. (1968)	Kireev (1964)
		-716.09	Naumov et al. (1974)	Butkevitsch (1967)
		-712.95		Wagman et al. (1969)
		-716.1	Woods and Garrels (1987)	Naumov et al. (1974)
		-713.00	Stern (2000)	Barin et al. (1977)
		-732.21 ± 3.10		Tareen et al. (1991)
		-114.36 ± 1.10[(1)]		Allada et al. (2002), Allada et al. (2006)
		-745.82 ± 1.68		Allada et al. (2002), Allada et al. (2006)
		-745.82 ± 1.68	Radha and Navrotsky (2013)	Allada et al. (2002)
Co(III)				
Synthetic Phases				
Co(II)				
$Co(HCO_3)_2$	$Co(HCO_3)_2$	-1451.85 ± 62.76	Estimated value of fictive compound	Wilcox and Bromley (1963)
		-1451.85	Karapet'yants and Karapet'yants (1970)	Wilcox and Bromley (1963)
Co-Al hydrotalcite	$Co_{0.756}Al_{0.244}(OH)_2(CO_3)_{0.1202}(NO_3)_{0.0018}\cdot 0.810(H_2O)$	957.89 ± 3.33		Allada et al. (2002)
	$Co_{0.756}Al_{0.244}(OH)_2(CO_3)_{0.1202}(NO_3)_{0\cdot 0018}\cdot 0.810H_2O$	–967.89 ± 3.33	Radha and Navrotsky (2013)	Allada et al. (2002)
	$Co_{0.68}Al_{0.32}(OH)_2(CO_3)_{0.16}\cdot 0.779 H_2O$	-1044.17 ± 2.54		Allada et al. (2002)
	$Co_{0.68}Al_{0.32}(OH)_2(CO_3)_{0.16}\cdot 0.78(H_2O)$	-1044.17 ± 2.54	Radha and Navrotsky (2013)	Allada et al. (2002)

Table 4b. Thermodynamic Properties of Cobalt Carbonate Minerals and Synthetic Solid Carbonates: Enthalpies of Formation (Continued)

Mineral Name	Formula	$\Delta H^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
	$Co_{0.756}Al_{0.244}(OH)_2(CO_3)_{0.122}$•0.80($5H_2O$)	-991.79 ± 1.72		Allada et al. (2002)
	$Co_{0.76}Al_{0.24}(OH)_2(CO_3)_{0.12}$•0.81($H_2O$)	-991.79 ± 1.72	Radha and Navrotsky (2013)	Allada et al. (2002)
	$Co_{0.68}Al_{0.32}(OH)_2(CO_3)_{0.16}$•0.78($H_2O$)	-1044.17 ± 2.54		Allada et al. (2006)
	$Co_{0.69}Al_{0.31}(OH)_2(CO_3)_{0.16}$•0.68($H_2O$)	-1006.26 ± 1.62		Allada et al. (2006)
	$Co_{0.70}Al_{0.30}(OH)_2(CO_3)_{0.16}$•0.23($H_2O$)	-877.34 ± 1.35		Allada et al. (2006)
	$Co_{0.76}Al_{0.24}(OH)_2(CO_3)_{0.12}$•0.81($H_2O$)	-991.79 ± 1.72		Allada et al. (2006)
	$Co_{0.80}Al_{0.20}(OH)_2(CO_3)_{0.10}$•0.76($H_2O$)	-933.36 ± 2.17		Allada et al. (2006)
	$Co_{0.83}Al_{0.17}(OH)_2(CO_3)_{0.09}$•0.29($H_2O$)	-777.09 ± 1.97		Allada et al. (2006)
Co(III)				

(1) Formation from the oxides

Table 4c. Thermodynamic Properties of Cobalt Carbonate Minerals and Synthetic Solid Carbonates: Entropies

Mineral		$S^0_{P_r,T_r}$ J K^{-1} gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
Minerals				
Co(II)				
Sphaerocobaltite	$CoCO_3$			
calculated		91.63		Zhuk (1954)
		91.63	Karpov et al. (1968)	Zhuk (1954)
		91.63	Karapet'yants and Karapet'yants (1970)	Zhuk (1954)
		88.5		Kostryukov and Kalinkina (1964)
		88.5	Karapet'yants and Karapet'yants (1970)	Kostryukov and Kalinkina (1964)
		88.62 ± 0.42	Naumov et al. (1974)	Kostryukov and Kalinkina (1964)
		88.6	Woods and Garrels (1987)	Naumov et al. (1974)
		87.86	Stern (2000)	Barin et al. (1977)
Synthetic Phases				
Co(II)				
Co(III)				

Table 5. Crystallographic Properties of Cobalt Carbonate Minerals and Synthetic Solid Carbonates

	Name	Formula	Reference
	Minerals		
	Co(II)		
1	Kolwezite	$Cu_{1.34}Co_{0.66}(CO_3)(OH)_2$	Deliens and Piret (1980), Gaines et al. (1997)
2	Sphaerocobaltite	$CoCO_3$	Graf (1961), Gaines et al. (1997)
3	Sphaerocobaltite		RRUFF ID: R060497.9 Mineralogy Database (http://webmineral.com/)
4	Sphaerocobaltite		Pertlik (1986)
	Co(III)		
5	Comblainite	$Ni^{II}_6Co^{III}_2(CO_3)(OH)_{16}•4(H_2O)$	Gaines et al. (1997)
6	Comblainite	$Ni^{II}_6Co^{III}_2(CO_3)(OH)_{16}•4(H_2O)$	Piret and Deliens (1980)

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
	Minerals									
	Co(II)									
1	Kolwezite	9.50	12.15	3.189	93.32	90.74	91.47	4	P1 or P-1	55.301
2	Sphaerocobaltite	4.6581		14.958				6	R3c	28.211
3	Sphaerocobaltite	4.630(8)		14.94(4)				6	R3c	27.838
4	Sphaerocobaltite	4.6618		14.963				6	R3c	28.265
	Co(III)									
5	Comblainite	6.08		45.58				3	R-3m or R3m,	292.92
6	Comblainite	3.038		22.79				3/8	R-3m, R3m, R32, R-3, or R3	292.53

	Name	Formula	Reference
	Synthetic Phases		
	Co(II)		
7			
	Co(III)		
8			

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
	Synthetic Phases									
	Co(II)									
7										
	Co(III)									
8										

[#]Calculated from cell constants, this work

Table 6. Carbonate Minerals containing greater than 10 wt.% Cobalt*

Name	Formula	Cobalt, wt.%	gfw	Thermodynamic Data	
				Est.	Meas.
Co(II)					
Kolwezite	$(Cu,Co^{II})_2(CO_3)(OH)_2$	17.84	218.07	No	No
Sphaerocobaltite	$Co^{II}CO_3$	49.55	118.94	No	yes
Co(III)					
Comblainite	$Ni^{II}_6Co^{III}_2(CO_3)(OH)_{16}•4(H_2O)$	13.48	874.19	No	No

*Data taken primarily from a compilation given by the Mineralogy Database (http://webmineral.com).

References

Al-Obadie, M.S. (1980). Thermodynamics of the formation of tris (malonato) cobaltate (III) and tris (carbonato) cobaltate (III). Inorganic Chemistry, 19(10), 2897-2898.

Allada, R.K., Navrotsky, A., Berbeco, H.T. and Casey, W.H. (2002). Thermochemistry and aqueous solubilities of hydrotalcite-like solids. Science, 296, 721-723.

Allada, R.K., Peltier, E., Navrotsky, A., Casey, W.H. Johnson, C.A., Berbeco, H.T. and Sparks, D.L. (2006). Calorimetric determination of the enthalpies of formation of hydrotalcite-like solids and their use in the geochemical modeling of metals in natural waters. Clays and Clay Minerals, 54(4), 409-417.

Barin, I., Knacke, O., and Kubaschewski, O. (1977). Thermodynamic properties of inorganic substances. Supplement. Springer Verlag, Berlin.

Butkevitsch, O. (1967). Studies on the aqueous solubility of metal carbonates. Part 1. The solubility of cobalt(II) carbonate. Suomen Kemistilehti, B40, 148-150.

Cosovic, B., Degobbis, D. Bilinski, H. and Branica, M. (1982). Inorganic cobalt species in seawater. Geochimica et Cosmochimica Acta, 46, 151-158.

De Carli, F., cited in Landolt-Bornstein. (1931). Physikalisch-chemische Tabellen. Julius Springer Berlin, 2nd Supplement, 2, 1519. (Cited in Kelley and Anderson, 1935.)

Deliens, M. and P. Piret (1980). La kolwézite, un hydroxycarbonate de cuivre et de cobalt analogue à la glaukosphaerite et à la rosasite. Bulletin de Mineralogie, 103, 179-184.

Gamsjäger, H. (1974). Wechselwirkung von Metalloxiden, -hydroxiden, -carbonaten und -sulfiden mit Wasser, Radex-Rundschau, 4, 274-285.

Gamsjäger, H. (1985). Solid state chemical model for the solubility behavior of homogeneous solid cobalt manganese carbonate mixtures. Berichte der Bunsen-Gesellschaft, 89(12), 1318-22.

Goskhimizdat. (1952). Chemical Reference, vol. 3. [In Russian]. (As cited in Zhuk, 1954).

Graf, D.L. (1961). Crystallographic tables for the rhombohedral carbonates. American Mineralogist, 46, 1283–1316.

Grauer, R. (1999). Solubility products of M(II)-Carbonates [edited and translated by U. Berner]. Paul Scherrer Institute, Waste Management Laboratory, PSI Bericht Nr. 99-04, ISSN 1019-0643, 24 p.

Hummel, W. and Curti, E. (2003). Nickel Aqueous Speciation and Solubility at Ambient Conditions: A Thermodynamic Elegy. Monatshefte für Chemie, 134, 941-973.

Johnson, C.A., and Glasser, F.P. (2003). Hydrotalcite-like minerals ($M_2Al(OH)_6(CO_3)_{0.5}.XH_2O$, where M = Mg, Zn, Co, Ni) in the environment: synthesis, characterization and thermodynamic stability. Clays and Clay Minerals, 51(1), 1-8.

Karapet'yants, M.Kh. (1953). Khimicheskaya Termodinamika (Chemical Thermodynamics) 2nd Edition. Goshkhimizdat. 611 p. [In Russian].

Karapet'yants, M.Kh. (1954a). Approximate method of calculation of the free energies and heats of formation of various substances. Zhurnal Fizicheskoi Khimii, 28, 353-358. [In Russian].

Karapet'yants, M.Kh. (1954b). Approximate method of calculation of entropy. Ph.D Thesis, Trudy Instituta - Moskovskii Khimiko-Tekhnologicheskii Institut imeni D. I. Mendeleeva, (No. 18), 27-34. [In Russian].

Karapet'yants, M.Kh. and Karapet'yants, M.L. (1970). Thermodynamic constants of Inorganic and Organic Compounds (trans. By J. Schmorak). Humphrey Science Publishers, Ann Arbor, Michigan. 461 p.

Karpov, I.K., Kashik, S.A. and Pampura, V.D. (1968). Thermodynamic Constants for Calculations in Geochemistry and Petrology. Izdva, Nauka, 143 p. [In Russian].

Kelley, K.K. and Anderson, C.T. (1935). Theoretical metallurgy. IV. Metal carbonates-correlations and applications of thermodynamic properties. U.S. Bureau of Mines Bulletin No. 384, 73 p.

Kelley, K.K. and King. E.G. (1961). Contribution to the Data on Theoretical Metallurgy. XIV. Entropies of the Elements and Inorganic Compounds. U.S. Bureau of Mines Bulletin No. 592, 149 p.

Kireev, V.A. (1964). Acid-base properties of oxides. Zhurnal Fizicheskoi Khimii, 38(8), 1881-1894. [In Russian].

Kostryukov, V.N. and Kalinkina, I.N. (1964). Heat capacity and entropy for manganese, iron, cobalt, and nickel carbonates at low temperatures: Zhurnal Fizicheskoi Khimii, 38, 780-781.

Latimer, W.M. (1952). The Oxidation States of the Elements and their Potentials in Aqueous Solutions. Second edition. Prentice Hall, New York, 392 p.

Lothenbach, B. and Winnefeld, F. (2006). Thermodynamic modelling of the hydration of Portland cement, Cement and Concrete Research, 36(2), 209-226.

McCutcheon, T.P. and Schuele, W.J. (1953). Complex Acids of Cobalt and Chromium. The Green Carbonatocobalt (III) Anion. Journal of the American Chemical Society, 75(8), 1845-1846.

Naumov, G.B., Ryzhenko, B.N. and Khodakovsky, I.L. (1974). Handbook of Thermodynamic Data. Natl. Tech. Inf. Service, 722176A, U.S. Dept. Commerce. 328 p.

Palmer, D.A. and van Eldik, R. (1983). The chemistry of metal carbonato and carbon dioxide complexes. Chemical Reviews, 83, 651-731.

Pertlik, F. (1986). Structures of hydrothermally synthesized cobalt(II) carbonate and nickel(II) carbonate. Acta Crystallographica, C42, 4-5.

Piret, P. and M. Deliens (1980). La comblainite, $(Ni^{2+}_{x}{}'Co^{3+}_{1-x})(OH)_2(CO_3)_{(1-x)/2}\bullet yH_2O$, nouveau mineral du groupe de la pyroaurite. Bulletin de Mineralogie, 103, 113–117.

Pourbaix, M. (1960). Standard free energies of formation at 25ºC. CEBELCOR Rapt. 684, Belgian Center for the Study of Corrosion, Brussels, 57 p.

Radha, A.V. and Navrotsky, A. (2013). Thermodynamics of carbonates. Reviews in Mineralogy and Geochemistry, 77(1), 73-121.

Reiterer, F. (1980). Lös1ichkeitskonstanten und freie Bildungsenthalpien neutraler Übergangsmetallcarbonate: $MnCO_3$, $FeCO_3$, $CoCO_3$, $NiCO_3$, $CuCO_3$, $ZnCO_3$. PhD thesis, Montanuniversität, Leoben, Austria.

Rossini, F.D., Wagman, D.D., Evans, W.H., Levine, S. and Jaffe, I. (1952). Selected values of chemical tbermodynamical properties. NBS Circular 500. 1268 p., Washington, D.C.

Smith, R.M. and Martell, A.E. (1976). Critical Stability Constants, Volume 4, Inorganic Complexes. Plenum Press: New York.

Stern, K.H. (2000). High Temperature Properties and Thermal Decomposition of Inorganic Salts with Oxyanions. 256 p. CRC Press LLC, 2000 N.W. Corporate Blvd., Boca Raton Florida 33431.

Tareen, J.A.K., Fazeli, A.R., Basavalingu, B. and Bhandage, G.T. (1991). Hydrothermal decomposition curves and thermodynamic data for spherocobaltite ($CoCO_3$) and gaspeite ($NiCO_3$), European Journal of Mineralogy, 3, 501-505.

Wagman, D.D., Evans, W.H., Parker, V.B., Halow, I., Bailey, S.M. and Schumm, R.H. (1969). Selected Values of Chemical Thermodynamic Properties. Tables for elements 35 through 53 in the standard order of arrangement. NBS Technical Note 270-4, U.S. Department of Commerce, National Bureau of Standards, 141 p.

Wilcox. D.E. and Bromley, L.A. (1963). Computer Estimation of heat and free energy for simple inorganic compounds. Industrial and Engineering Chemistry, 55(7), 32-39.

Woods, T.L. and Garrels, R.M. (1987). Thermodynamic Values at Low Temperature for Natural Inorganic Materials. An Uncritical Summary. Oxford University Press. 242 p. plus references.

Yoder, C.H. and Rowand, J.P. (2006). Application of the simple salt lattice energy approximation to the solubility of minerals. American Mineralogist, 91(5-6), 747-752.

Zhorov, V.A., Bezborodov, A.A. and Popov, N.I. (1976). Predominance area diagrams and equilibrium ratios of inorganic forms of cobalt and nickel in oceanic water. Okeanol, 16, 808-814. [In Russian].

Zhuk, N.P. (1954). Thermodynamic constants of sulfates, carbonates, chromates, bromates, iodates, oxalates, and other salts slightly soluble in water. Zhurnal Fizicheskoi Khimii, 28, 1690-1697. [In Russian].

COPPER

Table 1. Association Constants for Aqueous Carbonate Complexes in the System $Cu_2O/CuO-CO_2-H_2O$

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
$Cu^{2+} + CO_3^{2-} = CuCO_3(aq)$	6.42	-	Solubility		Scaife (1957)
	6.34	-	$I = 0$	Bilinski et al. (1976)	Scaife (1957)
	6.77 ± 0.08	-			Silman (1958)
	6.77	-	$I = 0$	Bilinski et al. (1976)	Silman (1958)
	6.77	-		Vieillard (1988)	Silman (1958)
	6.77	-		Zirino and Yamamoto (1972)	Sillen and Martell (1964)
	6.34	-		Vieillard (1988)	Sillen and Martell (1964, 1971)
	6.73				Schindler et al. (1968)
	6.73			Mattigod and Sposito (1977)	Schindler et al. (1968)
	6.73	-		Vieillard (1988)	Schindler et al. (1968)
	6.8 ± 0.1	-	ISE		Stiff (1971)
	6.8	-	Var.	Bilinski et al. (1976)	Stiff (1971)
	5.7 ± 0.2	-	DPP, 0.1 *M* KNO_3		Ernst et al. (1975)
	5.7	-	DPP	Bilinski et al. (1976)	Ernst et al. (1975)
	6.1 ± 0.2	-	DPASV, 0.1 *M* KNO_3		Ernst et al. (1975)
	6.1	-	DPASV	Bilinski et al. (1976)	Ernst et al. (1975)
	6.1	-	DPP, 0.1 *M* KNO_3		Bilinski et al. (1976)
	6.0	-	ASV, 0.1 *M* KNO_3		Bilinski et al. (1976)
	6.75 ± 0.02	-	$I = 0$	Palmer and Van Eldik (1983)	Smith and Martell (1976)
	6.73			McBride (1979)	Mattigod and Sposito (1977) and Novozamsky and Beek (1976)
	6.04	-	$I = 0.05$		Stella and Ganzeril-Valentini (1979)
	6.74				Sunda and Hanson (1979)

Table 1. Association Constants for Aqueous Carbonate Complexes in the System $Cu_2O/CuO-CO_2-H_2O$ (Continued)

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	6.78	-	I = 0	Palmer and Van Eldik (1983)	Sunda and Hanson (1979)
	6.8	-	I = 0.1	Palmer and Van Eldik (1983)	Van den Berg and Kramer (1979)
	6.8	-	DPASV. 0.01 M KNO_3		Van den Berg and Kramer (1979)
	6.89				Zuehlke and Kester (1983)
	6.89	-		Vieillard (1988)	Zuehlke and Kester (1983)
	6.73	-11.30	Estimate		Fouillac and Criaud (1984)
	6.82				Byrne and Miller (1985)
	6.73	-		Millero and Hawke (1992)	Byrne and Miller (1985)
	6.74	-		Vieillard (1988)	Grenthe (1985)
	4.91 ± 0.01	10.38 ± 1.21	I = that of seawater		Soli and Byrne (1989)
	6.73			Puigdomenech and Taxén (2000)	Ball and Nordstrom (1991)
	6.77			Puigdomenech and Taxén (2000)	Martell et al. (1997)
	6.75 ± 0.01	-			Powell et al. (2007)
	6.74 ± 0.01	-			Millero et al. (2010)
$Cu^{2+} + 2CO_3^{2-} = Cu(CO_3)_2^{2-}$	10.01 ± 0.08	-			Silman (1958)
	10.01	-	I = 0	Bilinski et al. (1976)	Silman (1958)
	10.01	-		Vieillard (1988)	Silman (1958)
	8.6	-	18ºC, Pol. 1.7 M KNO_3 (+ K_2CO_3 + $KHCO_3$)		Faucherre and Bonnaire (1959)
	8.6	-	18ºC. Pol., 1.7 M KNO_3,	Krishnamurty et al., 1970)	Faucherre and Bonnaire (1959
	9.83			Mattigod and Sposito (1977)	Schindler et al. (1968)
	9.83	-		Vieillard (1988)	Schindler et al. (1968)
	9.8	-	Pol./Ion Exchange, 1.8 N (K_2CO_3 + KNO_3)		Fromage and Fiorina (1969)

Table 1. Association Constants for Aqueous Carbonate Complexes in the System $Cu_2O/CuO-CO_2-H_2O$ (Continued)

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	10.0	-	Estimate		Zirino and Yamamoto (1972)
	8.1 ± 0.3	-	L# = 1.63, DPP, 0.1 *M* KNO_3		Ernst et al. (1975)
	8.2 ± 0.2	-	L# = 1.65, DPASV, 0.1 *M* KNO_3		Ernst et al. (1975)
	8.1	-	DPP	Bilinski et al. (1976)	Ernst et al. (1975)
	8.2	-	DPASV	Bilinski et al. (1976)	Ernst et al. (1975)
	9.7	-	DPP, 0.1 *M* KNO_3		Bilinski et al. (1976)
	10.0	-	ASV, 0.1 *M* KNO_3		Bilinski et al. (1976)
	8.6		18ºC, *I* = 1.7.	Palmer and Van Eldik (1983)	Smith and Martell (1976)
	9.92 ± 0.09		*I* = 0	Palmer and Van Eldik (1983)	Smith and Martell (1976)
	9.28	-	*I* = 0.05		Stella and Ganzeril-Valentini (1979)
	10.23				Sunda and Hanson (1979)
	10.24		*I* = 0	Palmer and Van Eldik (1983)	Sunda and Hanson (1979)
	10.6				Byrne and Miller (1985)
	10.41	-		Millero and Hawke (1992)	Byrne and Miller (1985)
	10.83	-		Vieillard (1988)	Grenthe (1985)
	9.83			Puigdomenech and Taxén (2000)	Ball and Nordstrom (1991)
	10.2			Puigdomenech and Taxén (2000)	Martell et al. (1997)
	10.30 ± 0.10	-			Powell et al. (2007)
	10.52 ± 0.06	-			Millero et al. (2010)
	7.2	-	Pol., 1 *M* KNO_3	Krishnamurty et al. (1970)	Meites (1950)
	10.5	-	Pol./Ion Exchange, 1.8 N (K_2CO_3 + KNO_3)		Fromage and Fiorina (1969)
$Cu^{2+} + CO_3^{2-} + H^+ = CuHCO_3^+$	>12.73	-	Solubility		Scaife (1957)

Table 1. Association Constants for Aqueous Carbonate Complexes in the System Cu_2O/CuO-CO_2-H_2O (Continued)

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	-	-	ISE. No evidence for existence.		Stiff (1971)
	13.0	-	Estimate		Zirino and Yamamoto (1972)
	12.53*	-10.46*	Estimate		Fouillac and Criaud (1984)
	12.13				Byrne and Miller (1985)
	12.8*	-		Vieillard (1988)	Zuehlke and Kester (1983)
	12.15*	-		Millero and Hawke (1992)	Byrne and Miller (1985)
	12.1 ± 0.1	-			Powell et al. (2007)
	12.20 ± 0.01	-			Millero et al. (2010)
$Cu^{2+} + HCO_3^- = Cu(HCO_3)^-$	2.10		Estimate		Mattigod and Sposito (1977)
		20.9		Palmer and Van Eldik (1983)	Rages (1978)
	2.08	23.4		Palmer and Van Eldik (1983)	Bauman (1981)
	2.7			Puigdomenech and Taxén (2000)	Ball and Nordstrom (1991)
	1.8			Puigdomenech and Taxén (2000)	Martell et al. (1997)
	6.27		I = 7.18 (lake water)		Mugabe et al. (1998)
$Cu^{2+} + 2HCO_3 = Cu(HCO_3)_2(aq)$	5.9	-	Pol./Ion Exchange, 1. N (K_2CO_3 + KNO_3)		Fromage and Fiorina (1969)
$Cu^{2+} + 2HCO_3 = Cu(HCO_3)_2(aq)$	7.46		I = 7.18 (lake water)		Mugabe et al. (1998)
$Cu^{2+} + 3HCO_3^- = Cu(HCO_3)^+$	9.84		I = 7.18 (lake water)		Mugabe et al. (1998)
$Cu^{2+} + 4HCO_3 = Cu(HCO_3)_4^{2-}$	11.52	-	Pol., 1 M KNO_3	Krishnamurty et al. (1970)	Meites (1950)
$Cu^{2+} + CO_3^{2-} + H_2O = Cu(OH)_2CO_3^{2-} + 2H^+$	≈15.				Silman (1958)

Table 1. Association Constants for Aqueous Carbonate Complexes in the System Cu_2O/CuO-CO_2-H_2O (Continued)

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
$Cu^{2+} + CO_3^{2-} + H_2O = Cu(OH)CO_3^- + H^+$	-2.79 ± 0.3	-		Powell et al. (2007)	Symes and Kester (1985)
$Cu(OH)_2 + 3CO_3^{2-} = 2(OH)^- + Cu(CO_3)_3^{4-}$	-7.18 ± 0.4	-	Pol., 1 *M* KNO_3		Meites (1950)
	-7.18	-		Latimer (1952)	Meites (1950)
$Cu^{2+} + 4HCO_3^- + 2K^+ = K_2Cu(HCO_3)_4(aq)$	11.52 ± 0.25	-	Pol., 1 *M* KNO_3		Meites (1950)
$K_2Cu(HCO_3)_4(aq) + HCO_3^- = K_2Cu(HCO_3)_5^- + 2K^+$	1.98	-	Pol., 1 *M* KNO_3		Meites (1950)
$Cu^{2+} + 2CO_3^{2-} + 2H_2O = [Cu(OH)_2(HCO_3)_2]^{2-}$	-	-	0.5 – 1.0 *M* $KHCO_3$. Evidence for complex. Incurrectly specified charge on complex.		Shirai (1961)

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

* Equation recast using bicarbonate dissociation equation from PHREEQC

Table 2. Solubility Constants of Solid Carbonates in the System $Cu_2O/CuO-CO_2-H_2O$

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
Minerals					
Aurichalcite					
$Zn_{2.73}Cu_{2.27}(CO_3)_2(OH)_6 = 2.73Zn^{2+} + 2.27Cu^{2+} + 2CO_3^{2-} + 6OH^-$	-90.1	-			Alwan et al. (1980)
Azurite					
$Cu_3(CO_3)_2(OH)_2 + 2H^+ = 3Cu^{2+} + 2CO_3^{2-} + 2H_2O$	-17.96	-	Natural material		Silman (1958)
	-17.96	-		Vieillard (1988)	Silman (1958)
	-16.88	-		Vieillard (1988)	Schindler et al. (1968)
	-16.9 ± 0.2	-		Powell et al. (2007)	Schindler et al. (1968)
	-11.4			Vieillard (1988)	Helgeson et al. (1978)
	-16.88			Vieillard (1988)	Reiterer et al. (1981)
	+3.10			Vieillard (1988)	Wagman et al. (1982)
	-17.8	-		Vieillard (1988)	Grenthe (1985)
	-19.46	-		Vieillard (1988)	Vink (1986)
	-18.4	-		Vieillard (1988)	Woods and Garrels (1986)
	-16.8	-	See note 1.		Vieillard (1988)
	-16.8	-			Vieillard et al. (1989)
	-16.91	-		Puigdomenech and Taxén (2000)	Ball and Nordstrom (1991), Martell et al. (1997), Baes and Mesmer (1976)
	-17.38 ± 0.30				Preis and Gamsjäger (2002)
	-18.52		Estimated		Yoder and Rowand (2006)
	-16.00		Estimated		Yoder et al. (2010)
$Cu_3(CO_3)_2(OH)_2 + 6H^+ = 3Cu^{2+} + 2CO_2 + 4H_2O$	19.41 ± 0.09	-			Schindler et al. (1968)
	19.41 ± 0.09			Naumov et al. (1974)	Schindler et al. (1968)

Table 2. Solubility Constants of Solid Carbonates in the System $Cu_2O/CuO-CO_2-H_2O$ (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
$2/3Cu_3(CO_3)_2(OH)_2 + 2H^+ = Cu^{2+} + 2/3CO_2 + 4/3H_2O$	6.30	-20.2			Preis and Gamsjäger (2001)
Caledonite					
$Pb_5Cu_2CO_3(SO_4)_3(OH)_6 + 6H^+ = 5Pb^{2+} + 2Cu^{2+} + CO_3^{2-} + 3SO_4^{2-} + 6H_2O$	-26.6	-	See note 2.		Abdul-Samad et al. (1982)
Juangodoyite					
$Na_2Cu(CO_3)_2 = 2Na^+ + Cu^{2+} + 2CO_3^{2-}$	-6.40		Estimated		Yoder and Rowand (2006)
Malachite					
$Cu_2CO_3(OH)_2 + 2H^+ = 2Cu^{2+} + CO_3^{2-} + 2H_2O$	-4.45	-	Synthetic material	Scaife (1957)	Free (1908)
	-5.75	-	Estimate for natural material	Silman (1958)	Free (1908)
	-5.35	-	Synthetic material	Silman (1958)	Free (1908)
	-3.90	-	Synthetic material		Scaife (1957)
	-4.71	-	Synthetic material	Silman (1958)	Scaife (1957)
	-3.9	-		Vieillard (1988)	Scaife (1957)
	-5.78	-	Natural material		Silman (1958)
	-5.78	-		Vieillard (1988)	Silman (1958)
	-5.16	-		Vieillard (1988)	Schindler et al. (1968)
	-5.16 ± 0.08	-		Powell et al. (2007)	Schindler et al. (1968)
	-6.19	-		Vieillard (1988)	Rickard (1971)
	-4.35	-		Vieillard (1988)	Helgeson et al. (1978)
	-3.249	-	*I* = 0.05. precipitated.		Stella and Ganzeril-Valentini (1979)
	-5.16			Vieillard (1988)	Reiterer et al. (1981)
	-3.94			Vieillard (1988)	Wagman et al. (1982)
	-5.46 ± 0.22	-			Symes and Kester (1984)
	-5.46	-		Vieillard (1988)	Symes and Kester (1984)
	-5.16	-		Vieillard (1988)	Grenthe (1985)

Table 2. Solubility Constants of Solid Carbonates in the System $Cu_2O/CuO-CO_2-H_2O$ (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	-5.97	-		Vieillard (1988)	Woods and Garrels (1986)
	-5.78	-		Vieillard (1988)	Vink (1986)
	-4.80	-		Vieillard (1988)	Vieillard et al. (1989)
	-5.18			Puigdomenech and Taxén (2000)	Ball and Nordstrom (1991)
	-5.3			Puigdomenech and Taxén (2000)	Martell et al. (1997)
	-5.46 ± 0.20	-			Preis and Gamsjäger (2002)
	-4.00		Estimated		Yoder and Rowand (2006)
	-6.00		Estimated		Yoder et al. (2010)
$0.5Cu_2CO_3(OH)_2 + 2H^+ = Cu^{2+} + 0.5CO_3(g) + 1.5H_2O$	6.49 ± 0.04	-		Naumov et al. (1974)	Schindler et al. (1968)
	6.34	-27.1			Preis and Gamsjäger (2001)
$Cu_2CO_3(OH)_2 + 2H^+ = 2Cu^{2+} + CO_3^{2-} + 2H_2O$	12.98 ± 0.08	-			Schindler et al. (1968)
Rosasite					
$Cu_{1.16}Zn_{0.84}CO_3(OH)_2 = 1.16Cu^{2+} + 0.84Zn^{2+} + CO_3^{2-} + 2OH^-$	-36.4	-			Alwan et al. (1980)
Synthetic Phases					
$CuCO_3$					
$CuCO_3 = Cu^{2+} + CO_3^{2}$			18°C, Solubility = 0.03% and 0.041% at $P(CO_2)$ = 1 and 56 atm., respectively		Haehnel (1924)
	-9.863	-	18°C	Kelley and Anderson (1935)	Haehnel (1924)
	-9.60			Latimer (1952)	Haehnel (1924)
	-9.627	-	Review. No correction for activity coefficients		Kelley and Anderson (1935)

Table 2. Solubility Constants of Solid Carbonates in the System $Cu_2O/CuO-CO_2-H_2O$ (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	-9.63			Zhuk (1954)	Goskhimizdat (1952)
	-9.63		I = 0	Palmer and Van Eldik (1983)	Smith and Martell (1976)
	-9.60	-		Vieillard (1988)	Helgeson et al. (1978)
	-11.43	-		Vieillard (1988)	Reiterer et al. (1981)
	-11.5	-		Puigdomenech and Taxén (2000)	Martell et al. (1997)
	-11.45 ± 0.10	-	Literature review		Grauer (1999)
	-11.45	-		Puigdomenech and Taxén (2000)	Grauer (1999)
	-10.00	-	Estimated		Yoder et al. (2010)
$CuCO_3 + 2H+ = Cu^{2+} + CO_{2(g)} + H_2O$	6.44	-	25°C, I = 0.	Gamsjäger (1974)	Schindler et al. (1968)
	7.16 ± 0.05		50°C, 1 M $NaClO_4$,	Gamsjäger (1985)	Reiterer (1980)
	6.70 ± 0.10	-	Phase prepared following Ehrhardt et al. (1973) and Seidel et al. (1974)		Reiterer et al. (1981)
$CuCO_3 + 2H+ = Cu^{2+} + CO_{2(g)} + H_2O$	6.95 ± 0.04		25°C, 0.20 M $NaClO_4$		Reiterer et al. (1981)
$K_2Cu(CO_3)_2$					
$K_2Cu(CO_3)_2 = 2K^+ + Cu^{2+} + 2CO_3^{2-}$	-2.00		Estimated		Yoder and Rowand (2006)
$K_2Cu(HCO_3)_4$					
$K_2Cu(HCO_3)_4 = 2K^+ + Cu^{2+} + 4HCO_3^-$	-11.52 ± 0.26	-			Meites (1950)
	-11.52			Latimer (1952)	Meites (1950)
$Cu_3CO_3(OH)_4$					
$Cu_3CO_3(OH)_4 + 4H^+ = 3Cu^{2+} + CO_3^{2-} + 4H_2O$	-1.70	-	Estimated		Yoder et al. (2010)
$Cu_3CO_3(OH)_4$					
$Cu_4CO_3(OH)_6 + 6H^+ = 4Cu^{2+} + CO_3^{2-} + 6H_2O$	2.48	-	Estimated		Yoder et al. (2010)

Table 2. Solubility Constants of Solid Carbonates in the System $Cu_2O/CuO-CO_2-H_2O$ (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
$\underline{Cu_5CO_3(OH)_8}$					
$Cu_5CO_3(OH)_8 + 8H^+ = 5Cu^{2+} + CO_3^{2-} + 8H_2O$	6.60	-	Estimated		Yoder et al. (2010)
$\underline{Cu_5(CO_3)_2(OH)}$					
$Cu_5(CO_3)_2(OH)_6 + 6H^+ = 5Cu^{2+} + CO_3^{2-} + 6H_2O$	-7.52	-	Estimated		Yoder et al. (2010)

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Note 1: Calculated from the solubility product for malachite by Vieillard et al. (1989), and fixing the equilibrium $P(CO_2)$ between malachite and azurite at 10^{-10} atm.

Note 2: Abdul-Samad et al. (1982) also determined the solubility of wherryite with an assumed formula: $PbCuCO_3(SO_4)_2O(OH,Cl)_2$. However, a subsequent crystallographic structure determination by Cooper and Hawthorne (1994) indicated that its composition is actually $Pb_7Cu_2(SO_4)_4(SiO_4)_2(OH)_2$.

Table 3a. Association Constants of Aqueous Carbonate Complexes in the System $Cu_2O/CuO-CO_2-H_2O$ extracted from Databases of Distribution-of-Species Codes

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Database	Source
$Cu^{2+} + CO_3^{2-} = CuCO_3(aq)$	6.73		MinteqA2	
	6.73		Wateq4f	
	3.37		V8.R6+	
	6.73	0	Minteq (2009)	
	6.77	0.	Minteq (2006)	NIST46.4, MTQ3.11
	-	-	Phreeqc (2009)	
	6.73	-	Wateq4f (2005)	
	-	-	ThermoChimie v.7.b	
			NAGRA/PSI (2001)	
	-	-	Data0.YMP.R5	
	-	-	Thermoddem (2009)	
$Cu^{2+} + 2CO_3^{2-} = Cu(CO_3)_2^{2-}$	9.83		MinteqA2	
	9.83		Wateq4f	
	10.48		V8.R6+	
	9.83	0	Minteq (2009)	
	10.2	0.	Minteq (2006)	NIST46.4, MTQ3.11
	-	-	Phreeqc (2009)	
	9.83	-	Wateq4f (2005)	
	-	-	ThermoChimie v.7.b	
	-	-	NAGRA/PSI (2001)	
	-	-	Data0.YMP.R5	
	-	-	Thermoddem (2009)	
$Cu^{2+} + CO_3^{2-} + H^+ = CuHCO_3^+$	13.16		MinteqA2	
	13.16		Wateq4f	
	-		V8.R6+	
	13.	0	Minteq (2009)	
	12.129	0.	Minteq (2006)	NIST46.4, MTQ3.11
	-	-	Phreeqc (2009)	
	13.029	-	Wateq4f (2005)	
	-	-	ThermoChimie v.7.b	
	-	-	NAGRA/PSI (2001)	
	-	-	Data0.YMP.R5	
	-	-	Thermoddem (2009)	
$Cu^{2+} + CO_3^{2-} + H_2O = CuCO_3(OH)_2^{2-} + 2H+$	13.11		V8.R6+	
	-	-	Minteq (2009)	
	-	-	Minteq (2006)	
	-	-	Phreeqc (2009)	
	-	-	Wateq4f (2005)	
	-	-	ThermoChimie v.7.b	
	-	-	NAGRA/PSI (2001)	

Table 3a. Association Constants of Aqueous Carbonate Complexes in the System Cu_2O/CuO-CO_2-H_2O extracted from Databases of Distribution-of-Species Codes (Continued)

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Database	Source
	-	-	Data0.YMP.R5	
	-	-	Thermoddem (2009)	

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Table 3b. Solubility Constants of Solid Carbonates in the System Cu_2O/CuO-CO_2-H_2O extracted from Databases of Distribution-of-Species Codes

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Database	Source
Minerals				
Azurite				
$Cu_3(CO_3)_2(OH)_2 + 2H^+ = 3Cu^{2+} + 2CO_3^{2-} + 2H_2O$	-17.40		MinteqA2	
	-16.17		Wateq4f	
	-11.50		V8.R6+	
	-16.92	-99.54	Minteq (2009)	
	-16.906	-95.22	Minteq (2006)	
	-	-	Phreeqc (2009)	
	-16.908	99.362	Wateq4f (2005)	
	-	-	ThermoChimie v.7.b	
	-	-	NAGRA/PSI (2001)	
	-11.4969	-	Data0.YMP.R5	Helgeson et al. (1978)
	-11.5385	-	Thermoddem (2009)	Helgeson et al. (1978)
Malachite				
$Cu_2CO_3(OH)_2 + 2H^+ = 2Cu^{2+} + CO_3^{2-} + 2H_2O$	-5.47		MinteqA2	
	-4.67		Wateq4f	
	-4.39		V8.R6+	
	-5.18	-65.31	Minteq (2009)	
	-5.306	76.38	Minteq (2006)	
	-	-	Phreeqc (2009)	
	-5.179	-67.777	Wateq4f (2005)	
	-	-	ThermoChimie v.7.b	
	-	-	NAGRA/PSI (2001)	
	-4.3889	-	Data0.YMP.R5	Helgeson et al. (1978)
	-4.4159	-	Thermoddem (2009)	Helgeson et al. (1978)
Synthetic Phases				
$Cu(CO_3)$				
$Cu(CO_3) = Cu^{2+} + CO_3^{2-}$	-9.63	-0	Minteq (2009)	
	-11.5	-0.	Minteq (2006)	
	-	-	Phreeqc (2009)	
	-9.63	-	Wateq4f (2005)	
	-	-	ThermoChimie v.7.b	
	-	-	NAGRA/PSI (2001)	
	-	-	Data0.YMP.R5	
	-	-	Thermoddem (2009)	

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Table 3c. Distribution-of-Species Codes: Database References

Database	Reference
Data0.com.V8.R6+	Wolery, T.J. (1994). EQ3NR, Letter report: EQ3/6 version 8.0. Differences from version 7. UCRL-ID-129749. Lawrence Livermore National Laboratory, Livermore, California. USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/LLNL.DAT
Data0.YMP.R5	BSC (Bechtel SAIC Company) (2007). Qualification of Thermodynamic Data for Geochemical Modeling of Mineral–Water Interactions in Dilute Systems. ANL-WIS-GS-000003 REV 01. Las Vegas, Nevada: Bechtel SAIC Company.DOC.20070619.0007.
MinteqA2	HydroGeoLogic, Inc. and Allison Geoscience Consultants, Inc. (1999). MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: User Manual Supplement for Version 4.0, Appendix A: thermodynamic database for MINTEQA2 V4.0, p. 44-74.
Minteq (2009)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/MINTEQ.DAT
Minteq (2006)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/minteq.v4.dat
NAGRA/PSI (2001)	Hummel, W., Berner, U., Curti, E., Pearson, F.J. and Thoenen, T. (2002). Nagra/PSI Chemical Thermodynamic Data Base 01/01. Universal Publishers/uPublish.com, Parkland, Florida. 565 p.
Phreeqc (2009)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/PHREEQC.DAT
ThermoChimie v.7.b	Duro, L., Grivém M. and Giffaut, E. (2010). ThermoChimie, the ANDRA thermodynamic database In Buckau G, Kienzler B, Duro L, Grivé M, Montoya V (eds). 2nd Annual Workshop Proceedings of the Collaborative Project “Redox Phenomena Controlling Systems” (7th EC FP CP Recosy) Larnaca (Cyprus) 16–19 March 2010. Karlsruhe: KIT Scientific Publishing, 275–283.
Thermoddem (2009)	Blanc P., Lassin A. and Piantone P. (2007) THERMODDEM a database devoted to waste minerals. BRGM (Orléans, France). For updates: http://thermoddem.brgm.fr
Wateq4f	Ball, J. W., & Nordstrom, D. K. (1991). User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters. U.S. GEOLOGICAL SURVEY, Open-File Report 91-183, Revised and reprinted - April, 2001. p. 81-94
Wateq4f (2005)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/WATEQ4F.DAT

Table 4a. Thermodynamic properties of Copper Carbonate Minerals and Synthetic Solid Carbonates: Gibbs Free Energies of Formation

Mineral		$\Delta G^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
Minerals				
Aurichalcite	$Zn_{2.73}Cu_{2.27}(CO_3)_2(OH)_6$	-2765.8		Alwan et al. (1980)
Azurite	$Cu_3(CO_3)_2(OH)_2$	-1438 ± 0.33		Silman (1958)
		-1438.2	Woods and Garrels (1987)	Silman (1958)
		-1438.04	Rickard (1971)	Garrels (1960)
		-1438.17 ± 2.09	Robie (1962, 1966)	Garrels (1960)
		-1438.17 ± 2.09	Karpov et al. (1968)	Robie (1962)
		-1419.4	Woods and Garrels (1987)	Reinert (1965)
		-1419.4	Vieillard (1988)	Reinert (1965)
		-1430.89 ± 5.02		Schindler et al. (1968)
		-1430.93	Naumov et al. (1974)	Schindler et al. (1968), Roth et al. (1941)
		-1430.9	Vieillard (1988)	Gedansky et al. (1970),
		-1430.9	Vieillard (1988)	Naumov et al. (1971)
		-1430.9	La Iglesia and Felix (1994)	Naumov et al. (1971)
		-1430.9	Woods and Garrels (1987)	Naumov et al. (1974)
			Woods and Garrels (1987)	Robie et al. (1978)
		-1399.2	Woods and Garrels (1987)	Helgeson et al. (1978)
		-1399.2	Vieillard (1988)	Helgeson et al. (1978)
		-1436.93	Vieillard (1988)	Lewis (1978)
		-1419.4	La Iglesia and Felix (1994)	Woods and Garrels (1987)
		-1315.5	Woods and Garrels (1987)	Wagman et al. (1982)
		-1315.5	Vieillard (1988)	Wagman et al. (1982)
		-1391.4 ± 2.2	Robie and Hemingway (1995)	Wagman et al. (1982)
		-1429.7	Woods and Garrels (1987)	Sangameswar and Barnes (1983)
		-1429.7	Vieillard (1988)	Sangameshwar and Barnes (1983)
		-1429.7	La Iglesia and Felix (1994)	Sangameshwar and Barnes (1983)
		-1429.22		Calculated from the solubility constant for azurite given by Vieillard (1988, Table 2)

Table 4a. Thermodynamic properties of Copper Carbonate Minerals and Synthetic Solid Carbonates: Gibbs Free Energies of Formation (Continued)

Mineral		$\Delta G^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
		-1438.2	Vieillard (1988)	Woods and Garrels (1986)
		-1388.7 ± 8.2		Kiseleva et al. (1992)
		-1431.43	Puigdomenech and Taxén (2000)	Kubaschewski et al. (1993)
		-1419.4 ± 3.8		La Iglesia and Felix (1994)
		-1434.2 ± 1.8		Preis and Gamsjäger (2002)
Caledonite	$Pb_5Cu_2CO_3(SO_4)_3(OH)_6$	-4328 ± 2		Abdul-Samad et al. (1982)
Malachite (natural)	$Cu_2CO_3(OH)_2$	-908.		Estimated by Garrels (1957)
		-905.59 ± 0.21		Silman (1958)
		-905.6	Woods and Garrels (1987)	Silman (1958)
		-905.58 ± 2.09	Robie (1962, 1966)	Garrels (1960)
		-907.93	Karpov et al. (1968)	Garrels (1960)
		-905.58 ± 2.09	Karpov et al. (1968)	Robie (1962)
		-893.90	Vieillard (1988)	Reinert (1965)
		-893.9	Woods and Garrels (1987)	Reinert (1965)
		-901.32 ± 0.46		Schindler et al. (1968)
		-901.28	Naumov et al. (1974)	Schindler et al. (1968), Roth et al. (1941)
		-893.70		Wagman et al. (1969)
		-901.20	Vieillard (1988)	Gedansky et al. (1970),
		-890.2 ± 2.2	Robie and Hemingway (1995)	Richardson and Brown (1974)
		-901.28	Vieillard (1988)	Naumov et al. (1971)
		-901.3	Woods and Garrels (1987)	Naumov et al. (1974)
		-901.3	La Iglesia and Felix (1994)	Naumov et al. (1974)
			Woods and Garrels (1987)	Robie et al. (1978)
		-896.2	Woods and Garrels (1987)	Helgeson et al. (1978)
		-896.23	Vieillard (1988)	Helgeson et al. (1978)
		-901.26	Vieillard (1988)	Lewis (1978)

Table 4a. Thermodynamic properties of Copper Carbonate Minerals and Synthetic Solid Carbonates: Gibbs Free Energies of Formation (Continued)

Mineral		$\Delta G^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
		-893.6	Woods and Garrels (1987)	Wagman et al. (1982)
		-893.6	Vieillard (1988)	Wagman et al. (1982)
		-893.9	La Iglesia and Felix (1994)	Wagman et al. (1982), Woods and Garrels (1987)
		-900.4	Woods and Garrels (1987)	Sangameswar and Barnes (1983)
		-900.40	Vieillard (1988)	Sangameshwar and Barnes (1983)
		-900.4	La Iglesia and Felix (1994)	Sangameswar and Barnes (1983)
		-903.7	Woods and Garrels (1987)	Symes and Kester (1984)
		-905.0		Woods and Garrels (1986)
		-905.0	Woods and Garrels (1987)	Woods and Garrels (1986)
		-905.00	Vieillard (1988)	Woods and Garrels (1986)
		-898.50		Calculated from the solubility constant for malachite given by Vieillard (1988, Table 2)
		-899.1		Calculated from reaction paratacamite-malachite by Vieillard (1988)
		-882.9 ± 6.4		Kiseleva et al. (1992)
		-896.2	La Iglesia and Felix (1994)	Helgeson et al. (1978)
		-903.7	La Iglesia and Felix (1994)	Woods and Garrels (1987)
		-905.0	La Iglesia and Felix (1994)	Woods and Garrels (1987)
		-902.35	Puigdomenech and Taxén (2000)	Kubaschewski et al. (1993)
Predicted		-901.4 ± 3.6		La Iglesia and Felix (1994)
		-903.3 ± 1.2		Preis and Gamsjäger (2002)
Rosasite	$Cu_{1.16}Zn_{0.84}CO_3(OH)_2$	-1100.5		Alwan et al. (1980)
Voglite	$Ca_2Cu(UO_2)(CO_3)_4 \cdot 6(H_2O)$	-5791.4 ± 35.0		Hemingway (1982)
Voglite	$Ca_3Cu(UO_2)(CO_3)_4$	-4469.0 ± 15.0		Van Genderen and Van der Weijden (1984)
Synthetic Phases				

Table 4a. Thermodynamic properties of Copper Carbonate Minerals and Synthetic Solid Carbonates: Gibbs Free Energies of Formation (Continued)

Mineral		$\Delta G^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
$CuCO_3$	$CuCO_3$	-516.22	Kelley and Anderson (1935)	Haehnel (1924)
		-516.22		Kelley and Anderson (1935)
		-517.98	Latimer (1952)	Rossini et al. (1952)?
		-517.98	Zhuk (1954)	Rossini et al. (1952), Karapet'yants (1953)
		-517.98	Karpov et al. (1968)	Rossini et al. (1952)
calculated		-518.06		Zhuk (1954)
		-518.06	Karapet'yants and Karapet'yants (1970)	Zhuk (1954)
		5.02	Karpov et al. (1968)	Kireev (1964)
		-519.15		Barin et al. (1973)
		-622.42	Stern (2000)	Barin et al. (1977)
		-518.3	Dobrydiev et al. (2005)	Ryabin et al. (1977)
monoclinic		-528.06 ± 0.25		Reiterer et al. (1981)
		-527.27	Calculated from the solubility constant for $CuCO_3$ given by Vieillard (1988) in Table 2	Reiterer et al. (1981)
		-528.20	Puigdomenech and Taxén (2000)	Kubaschewski et al. (1993)
$CuCO_3.K_2CO_3$	$CuCO_3.K_2CO_3$	-1608.75	Karapet'yants and Karapet'yants (1970)	Karapet'yants (1955)
$CuCO_3.Na_2CO_3$	$CuCO_3.Na_2CO_3$	-1579.04	Karapet'yants and Karapet'yants (1970)	Karapet'yants (1955)
$K_2Cu(HCO_3)_4$	$K_2Cu(HCO_3)_4$	-2913.9	Vieillard (1988)	Wagman et al. (1982)

(1) Formation from the oxides

Table 4b. Thermodynamic properties of Copper Carbonate Minerals and Synthetic Solid Carbonates: Enthalpies of Formation

Mineral		$\Delta H^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
Minerals				
Azurite	$Cu_3(CO_3)_2(OH)_2$	-1629.80		Calculated by Vieillard (1988) from the enthalpy of reaction ΔH_r = 87.36 kJ mol^{-1} for 3CuO(c) + H_2O(l) +2CO_2(g) = $Cu_3(CO_3)_2(OH)_2$(c) by Roth et al. (1941)
		-1627.58	Naumov et al. (1974)	Roth et al. (1941)
		1632.18		Wagman et al. (1969)
		-1632.180 ± 2.000	Robie et al. (1979)	Wagman et al. (1969)
		-1632.18 ± 2.00	Radha and Navrotsky (2013)	Wagman et al. (1969), Robie et al. (1978)
		-1627.6	Woods and Garrels (1987)	Naumov et al. (1974)
		-1627.6	La Iglesia and Felix (1994)	Naumov et al. (1974), Sangameswar and Barnes (1983)
		-1632.2	Woods and Garrels (1987)	Helgeson et al. (1978)
			La Iglesia and Felix (1994)	Helgeson et al. (1978)
		-1632.2	Woods and Garrels (1987)	Robie et al. (1978)
		-1632.2	Woods and Garrels (1987)	Wagman et al. (1982)
		-1632.2	La Iglesia and Felix (1994)	Wagman et al. (1982), Robie et al. (1978), Helgeson et al. (1978)
		-1632.2 ± 2.0	Robie and Hemingway (1995)	Wagman et al. (1982),
		-1627.6	Woods and Garrels (1987)	Sangameswar and Barnes (1983)
		-1629.5 ± 8.3		Kiseleva et al. (1992)
Predicted		-1641.6 ± 5.3		La Iglesia and Felix (1994)
		-1675.1 ± 5.1		Preis and Gamsjäger (2002)
Chalconatronite	$Na_2Cu(CO_3)_2$•3 (H_2O)	-2609.89	Vieillard (1988)	Wagman et al. (1982)
Juangodoyite	$Na_2Cu(CO_3)_2$	-1712.5	Vieillard (1988)	Wagman et al. (1982)
Malachite	$Cu_2CO_3(OH)_2$	-1055.58		Calculated by Vieillard (1988) from the enthalpy of reaction ΔH_r = 57.66 kJ mol^{-1} for 2CuO(c) + H_2O(l) +2CO_2(g) = $Cu_2(CO_3)_2(OH)_2$(c) by Richardson and Brown (1974)

Table 4b. Thermodynamic properties of Copper Carbonate Minerals and Synthetic Solid Carbonates: Enthalpies of Formation (Continued)

Mineral		$\Delta H^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
		-1048.51	Naumov et al. (1974)	Roth et al. (1941)
		-1051.44		Wagman et al. (1969)
		-1048.5	Woods and Garrels (1987)	Naumov et al. (1974)
		-1048.5	La Iglesia and Felix (1994)	Naumov et al. (1974)
synthetic		1053.9 ± 2.1		Richardson and Brown (1974)
		-1053.950 ± 2.090	Robie et al. (1979)	Richardson and Brown (1974),
		-1054 ± 2.1	Robie and Hemingway (1995)	Richardson and Brown (1974),
		-1053.95 ± 2.09	Radha and Navrotsky (2013)	Richardson and Brown (1974), Robie et al. (1978)
		-1054.0	Woods and Garrels (1987)	Robie et al. (1978)
		-1053.9	Woods and Garrels (1987)	Helgeson et al. (1978)
		-1063.9	La Iglesia and Felix (1994)	Helgeson et al. (1978)
		-1051.4	Woods and Garrels (1987)	Wagman et al. (1982)
		-1051.4	La Iglesia and Felix (1994)	Wagman et al. (1982)
		-1053.9	Woods and Garrels (1987)	Sangameswar and Barnes (1983)
		-1046.5 ± 6.0		Kiseleva et al. (1992)
Predicted		-1048.6 ± 5.0		La Iglesia and Felix (1994)
		-1067.1 ± 3.4		Preis and Gamsjäger (2002)
Voglite	$Ca_2Cu(UO_2)(CO_3)_4$•6(H_2O)			
Voglite	$Ca_3Cu(UO_2)(CO_3)_4$	-4830.0		Van Genderen and Van der Weijden (1984)
Synthetic Phases				
$\underline{CuCO_3}$	$CuCO_3$	-597.48		Kelley and Anderson (1935)
		-594.96	Latimer (1952)	Rossini et al. (1952)?
		-594.96	Zhuk (1954)	Rossini et al. (1952), Karapet'yants (1953)
		-46.02	Karpov et al. (1968)	Kireev (1964)

Table 4b. Thermodynamic properties of Copper Carbonate Minerals and Synthetic Solid Carbonates: Enthalpies of Formation (Continued)

Mineral		$\Delta H^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
		-596.22	Stern (2000)	Barin et al. (1977)
		-595.4	Dobrydiev et al. (2005)	Ryabin et al. (1977)
$\underline{Cu(HCO_3)_2}$	$Cu(HCO_3)_2$	-1347.25 ± 62.76	Estimated value of fictive compound	Wilcox and Bromley (1963)
		-1347.25	Karapet'yants and Karapet'yants (1970)	Wilcox and Bromley (1963)
$K_2Cu(CO_3)_2$, form 2, β	$K_2Cu(CO_3)_2$	-1733.4	Vieillard (1988)	Wagman et al. (1982)
$K_2Cu(CO_3)_2$, form 4, β	$K_2Cu(CO_3)_2$	-1741.8	Vieillard (1988)	Wagman et al. (1982)
$K_2Cu(CO_3)_2$, form 5, α	$K_2Cu(CO_3)_2$	-1744.3	Vieillard (1988)	Wagman et al. (1982)

Table 4c. Thermodynamic properties of Copper Carbonate Minerals and Synthetic Solid Carbonates: Entropies

Mineral		$S^0_{P_r,T_r}$	Secondary Reference	Primary Reference
Name	Formula	J K^{-1} gfw^{-1}		
Minerals				
Azurite	$Cu_3(CO_3)_2(OH)_2$	402.50		Naumov et al. (1974)
		402.5	Woods and Garrels (1987)	Naumov et al. (1974)
		-280.2	Woods and Garrels (1987)	Helgeson et al. (1978)
		388.9		Vieillard (1988)
		254.4 ± 3.8		Kiseleva et al. (1992)
		254.4 ± 3.8	Robie and Hemingway (1995)	Kiseleva et al. (1992)
		254.4	Puigdomenech and Taxén (2000)	Kiseleva et al. (1992)
		254.4 ± 3.8		Preis and Gamsjäger (2002)
Malachite	$Cu_2CO_3(OH)_2$	186.19		Wagman et al. (1969)
		221.75		Naumov et al. (1974)
		221.8	Woods and Garrels (1987)	Naumov et al. (1974)
		186.2	Woods and Garrels (1987)	Helgeson et al. (1978)
		186.2	Woods and Garrels (1987)	Wagman et al. (1982)
		188.4		Vieillard (1988)
		166.3 ± 2.5		Kiseleva et al. (1992)
		166.3 ± 2.5	Robie and Hemingway (1995)	Kiseleva et al. (1992)
		166.3	Puigdomenech and Taxén (2000)	Kiseleva et al. (1992)
		166.3 ± 2.5		Preis and Gamsjäger (2002)
Synthetic Phases				
$CuCO_3$	$CuCO_3$	74.06		Kelley and Anderson (1935)
		87.86	Latimer (1952)	Rossini et al. (1952)?
		87.86	Zhuk (1954)	Rossini et al. (1952), Karapet'yants (1953)
		87.86	Karpov et al. (1968)	Rossini et al. (1952)
estimate		92.05 ± 4.18		Kelley and King (1961)

Table 4c. Thermodynamic properties of Copper Carbonate Minerals and Synthetic Solid Carbonates: Entropies (Continued)

Mineral		$S^0_{P_r,T_r}$ J K^{-1} gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
calculated		88.70		Zhuk (1954)
		88.70	Karapet'yants and Karapet'yants (1970)	Zhuk (1954)
		92.05 ± 4.18	Karpov et al. (1968)	Kelley and King (1961)
		92.05	Karapet'yants and Karapet'yants (1970)	Kelley and King (1961)
		87.86	Stern (2000)	Barin et al. (1977)
		87.9	Puigdomenech and Taxén (2000)	Kubaschewski et al. (1993)

(1) Formation from the oxides

Table 5. Crystallographic Properties of Copper Carbonate Minerals and Synthetic Solid Carbonates

	Name	Formula	Reference
	Minerals		
1	Astrocyanite-Ce)	$Cu_2(Ce,Nd,La)_2(\mathbf{U}O_2)(CO_3)_5(OH)_2 \bullet 1.5(H_2O)$	Gaines et al. (1997), Deliens and Piret (1990)
2	Aurichalcite	$Zn_{2.73}Cu_{2.27}(CO_3)_2(OH)_6$	Gaines et al. (1997)
3	Aurichalcite	$Zn_{2.73}Cu_{2.27}(CO_3)_2(OH)_6$	Harding et al. (1994)
4	Aurichalcite	$Zn_{2.38}Cu_{2.62}(CO_3)_2(OH)_6$	Giester and Rieck. (2014)
5	Azurite	$Cu_3(CO_3)_2(OH)_2$	Gaines et al. (1997)
6	Azurite	$Cu_3(CO_3)_2(OH)_2$	Mineralogy Database (http://webmineral.com/)
7	Azurite	$Cu_3(CO_3)_2(OH)_2$	RRUFF ID: R050497.1, Mineralogy Database (http://webmineral.com/)
8	Azurite	$Cu_3(CO_3)_2(OH)_2$	Belokoneva et al. (2001)
9	Caledonite	$Pb_5Cu_2CO_3(SO_4)_3(OH)_6$	Gaines et al. (1997)
10	Caledonite	$Pb_5Cu_2CO_3(SO_4)_3(OH)_6$	Mineralogy Database (http://webmineral.com/)

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
	Minerals									
1	Astrocyanite-(Ce)	14.96		26.86				12	P 6/mmm	261.26
2	Aurichalcite	13.82	6.419	5.29		101.04		2	$P2_1/m$	138.69
3	Aurichalcite	13.82	6.419	5.29		101.04		2	$P2_1/m$	138.69
4	Aurichalcite	13.790(2)	6.414(2)	5.266(1)		100.99(1)		2	$P2_1/m$	137.68
5	Azurite	5.00	5.85	10.36		92.33		2	$P2_1/a$	91.169
6	Azurite	5.008	5.844	10.336		92.333		2	$P2_1/a$	91.010
7	Azurite	5.0095(2)	5.8455(2)	10.3441(5)		92.420(3)		2	$P2_1/a$	91.126
8	Azurite	5.010	5.850	10.353		92.41		2	$P2_1/a$	91.285
9	Caledonite	20.089	7.146	6.560				2	$Pmn2_1$	283.56
10	Caledonite	20.088	7.143	6.564				2	$Pmn2_1$	283.60

	Name	Formula	Reference
11	Caledonite	$Pb_5Cu_2CO_3(SO_4)_3(OH)_6$	Schofield et al. (2009)
12	Callaghanite	$Cu_2Mg_2(CO_3)(OH)_6•2(H_2O)$	Gaines et al. (1997)
13	Callaghanite	$Cu_2Mg_2(CO_3)(OH)_6•2(H_2O)$	Brunton (1973)
14	Carrboydite	$Ni_{6.50}Cu_{0.40}Al_{4.80}(SO_4)_{2.30}(CO_3)_{0.48}(OH)_{21.69}•3.67(H_2O)$	Nickel and Clarke (1976)
15	Carrboydite	$Ni_{13}Cu_1Al_9(SO_4)_4(CO_3)_2(OH)_{43}•7(H_2O)$, assumed	Gaines et al. (1997)
16	Carrboydite	$Ni_{10}Cu_4Al_9(SO_4)_4(CO_3)_2(OH)_{43}•7(H_2O)$	Mineralogy Database (http://webmineral.com/)
17	Chalconatronite	$Na_2Cu(CO_3)_2•3(H_2O)$	Gaines et al. (1997)
18	Chalconatronite	$Na_2Cu(CO_3)_2•3(H_2O)$	Mukhopadyhay and Bernal (2004)
19	Claraite	$Cu_2Zn(CO_3)(OH)_4•4(H_2O)$	Gaines et al. (1997)
20	Claraite	$Cu_2Zn(CO_3)(OH)_4•4(H_2O)$	Mineralogy Database (http://webmineral.com/)

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
11	Caledonite	20.085	7.141	6.563				2	$Pmn2_1$	286.44
12	Callaghanite	10.06	11.8	8.24		107.3		4	C2/c	140.60
13	Callaghanite	10.0060	11.7520	8.2132		107.38		4	C2/c	138.77
14	Carrboydite	9.14		10.34				1	hex	450.05
15	Carrboydite	9.14		10.34				1/2	hex	901.00
16	Carrboydite	18.28		20.68				4	hex	901.00
17	Chalconatronite	13.72	6.12	9.7		91.3		4	$P2_1/n$	
18	Chalconatronite	9.6933(3)	6.0296(2)	13.7863(4)		91.908(2)		4	$P2_1/n$	121.24
19	Claraite	26.22		21.56				66	P1 or P-1	117.13
20	Claraite	14.28	8.03	7.27	79.16	107.9	99.68	4	P1 or P-1	116.48

	Name	Formula	Reference
21	Claraite	$(Cu_{2.6}Zn_{0.4})(CO_3)(OH)_4 \bullet 4(H_2O)$	Walenta and Dunn (1982), Walenta (1999)
22	Georgeite (amorph)	$Cu^{II}5(CO_3)_3(OH)_4 \bullet 6(H_2O)$	Gaines et al. (1997)
23	Glaukosphaerite	$Cu_{1.5}Ni_{0.5}(CO_3)(OH)_2$	Gaines et al. (1997)
24	Glaukosphaerite	$Cu_{1.5}Ni_{0.5}(CO_3)(OH)_2$	Mineralogy Database (http://webmineral.com/)
25	Glaukosphaerite	$Cu_{1.5}Ni_{0.5}(CO_3)(OH)_2$	Perchiazzi and Merlino (2006)
26	Juangodoyite	$Na_2Cu(CO_3)_2$	Gaines et al. (1997)
27	Juangodoyite	$Na_2Cu(CO_3)_2$	Maslen et al. (1986)
28	Kolwezite	$Cu_{1.34}Co_{0.66}(CO_3)(OH)_2$	Deliens and Piret (1980), Gaines et al. (1997)
29	Malachite	$Cu_2CO_3(OH)_2$	Zigan et al. (1977)
30	Malachite	$Cu_2CO_3(OH)_2$	Gaines et al. (1997)

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
21	Claraite	14.28	8.03	7.27	79.16	107.9	99.68	4	P1 or P-1	116.54
22	Georgeite (amorph)	-	-	-	-	-	-	-	-	-
23	Glaukosphaerite	9.35	11.97	3.13		96.0		4	$P2_1/a$	52.451
24	Glaukosphaerite	9.34	11.93	3.07		90.0		4	$P2_1/a$	51.501
25	Glaukosphaerite	12.0613	9.3653	3.1361		90.085		4	$P2_1/a$	53.333
26	Juangodoyite	6.171	8.171	5.645		116.23		2	$P2_1/a$	76.883
27	Juangodoyite	6.170(2)	8.171(2)	5.648(2)		116.24(1)		2	$P2_1/a$	76.905
28	Kolwezite	9.50	12.15	3.189	93.32	90.74	91.47	4	P1 or P-1	55.301
29	Malachite	9.502	11.974	3.240		98.75		4	$P2_1/a$	54.854
30	Malachite	9.48	12.03	3.21		98.		4	$P2_1/a$	54.579

	Name	Formula	Reference
31	Malachite	$Cu_2CO_3(OH)_2$	Mineralogy Database (http://webmineral.com/)
32	Mcguinnessite	$(Mg,Cu)_2(CO_3)(OH)_2$	Gaines et al. (1997)
33	Mcguinnessite	$(Mg,Cu)_2(CO_3)(OH)_2$	Perchiazzi (2006)
34	Nakauriite	$(Cu)_8(SO_4)_4(CO_3)(OH)_6•48(H_2O)$	Suzuki et al. (1976)
35	Nakauriite	$(Cu)_8(SO_4)_4(CO_3)(OH)_6•48(H_2O)$	Peacor et al. (1982)
36	Rosasite	$Cu_{1.16}Zn_{0.84}CO_3(OH)_2$	Gaines et al. (1997)
37	Rosasite	$Cu_{1.16}Zn_{0.84}CO_3(OH)_2$	Mineralogy Database (http://webmineral.com/)
38	Rosasite	$Cu_{1.16}Zn_{0.84}CO_3(OH)_2$ (assumed)	Perchiazzi (2006)
39	Roubaultite	$Cu_2(UO_2)_3(CO_3)_2O_2(OH)_2•4(H_2O)$	Ginderow and Cesbron (1985)
40	Roubaultite	$Cu_2(UO_2)_3(CO_3)_2O_2(OH)_2•4(H_2O)$	RRUFF ID: R080131.9, Mineralogy Database (http://webmineral.com/)

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
31	Malachite	9.502	11.974	3.240		98.75		4	$P2_1/a$	54.854
32	Mcguinnessite	9.398	12.011	3.379		93.28		4	P2/a or $P2_1/a$	57.330
33	Mcguinnessite	12.9181	9.3923	3.1622		111.233		4	$P2_1/a$	
34	Nakauriite	14.585	11.47	16.22				2	Orthorh.	817.04
35	Nakauriite	9.62{1}	6.231(6)	7.857(8)		111.82(7)		1/3#	P?	790.00
36	Rosasite	9.366	12.116	3.127		90.06		4	$P2_1/m$ or $P2_1$	53.423
37	Rosasite	12.873	9.354	3.156		110.36		4	$P2_1/a$	53.641
38	Rosasite	12.8976(3)	9.3705(1)	3.1623(1)		110.262(3)		4	$P2_1/a$	53.980
39	Roubaultite	7.767	6.942	7.85	92.16	90.89	93.48	1	P-1	254.20
40	Roubaultite	7.765(2)	6.915(2)	7.840(2)	92.31(2)	90.89(2)	93.48(2)	1	triclin	252.80

	Name	Formula	Reference
41	Schulenbergite	$(Zn,Cu)_7(SO_4)_{1.5}(CO_3)_{0.5}(OH)_{10}•3(H_2O)$	Gaines et al. (1997)
42	Zn-Schulenbergite	$Zn_5Cu_2(SO_4)_{1.5}(CO_3)_{0.5}(OH)_{10}•3(H_2O)$	Ohnishi et al. (2007)
43	Tyrolite	$CaCu_5(AsO_4)_2(CO_3)(OH)_4•6H_2O$	Gaines et al. (1997)
44	Tyrolite	$CaCu_5(AsO_4)_2(CO_3)(OH)_4•6(H_2O)$	Guillemin (1956)
45	Clinotyrolite	$Ca_2Cu_9(AsO_4)_{3.8}(SO_4)_{0.3}(CO_3)(OH)_{9.9}•10.3(H_2O)$	Gaines et al. (1997)
46	Tyrolite-1M	$[Ca_2Cu_9(AsO_4)_4(OH)_8(CO_3)(H_2O)_{11}]•x(H_2O)$, x = 0.1	Krivovichev et al. (2006)
47	Tyrolite-2M	$[Ca_2Cu_9(AsO_4)_4(OH)_8(CO_3)(H_2O)_{11}]•x(H_2O)$, x = 0.1	Krivovichev et al. (2006)
48	Voglite	$Ca_3Cu(UO_2)(CO_3)_4•6(H_2O)$	Piret (1979)
49	Zincrosasite	$(Zn,Cu)_2(CO_3)(OH)_2$	Mineralogy Database (http://webmineral.com/)

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
41	Schulenbergite	8.249		7.183				1	P3 or P-3	254.91
42	Zn-Schulenbergite	8.292		7.271				1	hex	260.73
43	Tyrolite	10.50	54.71	5.59				8	Pmma	241.73
44	Tyrolite	10.212	55.510	5.602				8	Pmma	239.05
45	Clinotyrolite	10.513	5.56	27.61		94.0		2	P2/a	484.76
46	Tyrolite-1M	27.562(3)2	5.5682(7)	10.4662(15)	98.074(11)			2	P2/c	478.86
47	Tyrolite-2M	54.520(6)	5. 5638 (6)	10.4647(10)	96.432(9)			4	C2/c	474.90
48	Voglite	25.97	24.5	10.7		104.		16	$P2_1$ or $P2_1/m$	248.63
49	Zincrosasite	-	-	-	-	-	-	-	$P2_1/a$ (mono)	-

	Name	Formula	Reference
	Synthetic Phases		
50	$CuCO_3$	$CuCO_3$	Seidel et al. (1974)
51	$CuCO_3$	$CuCO_3$	Pistorius (1960)*
52	$TlCu(OH)CO_3$	$TlCu(OH)CO_3$	Adam and Zheng (1994)
53	$Tl_2Cu(CO_3)_2$	$Tl_2Cu(CO_3)_2$	Ehrhardt et al. (1981)
54	$Cu_6Al_2(OH)_{16}CO_3$	$Cu_6Al_2(OH)_{16}CO_3$	Frost et al. (2009)

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
	Synthetic Phases									
50	$CuCO_3$	6.092	4.493	7.030		101.34		4	$Pa\text{-}C^2_s$	28.404
51	$CuCO_3$	4.796(5)		15.48(1)				6	R3c	30.950
52	$TlCu(OH)CO_3$	10.849(1)		6.118(1)				6	$P6_3/m$	62.592
53	$Tl_2Cu(CO_3)_2$	7.583(1)	9.799(1)	9.119(1)		111.51(1)		4	$P2_1/c$	94.911
54	$Cu_6Al_2(OH)_{16}CO_3$									

*Note: Purported rhombohedral form of $CuCO_3$ identifed on the basis of an XRD pattern alone, whose "…rhombohedral lattice [had] nearly the same dimensions as siderite"

#Calculated from cell constants, this work.

Table 6. Carbonate Minerals containing greater than 10 wt.% Copper

Name	Formula	Copper, wt.%	gfw	Thermodynamic Data	
				Est.	Meas.
Ashburtonite	$HPb_4Cu^{II}{}_4Si_4O_{12}(HCO_3)_4(OH)_4Cl$	34.43	1735.88	no	no
Astrocyanite-(Ce)	$Cu_2(Ce,Nd,La)_2(UO_2)(CO_3)_5(OH)_2 \cdot 1.5(H_2O)$	32.37	951.38	no	no
Aurichalcite	$(Zn,Cu)_5(CO_3)_2(OH)_6$	34.00	546.71	no	yes
Azurite	$Cu_3(CO_3)_2(OH)_2$	55.31	344.67	no	yes
Caledonite	$Pb_5Cu_2(CO_3)(SO_4)_3(OH)_6$	14.64	1613.34	no	yes
Callaghanite	$Cu_2Mg_2(CO_3)(OH)_6 \cdot 2(H_2O)$	55.31	373.79	no	no
Camerolaite	$Cu_4Al_2[HSbO_4,SO_4](OH)_{10}(CO_3) \cdot 2(H_2O)$	57.48	738.34	no	no
Carbonatecyanotrichite	$Cu^{II}{}_4Al_2(CO_3,SO_4)(OH)_{12} \cdot 2(H_2O)$	40.96	620.53	no	no
Carrboydite	$(Ni,Cu)_{14}Al_9(SO_4,CO_3)_6(OH)_{43} \cdot 7(H_2O)$	22.41	2445.61	no	no
Chalconatronite	$Na_2Cu(CO_3)_2 \cdot 3(H_2O)$	42.93	283.59	no	yes
Claraite	$(Cu,Zn)_3(CO_3)(OH)_4 \cdot 4(H_2O)$	49.66	392.58	no	no
Decrespignyite-(Y)	$(Y,REE)_4Cu(CO_3)_4Cl(OH)_5 \cdot 2(H_2O)$	15.36	867.49	no	no
Ferrisurite	$(Pb,Cu)_{2-3}(CO_3)_{1.5-2}(OH,F)_{0.5-1}[(Fe,Al)_2Si_4O_{10}(OH)_2] \cdot n(H_2O)$	10.63	914.93	no	no
Gartrellite	$Pb(Cu,Fe{+}{+})_2(AsO_4,SO_4)_2(CO_3,H_2O)_{0.7}$	37.52	620.46	no	no
Georgeite	$Cu^{II}5(CO_3)_3(OH)_4 \cdot 6(H_2O)$	49.66	639.86	no	no
Glaukosphaerite	$(Cu,Ni)_2(CO_3)(OH)_2$	43.59	218.69	no	no
Juangodoyite	$Na_2Cu(CO_3)_2$	43.59	229.51	no	yes
Kolwezite	$(Cu,Co)_2(CO_3)(OH)_2$	39.05	218.07	no	no
Malachite	$Cu_2(CO_3)(OH)_2$	57.48	221.12	no	yes
Mcguinnessite	$(Mg,Cu)_2(CO_3)(OH)_2$	39.05	162.25	no	no
Nakauriite	$(Cu)_8(SO_4)_4(CO_3)(OH)_6 \cdot 48(H_2O)$	10.39		no	no
Numanoite	$Ca_4CuB_4O_6(OH)_6(CO_3)_2$	19.58	573.17	no	no
Paratooite-(La)	$REE_3(Ca,Sr)_2NaCu(CO_3)_8$	13.36	2146.77	no	no
Rosasite	$(Cu,Zn)_2(CO_3)(OH)_2$	42.93	222.04	no	yes
Roubaultite	$Cu_2(UO_2)_3(CO_3)_2O_2(OH)_2 \cdot 4(H_2O)$	27.13	1195.27	no	no
Schulenbergite	$(Cu,Zn)7(SO_4,CO_3)_2(OH)_{10} \cdot 3(H_2O)$	37.52	846.73	no	no
Schuilingite-(Nd)	$PbCu(Nd,Gd,Sm,Y)(CO_3)_3(OH) \cdot 1.5(H_2O)$	21.33	696.16	no	no
Surite	$(Pb,Cu)_{23}(CO_3)_{1.52}(OH,F)_{0.51}[(Al,Fe^{III})_2(Si,Al)_4O_{10}(OH)_2] \cdot n(H_2O)$	14.53	937.16	no	no
Tyrolite	$CaCu_5(AsO_4)_2(CO_3)(OH)_4 \cdot 6(H_2O)$	36.45	871.78	no	no
Voglite	$Ca_2Cu(UO_2)(CO_3)_4 \cdot 6(H_2O)$	14.91	761.86	yes	no
Zincrosasite	$(Zn,Cu)_2(CO_3)(OH)_2$	40.96	223.42	no	no
Zn-Schulenbergite	$(Zn,Cu)_7(SO_4,CO_3)_2(OH)_{10} \cdot 3(H_2O)$	36.45	852.26	no	no

Data taken primarily from a compilation given by the Mineralogy Database (http://webmineral.com).

References

Abdul-Samad, F., Thomas, J.H., Williams, P.A., Bideaux, R.A. and Symes, R.F. (1982). Mode of formation of some rare copper(II) and lead(II) minerals from aqueous solution, with particular reference to deposits at Tiger, Arizona. Transition Metal Chemistry, 7, 32-37.

Adam, A. and Zheng, Y.Q. (1994). $TlCu(OH)CO_3$ - Ein neues basisches Thallium-Kupfer-Carbonat. Zeitschrift für anorganische und allgemeine Chemie, 620, 1707-1713.

Alwan, A.K., Thomas, J.H. and Williams, P.A. (1980). Mineral Formation from Aqueous Solution. Part III. The Stability of Aurichalcite, $(Zn,Cu)_5(CO_3)_2(OH)_6$, and Rosasite $(Cu,Zn)_2(CO_3)(OH)_2$. Transition Metal Chemistry, 5, 3-5.

Baes, C.F., Jr. and Mesmer, R.E. (1976). The Hydrolysis of Cations. J. Wiley and Sons, New York, 489 p.

Ball, J.W. and Nordstrom, D. K. (1991). User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters. USGS-OFR-91-183, U.S. Geological Survey, Menlo Park, California.

Barin, I., Knacke, O and Kubaschewski, O. (1973). Thermochemical Properties of Inorganic Substances. Springer Verlag, Berlin. 921 p.

Barin, I., Knacke, O. and Kubaschewski, O. (1977). Thermodynamic properties of inorganic substances. Supplement. Springer Verlag, Berlin. 861 p.

Bauman, J.E., Jr. (1981). Thermodynamic measurements of carbonate equilibriums involving metal ions. US. Bureau of Mines, Information Circular No. 8853, 268-274.

Belokoneva, E.L., Gubina, Y.K, and Forsyth, J.B. (2001). The charge density distribution and antiferromagnetic properties of azurite $Cu_3[CO_3]_2(OH)_2$. Physics and Chemistry of Minerals, 28, 498-507.

Bilinski, H., Huston, R. and Stumm, W. (1976). Determination of the stability constants of some hydroxo and carbonato complexes of Pb(II), Cu(II), Cd(II), and Zn(II) in dilute solutions by anodic stripping voltammetry and differential pulse polarography. Analytica Chimica Acta, 84, 157-164.

Brunton, G.D. (1973). Refinement of the callaghanite structure. American Mineralogist, 58, 965-965.

Byrne, R.H. and Miller, W.L. (1985). Copper(II) carbonate complexation in seawater. Geochimica et Cosmochimica Acta, 49, 1837-1844.

Cooper, M. and Hawthorne, F.C. (1994). The crystal structure of wherryite, $Pb_7Cu_2(SO_4)_4(SiO_4)_2(OH)_2$, a mixed sulfate-silicate with $[^{[6]}M(TO_4)_2\ \phi]$ chains. Canadian Mineralogist, 32, 373-380.

Deliens, M. and Piret, P. (1980). La kolwézite, un hydroxycarbonate de cuivre et de cobalt analogue à la glaukosphaerite et à la rosasite. Bulletin de Mineralogie, 103, 179-184 (English abs.).

Deliens, M. and Piret, P. (1990). L'astrocyanite-(Ce), $Cu_2(TR)_2(UO_2)(CO_3)_5(OH)_2.1{,}5H_2O$, nouvelle espèce minérale de Kamoto, Shaba, Zaire. European Journal of Mineralogy, 2(3), 407-411.

Dobrydiev, S.V., Nilova, E.V. and Beskov, V.S. (2005). Calculation of $\Delta_f G^0(298)$ and $\Delta_f H^0(298)$ for sparingly soluble metal carbonates and oxalates in the solid state. Zhurnal Neorganicheskoi Khimii, 50(12), 2015-2018. [In Russian].

Ehrhardt, H., Johannes, W. and Seidel, H. (1973). Hochdrucksynthese von Kupfer(II)-Carbonat, Zeitschrift für Naturforschung, 28b, 682.

Ehrhardt, H., Lemor, R. and Seidel, H. (1981). Hochdrucksynthesen von Carbonaten. V [l]. Carbonatdarstellungen durch Schmelzreaktionen unter hohen CO_2-Drucken. Zeitschrift für anorganische und allgemeine Chemie, 477, 183-195.

Ernst, R., Allen, H.E. And Mancy, K.H. (1975). Characterization of trace metal species and measurement of trace metal stability constants by electrochemical techniques. Water Research, 9, 969-979.

Faucherre, J. and Bonnaire, Y. (1959). Sur la constitution des carbonates complexes de cuivre et de plomb. Comptes Rendus de l'Academie des Sciences de Paris, 248, 3705-3707.

Fouillac, A. and Criaud, A. (1984). Carbonate and bicarbonate trace metal complexes: Critical reevaluation of stability constants. Geochemical Journal, 18, 297-303.

Free, E.E. (1908). The solubility of precipitated basic copper carbonate in solutions of carbon dioxide. Journal of the American Chemical Society, 30, 1366-1374.

Fromage, F. and Fiorina, S. (1969). Sur les carbonato- et hydrogenocarbonatocuprates (II) de potassium. Comptes Rendus des Seances de l'Academie des Sciences, Serie C: Sciences Chimiques, 268(17), 1511-1513.

Frost, R.L., Soisnard, A., Voyer, N., Palmer, S.J. and Martensa, W.N. (2009). Thermo-Raman spectroscopy of selected layered double hydroxides of formula $Cu_6Al_2(OH)_{16}CO_3$ and $Zn_6A_{l2}(OH)_{16}CO_3$. Journal of Raman Spectroscopy, 40, 645-649.

Gaines, R.V., Skinner, H.C.W., Foord, E.E., Mason, B., Rosenzweig, A. King, V.T. and Dowty, E. (1997). Dana's New Mineralogy (Eighth edition). John Wiley and Sons, Inc., New York. 1819 p.

Gamsjäger, H. (1974). Wechselwirkung von Metalloxiden, -hydroxiden, -carbonaten und -sulfiden mit Wasser. Radex-Rundschau, 4, 274-285.

Gamsjäger, H. (1985). Solid state chemical model for the solubility behavior of homogeneous solid cobalt manganese carbonate mixtures. Berichte der Bunsen-Gesellschaft, 89(12), 1318-22.

Garrels, R.M. (1957). Some free energy values from geologic relations. American Mineralogist, 42, 780-791.

Garrels, R.M. (1960). Mineral Equilibria at Low Temperature and Pressure. Harper and Brothers, New York, 254 p.

Gedansky, L.M., Wooley, E.M. and Hepler, G.H. (1970). Thermochemistry of compounds and aqueous ions of copper. 1. Chemical Thermodynamics, 2, 561-576.

Ginderow, D.A.R.I.A., and Cesbron, F. (1985). Structure de la roubaultite, $Cu_2(UO_2)_3(CO_3)_2O_2(OH)_2.4H_2O$. Acta Crystallographica Section C: Crystal Structure Communications, 41(5), 654-657.

Goskhimizdat. (1952). Chemical Reference, vol. 3. [In Russian]. (As cited in Zhuk, 1954).

Grauer, R., (1999). Solubility products of M(II) carbonates (edited and translated by U. Berner). Waste Management laboratory, PSI Bericht Nr. 99-04, January 1999, ISSN 1019-0643.

Grenthe, I. (1985). Personal communication with Vieillard (1988).

Guillemin, C. (1956). Contribution a la mineralogie des arsenates, phosphates et vanadates de cuivre. Bulletin de la Société Française de Minéralogie et de la Cristallographie, 79, 7-95.

Haehnel, O. (1924). Über die Löslichkeit der Carbonate des Strontiums, des Bariums und der Schwermetalle in Wasser unter hohen Kohlendioxyddrucken sowie über die Eigenschaften solcher Lösungen. Journal für praktische Chemie (Leipzig), 108, 187-193.

Harding M M., Kariuki, B M., Cernik, R, and Cressey G. (1994). The structure of aurichalcite, $(Cu,Zn)_5(OH)_6(CO_3)_2$, determined from a microcrystal. Acta Crystallographica, B50, 673-676.

Helgeson, H.C., Delany, J.M., Nesbith.W. and Bird, D.K. (1978). Summary and critique of the thermodynamic properties of the rock forming minerals. American Journal of Science, 278-A, 227 p.

Hemingway, B.S. (1982). Thermodynamic properties of selected uranium compounds and aqueous species at 298.15 K and I bar and at higher temperatures. Preliminary models for the origin of coffinite deposits. U.S. Geological Survey, Open File Report 82-619, (1982), 89 p.

Karapet'yants, M. Kh. (1953). Khimicheskaya Termodinamika (Chemical Thermodynamics). 2nd Edition. Goshkhimizdat. 611 p. [In Russian].

Karapet'yants, M. Kh. (1955). Approximate method for the calculation of the isobaric potential and heat of formation of different substances. Trudy Instituta - Moskovskii Khimiko-Tekhnologicheskii Institut imeni D. I. Mendeleeva, No. 20, p. 10-28.

Karapet'yants, M.Kh. and Karapet'yants, M.L. (1970). Thermodynamic constants of Inorganic and Organic Compounds (trans. By J. Schmorak). Humphrey Science Publishers, Ann Arbor, Michigan. 461 p.

Karpov, I.K., Kashik, S.A. and Pampura, V.D. (1968). Thermodynamic Constants for Calculations in Geochemistry and Petrology. [In Russian] Izdva, Nauka, 143 p.

Kelley, K.K. and Anderson, C.T. (1935). Theoretical metallurgy. IV. Metal carbonates - Correlations and applications of thermodynamic properties. Bureau of Mines Bulletin No. 384, 73 p.

Kelley, K.K. and King. E.G. (1961). Contribution to the Data on Theoretical Metallurgy. XIV. Entropies of the Elements and Inorganic Compounds. U.S Bureau of Mines Bulletin No. 592, 149 p.

Kireev, V.A. (1964). Acid-base properties of oxides. Zhurnal Fizicheskoi Khimii, 38(8), 1881-1894. [In Russian].

Kiseleva, I.A., Ogorodova, L.P., Melchakova, L.V., Bisengalieva, M.R. and Becturganov, N.S. (1992). Thermodynamic properties of copper carbonates - malachite $Cu_2(OH)_2CO_3$ and azurite $Cu_3(OH)_2(CO_3)$. Physics and Chemistry of Minerals, 19, 322-333.

Krishnamurty, K.V., Harris, G.M. and Sastri, V.S. (1970). The chemistry of the metal carbonato complexes. Chemical Reviews, 70(2), 171-197.

Krivovichev, S.V., Chernyshov, D.Y., Dobelin, N., Armbruster, T., Kahlenberg, V., Kaindl, R., Tessadri, R. and Kaltenhauser, G. (2006). Crystal chemistry and polytypism of tyrolite. American Mineralogist, 91, 1378-1384.

Kubaschewski, O., Alcock, C.B. and Spencer, P.J. (1993). Materials Thermochemistry (Sixth edition). Pergamon Press, Oxford, 363 p.

La Iglesia, A. and Félix, J.F. (1994). Estimation of thermodynamic properties of mineral carbonates at high and low temperatures from the sum of polyhedral contributions. Geochimica et Cosmochimica Acta, 58(19), 3983-3991.

Latimer, W.M. (1952). The Oxidation States of the Elements and their Potentials in Aqueous Solutions. Second edition. Prentice Hall, New York, 392 p.

Lewis, D. (1978). The thermodynamics of the system Cu-H_2O-CO_3^{2-} at elevated temperatures: a preliminary investigation in copper as cannister material for unreprocessed nuclear waste. Rep. K.B.S.-90.

Martell, A.E., Smith, R.M. and Motekaitis, R.J. (1997). Critically selected stability constants of metal complexes database. Version 4.0. National Institute of Standards and Technology (NIST); Texas A & M University. (http://www.nist.gov/srd).

Maslen, E N., Spadaccini, N. and Watson, K J. (1986). Electron density in non-ideal metal complexes. II. Sodium bis(carbonato)cuprate(II). Acta Crystallographica, B42, 430-436.

Mattigod, S.V. and Sposito, G. (1977). Estimated association constants for some complexes of trace metals with inorganic ligands. Soil Science Society of America Journal, 41(6), 1092-1097.

McBride, M.B. (1979). Chemisorption and precipitation of Mn^{2+} at $CaCO_3$ surfaces. Soil Science Society of America Journal, 43, 693-698.

Meites, L. (1950). Polarographic studies of metal complexes. III**.** The copper(II) oxalates and carbonates. Journal of the American Chemical Society, 72, 184-189.

Millero, F.J. and Hawke, D.J. (1992). Ionic interactions of divalent metals in natural waters. Marine Chemistry, 40, 19-48.

Millero, F.J., Santana-Casiano, J.M. and González-Dávila, M. (2010). The formation of Cu(II) complexes with carbonate and bicarbonate ions in $NaClO_4$ solutions. Journal of Solution Chemistry, 39, 543-558.

Mugabe, R., Nyangababo, T. J. and Schroeder, K.H. (1998). Voltammetric study of copper complexation by natural inorganic ligands in a salt lake. International Journal of Environmental Studies, 55(3), 247-253.

Mukhopadyhay, U. and Bernala, I. (2004). A totally unexpected synthesis of single crystals of the mineral Chalconatronite, $Na_2[Cu(CO_3)_2]\cdot 3H_2O$, from a solution of a copper coordination compound and atmospheric CO_2, at room temperature. Journal of Coordination Chemistry, 57(5), 353-360.

Naumov, G.B., Ryzhenko, B.N. and Khodakovsky, J.L. (1971). Handbook of thermodynamic quantities for geology. Moscow Atomic Press, 240 p. [in Russian].

Naumov, G.B., Ryzhenko, B.N. and Khodakovsky, 1.L. (1974). Handbook of Thermodynamic Data. National Technical Information Service, 722176A, U.S. Dept. Commerce. 328 p.

Nickel, E.H. and Clarke, R.M. (1976). Carrboydite, a hydrated sulfate of nickel and aluminum: a new mineral from Western Australia. American Mineralogist, 61, 366-372.

Novozamsky, I. and Beek, J. (1976). Common solubility equilibria in soils. In Soil Chemistry A. Basic Elements (G.H. Bolt and M.G. Bruggenwert, Eds.), 95-125. Elsevier. New York.

Ohnishi, M., Kusachi, I., Kobayashi, S. and Yamakawa, J. (2007). Mineral chemistry of schulenbergite and its Zn-dominant analogue from the Hirao mine, Osaka, Japan. Journal of Mineralogical and

Petrological Sciences, 102(4), 233-239.

Palmer, D.A. and van Eldik, R. (1983). The chemistry of metal carbonato and carbon dioxide complexes. Chemical Reviews, 83, 651-731.

Peacor, D.R., Simmons, W.B., Essene, E.J. and Heinrich, E.W. (1982). New data on and discreditation of "texasite," "albrittonite," "cuproartinite," "cuprohydromagnesite," and "yttromicrolite," with corrected data on nickelbischofite, rowlandite, and yttrocrasite. American Mineralogist, 67(1-2), 156-169.

Perchiazzi, N. (2006). Crystal structure determination and Rietveld refinement of rosasite and mcguinnessite. Zeitschrift für Kristallographie Supplement, 23, 505-510.

Perchiazzi, N. and Merlino, S. (2006). The malachite-rosasite group: crystal structures of glaukosphaerite and pokrovskite. European Journal of Mineralogy, 18, 787-792.

Piret, P. (1979). New crystal data for Ca, Cu, UO_2 hydrated carbonate: voglite. Journal of Applied Crystallography, 12(2), 616.

Pistorius, C.W.F.T. (1960). Synthesis at high pressure and lattice constants of normal cupric carbonate. Experientia, XVI, 447.

Powell, K.J., Brown, P.L., Byrne, R.H., Gajda, T., Hefter, G., Sjöberg, S. and Wanner, H. (2007). Chemical speciation of environmentally significant metals with inorganic ligands. Part 2: The Cu^{2+}-OH^-, Cl^-, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-} systems. Pure and Applied Chemistry, 79(5), 895-950.

Preis, W. and Gamsjäger, H. (2001). Thermodynamic investigation of phase equilibria in metal carbonate-water-carbon dioxide systems (Invited Review). Monatshefte für Chemie, 132, 1327-1346.

Preis, W. and Gamsjäger, H. (2002). Solid-solute phase equilibria in aqueous solution. XVI. Thermodynamic properties of malachite and azurite-predominance diagrams for the system Cu^{2+}-H_2O-CO_2. Journal of Chemical Thermodynamics, 34, 631-650.

Puigdomenech, I. and Taxén, C. (2000). Thermodynamic data for copper. Implications for the corrosion of copper under repository conditions. Technical Report TR-00-13, Swedish Nuclear Fuel and Waste Management Co., Stockholm, Sweden. 96 p.

Radha, A.V. and Navrotsky, A. (2013). Thermodynamics of carbonates. Reviews in Mineralogy and Geochemistry, 77(1), 73-121.

Rages, D. (1978). M.A. Thesis, University of Missouri-Columbia.

Reinert. M. (1965). Über die Bestimmung der Loslichkeit schwehrlöslicher Salze mit basischen Anionen. Unpublished Ph.D. thesis, Universität Berne.

Reiterer, F. (1980). Lös1ichkeitskonstanten und freie Bildungsenthalpien neutraler Übergangsmetallcarbonate: $MnCO_3$, $FeCO_3$, $CoCO_3$, $NiCO_3$, $CuCO_3$, $ZnCO_3$. PhD thesis, Montanuniversität, Leoben, Austria.

Reiterer, F., Johannes, W., and Gamsjäger, H. (1981). Semi~microdetermination of solubility constants of copper (II) carbonate and iron (II) carbonate. Microchimica Acta, 1(1-2), 63-72.

Richardson, D.W. and Brown, R.R. (1974). Enthalpy of formation of malachite [$Cu_2(CO_3)(OH)_2$]. U.S. Bureau of Mines Report of Investigations 7851, 5 p.

Rickard, D.T. (1971). The chemistry of copper in natural aqueous solutions. In Acta Universitatus.

Stockholmiensis, Stockholm Contributions in Geology (Ivar Hessland, Ed.), XXIII, 1-64. University of Stockholm, Stockholm, Sweden.

Robie, R.A. (1962). Thermodynamic properties of minerals. U.S. Geological Survey Open File Report TEI-816. 31 p.

Robie, R.A. (1966). Section 20: Thermodynamic properties of minerals. Handbook of Physical Constants, Geological Society of America Memoirs, 97, 437-458.

Robie, R.A. and Hemingway, B.S. (1995). Thermodynamic properties of minerals and related substances at 298.15 K and 1 Bar (10^5 Pascals) pressure and at higher temperatures. U.S. Geological Survey Bulletin No. 2131. United States Government Printing Office: Washington, DC. 461 p.

Robie R.A., Hemingway B.S. and Fisher J.R. (1978). Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 Pa) pressure and at higher temperatures. U.S. Geological Survey Bulletin No.1452. U.S. Government Printing Office, Washington, DC. 456 p.

Rossini, F.D., Wagman D.D., Evans W.H., Levine S. and Jaffe I. (1952). Selected values of chemical tbermodynamical properties. NBS Circular 500. 1268 p., Washington, D.C.

Roth, W.A., Berendt, H. and Wirths, G. (1941). Die Bildungswarmen einiger mineralischer und kunstlicher Carbonate. Zeitschrift für Elektrochemie, 47, 185-190.

Ryabin, V.A., Ostroumov, M.A. and Svit, T.F. (1977). Thermodynamic Properties of Substances: Handbook (Termodinamicheskie Svoistva Veshchestv: Spravochnik). Khimiya, Leningr. Otd. Leningrad, USSR 389 p. [In Russian].

Sangameswhar. S.R. and Barnes, H.L. (1983). Supergene processes in zinc - lead - silver sulfide ores in carbonates. Economic Geology, 78, 1379-1397.

Scaife, J.F. (1957). The solubility of malachite. Canadian Journal of Chemistry, 35, 1332-1340.

Schindler, P., Reinert, M. and Gamsjäger, H. (1968). Zur Thermodynamik der Metallcarbonate 2: Löslichkeitskonstanten und Freiebildungsenthalpien von $Cu_2(OH)_2CO_3$ (Malachit) und $Cu_3(CO_3)_2(OH)_2$ (Azurit) bei 25°C. Helvetica Chimica Acta, 51, 1845-1856.

Schofield, P.F., Wilson, C.C., Knight, K.S. and Kirk, C.A. (2009). Proton location and hydrogen bonding in the hydrous lead copper sulfates linarite, $PbCu(SO_4)(OH)_2$, and caledonite, $Pb_5Cu_2(SO_4)_3CO_3(OH)_6$. Canadian Mineralogist, 47,649-662.

Seidel, H., Viswanathan, K., Johannes, W. and Ehrhardt, H. (1974). Darstellung, Struktur und Eigenschaften von Kupfer(l1)-Carbonat. Zeitschrift für anorganische und allgemeine Chemie, 410, 138-148.

Shirai, H. (1961). The reduction waves of copper and lead ions in potassium hydrogen carbonate solution. Nippon Kagaku Zasshi, 82, 1179-1182. [Cited in Chemical Abstracts].

Sillen, L.G. and Martell, A.E. (1964). Stability constants of metal-ions complexes. The Chemical Society, Burlington House, London, 356 p.

Sillen, L.G. and Martell, A.E. (1971). Stability constants of metal-ions complexes. Supplement n° 1. The Chemical Society, Burlington House, London, 865 p.

Silman, J.F.B. (1958). The stabilities of some oxidized copper minerals in aqueous solutions at 25ºC and 1 atmosphere total pressure. Unpublished PhD thesis, Harvard University, Cambridge, Massachusetts,

98 p.

Smith, R.M. and Martell, A.E. (1976). Critical Stability Constants, Volume 4, Inorganic Complexes. Plenum Press, New York.

Soli, A.L. and Byrne, R.H. (1989). Temperature dependence of Cu(II) complexation in natural seawater. Limnology and Oceanography, 34, 239-244.

Stella, R. and Ganzeril-Valentini M.T. (1979). Copper ion-selective electrode for determination of inorganic copper species in freshwater. Analytical Chemistry, 51, 2148-2151.

Stern, K.H. (2000). High Temperature Properties and Thermal Decomposition of Inorganic Salts with Oxyanions. 256 p. CRC Press LLC, 2000 N.W. Corporate Blvd., Boca Raton Florida 33431.

Stiff, M.J. (1971). Copper/bicarbonate equilibria in solutions of bicarbonate ion at concentrations similar to those found in natural water. Water Research, 5, 171-176.

Sunda, W.G. and Hanson, P.J. (1979). Chemical speciation of copper in river water. In Chemical Modeling in Aqueous Systems (E.A. Jenne, Ed.). Washington DC, 147-180.

Suzuki, J., Ito, M. and Sugiura, T. (1976). A new copper sulfate-carbonate hydroxide hydrate mineral, $(Mn,Ni,Cu)_8(SO_4)_4(CO_3)(OH)_6.48H_2O$, from Nakauri, Achi Prefecture, Japan. Journal of Japanese Association of Mineralogists, Petrologists and Economic Geologists, 71, 183-192. [In English].

Symes, J.L. and Kester, D.R. (1984). Thermodynamic stability studies of the basic copper carbonate mineral, malachite. Geochimica et Cosmochimica Acta, 48, 2219-2229.

Symes, J.L. and Kester, D.R. (1985). Copper(II) interaction with carbonate species based on malachite solubility in perchlorate medium at the ionic strength of seawater. Marine Chemistry, 16, 189-211.

van den Berg, C.M.G. and Kramer, J.R. (1979). Determination of complexing capacities of ligands in natural waters and conditional stability constants of the copper complexes by means of manganese dioxide. Analytica Chimica Acta, 106. 113-120.

Van Genderen, A.C.G. and Van der Weijden, C.H. (1984). Prediction of Gibbs energies of formation and stability constants of some secondary uranium minerals containing the uranyl group. Uranium, 1(3), 249-256.

Vieillard, P. (1988). Proprietes thermodynamiques des composes du cuivre. Atlas de donnees thermodynamiques. Sciences Geologiques, Bulletin, 41(3-4), 289-308.

Vieillard, P., Koud, J.M., Nahon, D. and Tardy, Y. (1989). Petrologie, mineralogie et geochimie des depots de cuivre du bassin de Niari (a paraitre).

Vink, B.W. (1986). Stability relations of malachite and azurite. Mineralogical Magazine, 50, 41-47.

Wagman, D.D., Evans, W.H., Parker, V.B., Halow, I., Bailey, S.M. and Schumm, R.H. (1969). Selected values of chemical thermodynamic properties. Tables for elements 35 through 53 in the standard order of arrangement. NBS Technical Note 270-4, U.S. Department of Commerce, National Bureau of Standards, 141 p.

Wagman, D.D., Evans, W.H., Parker, V.B., Schumm, R.H., Halow, I., Bailey, S.M., Churney, K.L. and Nuttall, R.L. (1982). The NBS Tables of Chemical Thermodynamic Properties: Selected Values for Inorganic and C1 and C2 Organic Substances in SI Units. American Chemical Society and the

American Institute of Physics for the National Bureau of Standards (Journal of Physical Chemical Reference Data, 11, supp. 2, 392 p.).

Walenta, K. (1999). On the lattice constants of claraite. Der Erzgräber, 13, 20-22. [in German].

Walenta, K. and Dunn, P.J. (1982). Claraite, a new carbonate mineral from the Clara Mine. (Central Black Forest). Chemie der Erde. 41, 97-102.

Wilcox, D.E. and Bromley, L.A. (1963). Computer Estimation of heat and free energy for simple inorganic compounds. Industrial and Engineering Chemistry, 55(7), 32-39.

Woods, T.L. and Garrels, R.M. (1986). Phase relations of some cupric hydroxy minerals. Economic Geology, 81(8), 1989-2007.

Woods, T.L. and Garrels, R.M. (1987). Thermodynamic Values at Low Temperature for Natural Inorganic Materials. An Uncritical Summary. Oxford University Press. 242 p. plus references.

Yoder, C.H. and Rowand, J.P. (2006). Application of the simple salt lattice energy approximation to the solubility of minerals. American Mineralogist, 91(5-6), 747-752.

Yoder, C.H., Gotlieb, N.R. and Rowand, A.L. (2010). The relative stability of stoichiometrically related natural and synthetic double salts. American Mineralogist, 95(1), 47-51.

Zhuk, N.P. (1954). Thermodynamic constants of sulfates, carbonates, chromates, bromates, iodates, oxalates, and other salts slightly soluble in water. Zhurnal Fizicheskoi Khimii, 28, 1690-1697. [In Russian].

Zigan, F, Joswig W, Schuster, H U, and Mason, S.A. (1977). Verfeinerung der Struktur von Malachit, $Cu_2(OH)_2CO_3$, durch Neutronenbeugung. Zeitschrift fur Kristallographie 145, p. 412-426.

Zirino, A. and Yamamoto, S. (1972). A pH-dependent model for the chemical speciation of copper, zinc, cadmium, and lead in seawater. Limnology and Oceanography, 17, 661-671.

Zuehlke, R.W. and Kester, D.R. (1983). Ultraviolet spectroscopic determination of the stability constants for copper carbonate and bicarbonate complexes up to the ionic strength of sea water. Marine Chemistry, 13, 203-226.

IRON

Table 1. Association Constants for Aqueous Carbonate Complexes in the System FeO/Fe_2O_3-CO_2-H_2O

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
Fe(II)					
$Fe^{2+} + CO_3^{2-} = FeCO_3(aq)$	4.83	-		Nordstrom et al. (1990)	Langmuir (1969)
	6.57		Estimate		Mattigod and Sposito (1977)
	6.57		$FeHCO_3^+$, $FeCO_3(aq)$, $Fe(CO_3)_2^{2-}$, $FeOH^+$,$Fe(OH)_2(aq)$, $Fe(OH)_3^-$, $Fe(OH)_4^{2-}$	Fosbøl et al. (2010)	Mattigod and Sposito (1977)
	4.00	-		Fouillac and Criaud (1984)	Serebrennikov (1977)
	4		$FeHCO_3^+$, $FeCO_3(aq)$	Fosbøl et al. (2010)	Serebrennikov (1977)
	4.73		$FeCO_3(aq)$, $FeOH^+$, $Fe(OH)_2(aq)$, $Fe(OH)_3^-$, $Fe(OH)_4^2$	Fosbøl et al. (2010)	Turner et al. (1981)
	4.73	-0.29	Estimate		Fouillac and Criaud (1984)
	4.73		25°C, I = 0	Wersin et al. (1989)	Fouillac and Criaud (1984)
	4.73		$FeHCO_3^+$, $FeCO_3(aq)$	Fosbøl et al. (2010)	Fouillac and Criaud (1984)
	4.38		$FeHCO_3^+$, $FeCO_3(aq)$, $FeOH^+$	Fosbøl et al. (2010)	Nordstrom et al. (1990)
	5.5 ± 0.2	-		Bruno et al. (1992)	Bruno et al. (1992)
	5.45	-		Millero and Hawke (1992) Also cited by Millero et al. (1995)	Bruno (personal communication)
	5.69	-	Re-evaluation of data	King (1998)	Bruno et al. (1992)
	5.9 ± 0.2	-	Re-evaluation of data, in $NaClO_4$ soln.	Silva et al. (2002)	Bruno et al. (1992)
	5.5		$FeCO_3(aq)$, $Fe(CO_3)_2^{2-}$,	Fosbøl et al. (2010)	Bruno et al. (1992)
	5.45		$FeHCO_3^+$, $FeCO_3(aq)$, $Fe(CO_3)_2^{2-}$, $FeOH^+$, Fe(OH)2(aq)	Fosbøl et al. (2010)	Millero and Hawke (1992)
	5.3	-		Preis and Gamsäger (2002)	Source not cited
	5.3		$FeCO_3(aq)$, $Fe(CO_3)_2^{2-}$	Fosbøl et al. (2010)	Preis and Gamsja¨ger 2002
	6.3 ± 0.2	-	Sol., in NaCl soln.		Silva et al. (2002)
	6.3		$FeCO_3(aq)$ maybe more	Fosbøl et al. (2010)	Silva et al. (2002)

Table 1. Association Constants for Aqueous Carbonate Complexes in the System FeO/Fe_2O_3-CO_2-H_2O (Continued)

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
$Fe^{2+} + CO_2(g) + H_2O = FeCO_3(aq) + 2H^+$	-12.9 ± 0.12	-	1 *M* $NaClO_4$		Bruno et al. (1992)
$Fe^{2+} + 2CO_3^{2-} = Fe(CO_3)_2^{2-}$	9.51		Estimate		Mattigod and Sposito (1977)
	9.51		$FeHCO_3^+$, $FeCO_3(aq)$, $Fe(CO_3)_2^{2-}$, $FeOH^+$,$Fe(OH)_2(aq)$, $Fe(OH)_3^-$, $Fe(OH)_4^{2-}$	Fosbøl et al. (2010)	Mattigod and Sposito (1977)
	7.1 ± 0.2	-			Bruno et al. (1992)
	7.17	-		Millero and Hawke (1992)	Bruno (personal communication)
	7.45	-	Re-evaluation of data	King (1998)	Bruno et al. (1992)
	7.16	-		Millero et al. (1995)	Millero and Hawke (1992)
	7.1	-	Source not cited		Preis and Gamsjäger (2002)
	7.1		$FeCO_3(aq)$, $Fe(CO_3)_2^{2-}$,	Fosbøl et al. (2010)	Bruno et al. (1992)
	7.17		$FeHCO_3^+$, $FeCO_3(aq)$, $Fe(CO_3)_2^{2-}$, $FeOH^+$, $Fe(OH)_2(aq)$	Fosbøl et al. (2010)	Millero and Hawke 1992
	7.1		$FeCO_3(aq)$, $Fe(CO_3)_2^{2-}$	Fosbøl et al. (2010)	Preis and Gamsja¨ger (2002)
$Fe^{2+} + 2CO_2(g) + 2H_2O = Fe(CO_3)_2^{2-} + 4H^+$	-28.4 ± 0.10	-	1 *M* $NaClO_4$		Bruno et al. (1992)
$Fe^{2+} + CO_3^{2-} + H^+ = FeHCO_3^+$	12.50	-10.55	Estimate		Fouillac and Criaud (1984)
	12.3*	-		Nordstrom et al. (1990)	Fouillac and Criaud (1984)
	11.78*	-			Millero and Hawke (1992)
	11.80*	-		Millero et al. (1995)	Millero and Hawke (1992)
$Fe^{2+} + HCO_3^- = FeHCO_3^+$	2.05		Estimate		Mattigod and Sposito (1977)
	2.05		$FeHCO_3^+$, $FeCO_3(aq)$, $Fe(CO_3)_2^{2-}$, $FeOH^+$,$Fe(OH)_2(aq)$, $Fe(OH)_3^-$, $Fe(OH)_4^{2-}$	Fosbøl et al. (2010)	Mattigod and Sposito (1977)
	2		$FeHCO_3^+$, $FeCO_3(aq)$	Fosbøl et al. (2010)	Serebrennikov (1977)

Table 1. Association Constants for Aqueous Carbonate Complexes in the System FeO/Fe_2O_3-CO_2-H_2O (Continued)

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	1 – 1.5	-	0.1 *M* NaCl?		Johnson and Bauman (1978)
	1 – 1.5	-		Palmer and Van Eldik (1983)	Johnson and Bauman (1978)
	2.0		25°C, *I* = 0	Wersin et al. (1989)	Fouillac and Criaud (1984)
	2.17		$FeHCO_3^+$, $FeCO_3$(aq)	Fosbøl et al. (2010)	Fouillac and Criaud (1984)
	2		$FeHCO_3^+$, $FeCO_3$(aq), $FeOH^+$	Fosbøl et al. (2010)	Nordstrom et al. (1990)
	1.47		$FeHCO_3^+$, $FeCO_3$(aq), $Fe(CO_3)_2^{2-}$, $FeOH^+$, $Fe(OH)_2$(aq)	Fosbøl et al. (2010)	Millero and Hawke (1992)
$Fe^{2+} + CO_3^{2-} + OH^- = FeCO_3OH^-$	9.97	-	Re-evaluation of data	King (1998)	Bruno et al. (1992)
Fe(III)					
$2Fe^{3+} + 3H_2O + 3CO_3^{2-} = Fe_2(OH)_3(CO_3)_3^{3-} + 3H^+$	-	-	Evidence for the existence of. Preparative, Sol., Sat. $(NH_4)_2CO_3$	Krishnamurty et al. (1970)	Zvyagintsev and Lopatto (1962)
$4Fe^{3+} + 3H_2O + 6CO_3^{2-} = Fe_4O_3(CO_3)_6^{6-} + 6H^+$	-	-	Evidence for the existence of. Preparative, Sol., Sat. $(NH_4)_2CO_3$	Krishnamurty et al. (1970)	Zvyagintsev and Lopatto (1962)

(1) At standard state (25°C, 1 atm, *I* = 0), unless otherwise noted.

* Equation recast using bicarbonate dissociation equation from PHREEQC

Table 2. Solubility Constants of Solid Carbonates in the System FeO/Fe_2O_3-CO_2-H_2O

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
Minerals					
Fe(II)					
Siderite					
$FeCO_3(cr) = Fe^{2+} + CO_3^{2-}$					
	10.46	-	30ºC. Uncorrected for complex speciation and Ionic strength		Smith (1918)
	-10.503	-		Kelley and Anderson (1935)	Smith (1918)
	-10.55	-	30ºC, recalculation	Bénézeth et al. (2009)	Smith (1918)
	10.46	-	25ºC.	Braun (1991)	Smith (1918)
	-10.65 ± 0.03	-	30ºC, Sol.	Langmuir (1969)	Smith (1918)
	-10.57 ± 0.03	-	25ºC, Sol.	Langmuir (1969)	Smith (1918)
	-10.89	-10.38		Nordstrom et al. (1990)	Smith (1918)
	-10.46		30°C	Fosbøl et al. (2010)	Smith (1918)
			18°C. Solubility = 0.072 and 0.077% at $P(CO_2)$ = 1 and 56 atm., respectively		Haehnel (1924)
	-9.57		18°C	Fosbøl et al. (2010)	Tillmans and Klarmann (1924)
	-10.67, -10.5		30°C	Fosbøl et al. (2010)	Kelley and Anderson (1935)
	-10.676	-	Review. No correction for activity coefficients		Kelley and Anderson (1935)
	-10.68		In agreement with Kelley and Anderson (1935)		Latimer (1952)
	-10.68		Not reported	Jensen et al. (2002)	Latimer (1952)
	-10.68	-19.37		Fosbøl et al. (2010)	Latimer (1952)
	-10.68	-		Zhuk (1954)	Goskhimizdat (1952)
	-10.67			Fosbøl et al. (2010)	Robie and Waldbaum (1968)
	-10.69	21.05	Thermodynamic calculations		Helgeson (1969)
	-10.70	-		Braun (1991)	Helgeson (1969)

Table 2. Solubility Constants of Solid Carbonates in the System FeO/Fe_2O_3-CO_2-H_2O (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	-10.69	-21.05		Fosbøl et al. (2010)	Helgeson (1969)
	-10.55	-		Preis and Gamsjäger (2002)	Langmuir (1969)
	-10.55 ± 0.03	-25.2 ± 3.1	Sol.		Langmuir (1969)
	-10.45			Naumov et al. (1974)	Langmuir (1969)
	-10.55	-25.20	$FeOH^+$, $Fe(OH)_2(aq)$, $Fe(OH)_3^-$, $Fe(OH)_4^{-2}$	Fosbøl et al. (2010)	Langmuir (1969)
	-10.45		Precipitated. See note	Nordstrom et al. (1990),	Singer and Stumm (1970)
	-10.24	-		by Braun (1991)	Singer and Stumm (1970)
	-10.24	-		Bénézeth et al. (2009)	Singer and Stumm (1970)
	-10.24	-19.37		Fosbøl et al. (2010)	Singer and Stumm (1970)
	-10.7	-	Calculated from DG data by Berner (1967)		Emerson (1976)
	-10.7	-	I = 0	Palmer and Van Eldik (1983)	Smith and Martell (1976)
	-10.68			Fosbøl et al. (2010)	Martell and Smith (1976)
	-10.54		$FeHCO_3^+$, $FeCO_3(aq)$,	Fosbøl et al. (2010)	Serebrennikov (1977)
	-10.40 ± 0.05	-	20ºC. Sol.		Bardy and Péré (1978)
	-10.46	-	Sol., extrapolated to 25ºC		Bardy and Péré (1978)
	-10.37	-	based on regression of data	Haarberg et al. (1990)	Bardy and Pere (1976), Wagman et al. (1982) and Greenberg and Tomson (1992)
	-10.40		20ºC. Sol.	Braun (1991)	Bardy and Péré (1978)
	-10.40	-	20ºC. Sol.	Bénézeth et al. (2009)	Bardy and Péré (1978)
	-10.46			Fosbøl et al. (2010)	Bardy and Pe´ re´ (1976)
	-10.99			Suess (1979)	Murray et al. (1978)
	-10.5	-29.26		Fosbøl et al. (2010)	Robie et al. (1978)
	-10.5	-25.67	FeOH+	Fosbøl et al. (2010)	Wagman et al. (1982)
	-10.45		Precipitation from supersaturated solutions	Jensen et al. (2002)	Nordstrom et al. (1990), Singer and Stumm (1970)

Table 2. Solubility Constants of Solid Carbonates in the System FeO/Fe_2O_3-CO_2-H_2O (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	-10.89		Resuspension of wet crystals	Jensen et al. (2002)	Nordstrom et al. (1990), Smith (1918)
	-10.45	-10.38	$FeHCO_3^+$, $FeCO_3$(aq), FeOH+	Fosbøl et al. (2010)	Nordstrom et al. (1990)
	-10.91			Fosbøl et al. (2010)	Reiterer (1980)
	-11.20		Resuspension of dry crystals	Jensen et al. (2002)	Reiterer et al. (1981)
	-10.6			Fosbøl et al. (2010)	Robie et al. (1984)
	-10.60	-	Recalculation from Smith (1918) and Langmuir (1969)	Bénézeth et al. (2009)	Robie et al. (1984)
	-10.56	-22.8	$FeHCO_3^+$, $FeCO_3$(aq), FeOH+,$Fe(OH)_2$(aq)	Fosbøl et al. (2010)	Greenberg (1986)
	-10.605, -10.58	-22.9	$FeHCO_3^+$, $FeCO_3$(aq), FeOH+,Fe(OH)2(aq)	Fosbøl et al. (2010)	Greenberg and Tomson (1986)
	-10.37			Fosbøl et al. (2010)	Haarberg et al. (1990)
	-11.0	-	Sol.		Braun (1991)
	-10.99		Resuspension of crystals	Jensen et al. (2002)	Braun (1991)
	-11.11	-	30ºC	Bénézeth et al. (2009)	Braun (1991)
	-10.98	-	25°C, *I* = 0. Temperature extrapolation	Sun et al. (2009)	Braun (1991)
	-10.99			Fosbøl et al. (2010)	Braun 1991
	-10.45	-30.14	$FeHCO_3^+$, $FeOH^+$	Fosbøl et al. (2010)	Johnson and Tomson (1991)
	-10.8 ± 0.2	-			Bruno et al. (1992)
	-10.80		Resuspension of dry crystals	Jensen et al. (2002)	Bruno et al. (1992)
	-10.8		$FeCO_3$(aq), $Fe(CO_3)_2^{2-}$	Fosbøl et al. (2010)	Bruno et al. (1992)
	-10.78 ± 0.01	-9.46 ± 2.			Greenberg and Tomson (1992)
	-10.78		25°C, *I* = 0. Temperature extrapolation	Sun et al. (2009)	Greenberg and Tomson (1992)
	-10.77		Precipitation from supersaturated solutions	Jensen et al. (2002)	Greenberg and Tomson (1992)
	-10.78	-9.46	$FeHCO_3^+$, $FeCO_3$(aq), $FeOH^+$	Fosbøl et al. (2010)	Greenberg and Tomson (1992)

Table 2. Solubility Constants of Solid Carbonates in the System FeO/Fe_2O_3-CO_2-H_2O (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	-11.0 – -11.2		$FeHCO_3^+$, $FeCO_3$(aq), $FeOH^+$	Fosbøl et al. (2010)	Ptacek (1992)
	-11.06 ± 0.13	-	<0.01 - >6 *M* NaCl		Ptacek and Reardon (1992)
	-11.08 ± 0.12	-	,0.01 - >2.2 *M* Na_2SO_4		Ptacek and Reardon (1992)
	-10.93		Resuspension of wet crystals	Jensen et al. (2002)	Ptacek and Reardon (1992)
	-10.93	-		Bénézeth et al. (2009)	Ptacek and Reardon (1992)
	-11.06		$FeHCO_3^+$, $FeCO_3$(aq), $FeOH^+$	Fosbøl et al. (2010)	Ptacek and Reardon (1992)
	-11.03 ± 0.26	-			Ptacek and Blowes (1994)
	-11.03		Resuspension of wet crystals	Jensen et al. (2002)	Ptacek and Blowes (1994)
	-11.03	-		Bénézeth et al. (2009)	Ptacek and Blowes (1994)
	-11.03	-10.38	$FeHCO_3^+$, $FeCO_3$(aq), $FeOH^+$	Fosbøl et al. (2010)	Ptacek and Blowes (1994)
	-11.53	-10.4	Unknown	Fosbøl et al. (2010)	Robie and Hemingway (1995)
	-10.66		Unknown speciation	Fosbøl et al. (2010)	Garber et al. (1996)
	-10.8 ± 0.2	-	Literature review		Grauer (1999)
	-10.8		$FeCO_3$(aq), $Fe(CO_3)_2^{2-}$	Fosbøl et al. (2010)	Grauer (1999)
	-11.03 ± 0.10	-	dried crystals		Jensen et al. (2002)
	-10.43 ± 0.15	-	wet crystals		Jensen et al. (2002)
	-11.03	-	dried crystals	Bénézeth et al. (2009)	Jensen et al. (2002)
	-10.43	-	wet crystals	Bénézeth et al. (2009)	Jensen et al. (2002)
	-11.03, -10.43		$FeHCO_3^+$, $FeCO_3$(aq), maybe $FeOH^+$	Fosbøl et al. (2010)	Jensen et al. (2002)
	-10.59 ± 0.10	-	After work by other investigators		Preis and Gamsjäger (2002)
	-10.59	-13.23	$FeCO_3$(aq), $Fe(CO_3)_2^{2-}$	Fosbøl et al. (2010)	Preis and Gamsjäger (2002)
	-10.90	-		Bénézeth et al. (2009)	Silva et al. (2002)
	-10.90 ± 0.15	-			Silva et al. (2002)
	-10.90		25°C, ionic strength extrapolation	Sun et al. (2009)	Silva et al. (2002)
	-10.9		$FeCO_3$(aq) maybe more	Fosbøl et al. (2010)	Silva et al. (2002)

Table 2. Solubility Constants of Solid Carbonates in the System FeO/Fe_2O_3-CO_2-H_2O (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	-11.06		$FeCO_3$(aq), $FeOH^+$	Fosbøl et al. (2010)	Marion et al. (2003)
	-10.59		Unknown	Fosbøl et al. (2010)	Sun and Nesic (2004)
	-10.90	-			Bénézeth et al. (2009)
	-10.89		25°C, *I* = 0. Ave. of 9 independent studies from literature	Sun et al. (2009)	Smith (1918), Latimer (1952), Braun (1991), Bruno et al. (1992), Greenberg and Tomson (1992), Ptacek and Reardon (1992), Ptacek and Blowes (1994), Jensen et al. (2002), Silva et al. (2002),
	-10.89	-	25°C, *I* = 0. Temperature extrapolation		Sun et al. (2009)
$FeCO_3$(cr) + H+ = Fe^{2+} + HCO_3^-	-0.23		25°C, *I* = 0	Wersin et al. (1989)	Langmuir (1969)
$FeCO_3$(cr) + 2H+ = Fe^{2+} + CO_2(g) + H_2O	8.58	-	25°C, *I* = 0	Gamsjäger (1974)	Latimer (1952), Larson et al. (1968)
	7.47	-	25°C, *I* = 0	Gamsjäger (1974)	Latimer (1952), Randall and Frandsen (1932)
	7.61 ± 0.04		50°C, 1 *M* $NaClO_4$,	Gamsjäger (1985)	Reiterer (1980)
	7.61 ± 0.05	-	50ºC and *I* = 1.0 mole/kg $NaClO_4$		Reiterer et al. (1981)
	7.61	-	50ºC	Braun (1991)	Reiterer et al. (1981)
	7.59	-	1 *M* $NaClO_4$		Bruno et al. (1992)
	7.56	-17.3			Preis and Gamsjäger (2001)
Fe(III)					
Hydrotalcite-CO_3 (-Pyroaurite)					
$Mg_3Al_{0.896}Fe_{0.097}(CO_3)_{0.336}(OH)_{8.305}$•2.51($H_2O$) = $3Mg^{2+}$ + $0.896Al^{3+}$ + $0.097Fe^{3+}$ + $0.336CO_3^{2-}$ + $8.305(OH)^-$ + $2.51H_2O$	−68.76 ± 3.55	-	Solubility		Rozov et al. (2010)

Table 2. Solubility Constants of Solid Carbonates in the System FeO/Fe_2O_3-CO_2-H_2O (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
$Mg_3Al_{0.827}Fe_{0.192}(CO_3)_{0.536}(OH)_{7.987}\cdot 2.62(H_2O) = 3Mg^{2+} + 0.827Al^{3+} + 0.192Fe^{3+} + 0.536CO_3^{2-} + 7.987(OH)^- + 2.62H_2O$	−67.79 ± 3.62	-	Solubility		Rozov et al. (2010)
$Mg_3Al_{0.802}Fe_{0.205}(CO_3)_{0.537}(OH)_{7.946}\cdot 2.67(H_2O) = 3Mg^{2+} + 0.802Al^{3+} + 0.205Fe^{3+} + 0.537CO_3^{2-} + 7.946(OH)^- + 2.67H_2O$	−71.61 ± 3.75	-	Solubility		Rozov et al. (2010)
$Mg_3Al_{0.695}Fe_{0.304}(CO_3)_{0.481}(OH)_{8.034}\cdot 2.52(H_2O) = 3Mg^{2+} + 0.695Al^{3+} + 0.304Fe^{3+} + 0.481CO_3^{2-} + 8.034(OH)^- + 2.52H_2O$	−70.83 ± 3.61	-	Solubility		Rozov et al. (2010)
$Mg_3Al_{0.625}Fe_{0.394}(CO_3)_{0.553}(OH)_{7.95}\cdot 2.50(H_2O) = 3Mg^{2+} + 0.625Al^{3+} + 0.394Fe^{3+} + 0.553CO_3^{2-} + 7.950(OH)^- + 2.50H_2O$	−68.7 ± 3.65	-	Solubility		Rozov et al. (2010)
$Mg_3Al_{0.502}Fe_{0.496}(CO_3)_{0.361}(OH)_{8.276}\cdot 2.45(H_2O) = 3Mg^{2+} + 0.502Al^{3+} + 0.496Fe^{3+} + 0.361CO_3^{2-} + 8.276(OH)^- + 2.45H_2O$	−69.25 ± 3.63	-	Solubility		Rozov et al. (2010)
$Mg_3Al_{0.415}Fe_{0.619}(CO_3)_{0.531}(OH)_{8.039}\cdot 2.47(H_2O) = 3Mg^{2+} + 0.415Al^{3+} + 0.619Fe^{3+} + 0.531CO_3^{2-} + 8.039(OH)^- + 2.47H_2O$	−69.51 ± 3.74	-	Solubility		Rozov et al. (2010)
$Mg_3Al_{0.299}Fe_{0.703}(CO_3)_{0.248}(OH)_{8.509}\cdot 2.55(H_2O) = 3Mg^{2+} + 0.299Al^{3+} + 0.619Fe^{3+} + 0.248CO_3^{2-} + 8.509(OH)^- + 2.55H_2O$	−70.09 ± 3.68	-	Solubility		Rozov et al. (2010)
$Mg_3Al_{0.207}Fe_{0.839}(CO_3)_{0.491}(OH)_{8.157}\cdot 2.55(H_2O) = 3Mg^{2+} + 0.207Al^{3+} + 0.839Fe^{3+} + 0.491CO_3^{2-} + 8.157(OH)^- + 2.55H_2O$	−70.23 ± 3.81	-	Solubility		Rozov et al. (2010)
$Mg_3Al_{0.108}Fe_{0.902}(CO_3)_{0.342}(OH)_{8.344}\cdot 2.64(H_2O) = 3Mg^{2+} + 0.108Al^{3+} + 0.902Fe^{3+} + 0.342CO_3^{2-} + 8.334(OH)^- + 2.64H_2O$	−70.38 ± 3.53	-	Solubility		Rozov et al. (2010)
$Mg_3Fe_{1.086}(CO_3)_{0.343}(OH)_{8.570}\cdot 2.15(H_2O) = 3Mg^{2+} + 1.086Fe^{3+} + 0.343CO_3^{2-} + 8.570(OH)^- + 2.15H_2O$	−72.36 ± 3.99	-	Solubility		Rozov et al. (2010)
Synthetic Phases					
Fe(II)					
Fe(III)					
Fe–monocarbonate					

Table 2. Solubility Constants of Solid Carbonates in the System FeO/Fe_2O_3-CO_2-H_2O (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
$Ca_4[Fe(OH)_6]_2(CO_3)•6(H_2O) = 4Ca^{2+} + 2Fe(OH)_4^- + CO_3^{2-} + 4OH^- + 6H_2O$	-35.5 ± 0.3	-	Solubility,	-	Moschner et al. (2008)
$Ca_4Fe_2(CO_3)(OH)_{12}•6(H_2O) = 4Ca^{2+} + 2Fe(OH)_4^- + CO_3^{2-} + 4OH^- + 6H_2O$	−34.59	-	Solubility	-	Dilnesa et al. (2011)
Fe–Hemicarbonate					
$Ca_4Fe_2O_{6.5}(CO_3)_{0.5}•11.5(H_2O) = 4Ca^{2+} + 2Fe(OH)_4^- + 0.5CO_3^{2-} + 5OH^- + 5H_2O$	-33.1	-	Estimated	-	Lothenbach et al. (2008)
$Ca_4Fe_2(CO_3)_{0.5}(OH)_{13.5}•5(H_2O) = 4Ca^{2+} + 2Fe(OH)_4^- + 0.5CO_3^{2-} + 5OH^- + 5.5H_2O$	-33.1	-	Estimated	-	Lothenbach (2010)
$Ca_4Fe_2(CO_3)_{0.5}(OH)_{12}•4(H_2O) = 4Ca^{2+} + 2Fe(OH)_4^- + 0.5CO_3^{2-} + 5OH^- + 3.5H_2O$	−30.83	-	Solubility	-	Dilnesa et al. (2011)

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Note: Log K of Smith (1918) recalculated using Nordstrom et al. (1990) aqueous model at 303 K, adjusted to 298 K using DH0r calculated using ion values from Wagman et al. (1982) and Robie et al. (1984) for solid.

Table 3a. Association Constants of Aqueous Carbonate Complexes in the System FeO/Fe_2O_3-CO_2-H_2O extracted from Databases of Distribution-of-Species Codes

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Database	Source
Fe(II)				
$Fe^{2+} + CO_3^{2-} = FeCO_3(aq)$			Minteq (2009)	
			Minteq (2006)	NIST46.4
	4.380	-	Phreeqc (2009)	not cited
	4.38	-	Wateq4f (2005)	not cited
	5.69	-5.764	ThermoChimie v.7.b	#99CHIb
			NAGRA/PSI (2001)	
	5.4500	-	Data0.YMP.R5	Millero et al. (1995)
			Thermoddem (2009)	Sverjensky et al. (1997)
$Fe^{2+} + 2CO_3^{2-} = Fe(CO_3)_2^{2-}$	-	-	Minteq (2009)	
	-	-	Minteq (2006)	
	-	-	Phreeqc (2009)	
	-	-	Wateq4f (2005)	
	7.45	-	ThermoChimie v.7.b	#98KIN in 99CHIb
	-	-	NAGRA/PSI (2001)	
	7.1600	-	Data0.YMP.R5	Millero et al. (1995)
			Thermoddem (2009)	
$Fe^{2+} + CO_3^{2-} + H^+ = FeHCO_3^+$	-	-	Minteq (2009)	
	11.429	0	Minteq (2006)	NIST46.4; MTQ3.11
	12.329	-	Phreeqc (2009)	not cited
	12.329	-	Wateq4f (2005)	not cited
	11.77	-	ThermoChimie v.7.b	#95CHI
			NAGRA/PSI (2001)	
	11.799	-	Data0.YMP.R5	Millero et al. (1995)
			Thermoddem (2009)	Shock and Koretsky (1995)
$Fe^{2+} + CO_3^{2-} + H_2O = FeOHCO_3^- + H^+$	-	-	Minteq (2009)	
		0	Minteq (2006)	
		-	Phreeqc (2009)	
			Wateq4f (2005)	
	-4.03	-	ThermoChimie v.7.b	#98KIN in 99CHIb
			NAGRA/PSI (2001)	
		-	Data0.YMP.R5	
			Thermoddem (2009)	
Fe(III)				
$Fe^{2+} + CO_3^{2-} = FeCO_3(aq)$			Minteq (2009)	
			Minteq (2006)	
		-	Phreeqc (2009)	
			Wateq4f (2005)	
			ThermoChimie v.7.b	
			NAGRA/PSI (2001)	

Table 3a. Association Constants of Aqueous Carbonate Complexes in the System FeO/Fe_2O_3-CO_2-H_2O extracted from Databases of Distribution-of-Species Codes (Continued)

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Database	Source
		-	Data0.YMP.R5	
			Thermoddem (2009)	
$Fe^{3+} + 3CO_3^{2-} = Fe(CO_3)_3^{3-}$		-	Minteq (2009)	
		-	Minteq (2006)	
		-	Phreeqc (2009)	
		-	Wateq4f (2005)	
	24.24	-	ThermoChimie v.7.b	#05GRI
		-	NAGRA/PSI (2001)	
		-	Data0.YMP.R5	
			Thermoddem (2009)	
$Fe^{3+} + CO_3^{2} + H_2O = FeCO_3OH^{-} + H^{+}$		-	Minteq (2009)	
		0	Minteq (2006)	
		-	Phreeqc (2009)	
			Wateq4f (2005)	
	10.76	-	ThermoChimie v.7.b	#05GRI
			NAGRA/PSI (2001)	
		-	Data0.YMP.R5	
			Thermoddem (2009)	

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Table 3b. Solubility Constants of Solid Carbonates in the System FeO/Fe_2O_3-CO_2-H_2O extracted from Databases of Distribution-of-Species Codes

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Database	Source
Siderite				
$FeCO_3(s) = Fe^{2+} + CO_3^{2-}$	-10.55	-22.292	Minteq (2009)	not cited
	-10.24	-16.	Minteq (2006)	not cited
	-10.890	-10.376	Phreeqc (2009)	not cited
	-10.89	-10.376	Wateq4f (2005)	not cited
Siderite(d)(3): $FeCO_3(s) = Fe^{2+} + CO_3^{2-}$	-10.45	-	Wateq4f (2005)	not cited
	-10.8	-12.012	ThermoChimie v.7.b	Bruno et al. (1992)
			NAGRA/PSI (2001)	
	-10.5200	-	Data0.YMP.R5	Helgeson et al. (1978); Helgeson (1985)
			Thermoddem (2009)	

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Table 3c. Distribution-of-Species Codes: Database References

Database	Reference
Data0.com.V8.R6+	Wolery, T.J. (1994). EQ3NR, Letter report: EQ3/6 version 8.0. Differences from version 7. UCRL-ID-129749. Lawrence Livermore National Laboratory, Livermore, California. USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/LLNL.DAT
Data0.YMP.R5	BSC (Bechtel SAIC Company) (2007). Qualification of Thermodynamic Data for Geochemical Modeling of Mineral–Water Interactions in Dilute Systems. ANL-WIS-GS-000003 REV 01. Las Vegas, Nevada: Bechtel SAIC Company.DOC.20070619.0007.
MinteqA2	HydroGeoLogic, Inc. and Allison Geoscience Consultants, Inc. (1999). MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: User Manual Supplement for Version 4.0, Appendix A: thermodynamic database for MINTEQA2 V4.0, p. 44-74.
Minteq (2009)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/MINTEQ.DAT
Minteq (2006)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/minteq.v4.dat
NAGRA/PSI (2001)	Hummel, W., Berner, U., Curti, E., Pearson, F.J. and Thoenen, T. (2002). Nagra/PSI Chemical Thermodynamic Data Base 01/01. Universal Publishers/uPublish.com, Parkland, Florida. 565 p.
Phreeqc (2009)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/PHREEQC.DAT
ThermoChimie v.7.b	Duro, L., Grivém M. and Giffaut, E. (2010). ThermoChimie, the ANDRA thermodynamic database In Buckau G, Kienzler B, Duro L, Grivé M, Montoya V (eds). 2nd Annual Workshop Proceedings of the Collaborative Project “Redox Phenomena Controlling Systems” (7th EC FP CP Recosy) Larnaca (Cyprus) 16–19 March 2010. Karlsruhe: KIT Scientific Publishing, 275–283.
Thermoddem (2009)	Blanc P., Lassin A. and Piantone P. (2007) THERMODDEM a database devoted to waste minerals. BRGM (Orléans, France). For updates: http://thermoddem.brgm.fr
Wateq4f	Ball, J. W., & Nordstrom, D. K. (1991). User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters. U.S. GEOLOGICAL SURVEY, Open-File Report 91-183, Revised and reprinted - April, 2001. p. 81-94
Wateq4f (2005)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/WATEQ4F.DAT

Table 4a. Thermodynamic properties of Iron Carbonate Minerals and Synthetic Solid Carbonates: Gibbs Free Energies of Formation

Mineral		$\Delta G^0_{f,P_r,T_r}$ kJ/gfw $^{-1}$	Secondary Reference	Primary Reference
Name	Formula			
Minerals				
Fe(II)				
Ankerite		-1819.29		Holland and Powell (1990)
predicted		-1807.4 ± 3.0		La Iglesia and Felix (1994)
		-1819.29		Holland and Powell (1998)
Fe Dolomite		-1817.2	La Iglesia and Felix (1994)	Holland and Powell (1990)
Siderite	$Fe^{II}CO_3$	-673.75	Kelley and Anderson (1935)	Smith (1918)
		-678.94	Mel'nik (1972)	Smith (1918), Kelley and Anderson (1935)
synthetic		-673.75		Kelley and Anderson (1935)
		-673.75	Fosbøl et al. (2010)	Kelley and Anderson (1935)
		-673.88	Fosbøl et al. (2010)	Latimer (1952)
		-673.88	Latimer (1952)	Rossini et al. (1952)?
		-673.88	Zhuk (1954)	Rossini et al. (1952), Karapet'yants (1953)
		-673.88 ± 3.35	Robie (1962, 1966). Data from Kelley and King (1961).corrected for magnetic contribution to entropy	Rossini et al. (1952), Kelley and King (1961)
		-673.88	Karpov et al. (1968)	Rossini et al. (1952)
		-673.88	Mel'nik (1972)	Rossini et al. (1952), Latimer (1952), Krestovnikov et al. (1963), Nikolaev and Dolivo-Dobovolskii (1961)
		-35.15[(1)]	Mel'nik (1972)	Rossini et al. (1952), Latimer (1952), Krestovnikov et al. (1963), Nikolaev and Dolivo-Dobovolskii (1961)
		-673.9	Woods and Garrels (1987)	Rossini et al. (1952)
calculated		-674.00		Zhuk (1954)
		-674.00	Karpov et al. (1968)	Zhuk (1954)

Table 4a. Thermodynamic properties of Iron Carbonate Minerals and Synthetic Solid Carbonates: Gibbs Free Energies of Formation (Continued)

Mineral		$\Delta G^0_{f,P_r,T_r}$ kJ/gfw $^{-1}$	Secondary Reference	Primary Reference
Name	Formula			
		-674.00	Karapet'yants and Karapet'yants (1970)	Zhuk (1954)
		-35.15(1)	Karpov et al. (1968)	Kireev (1964)
		-673.75 ± 2.09	Mel'nik (1972)	Robie and Waldbaum (1968)
		-34.18(1)	Mel'nik (1972)	Robie and Waldbaum (1968)
		-673.749	Fosbøl et al. (2010)	Robie and Waldbaum (1968)
		-666.72	Mel'nik (1972)	Wagman et al. (1969)
		-27.20(1)	Mel'nik (1972)	Wagman et al. (1969)
		-679.64 ± 2.13		Langmuir (1969)
		-677.64	Mel'nik (1972)	Langmuir (1969)
		-679.44	Fosbøl et al. (2010)	Langmuir (1969)
		-680.32	Naumov et al. (1974)	Langmuir (1969)
		-666.72		Wagman et al. (1969)
		-666.698 ± 2.092	Robie et al. (1979)	Wagman et al. (1969), Kelley and Anderson (1935)
		-666.72	Fosbøl et al. (2010)	Wagman et al. (1969)
		-680.32	Mel'nik (1972)	Naumov et al. (1971)
		-40.79(1)	Mel'nik (1972)	Naumov et al. (1971)
		-676.51	Mel'nik (1972)	Singer and Stumm (1970)
		-671.53	Fosbøl et al. (2010)	Singer and Stumm (1970)
		-697.05	Fosbøl et al. (2010)	French (1971)
		-666.72	Barin et al. (1977),	Stull and Prophet (1971)
recommended value		-679.48		Mel'nik (1972)
recommended value		-40.84(1)		Mel'nik (1972)
spherulitic, recommended value	$FeCO_3$•n(H_2O), as $FeCO_3$	-676.55		Mel'nik (1972)
Amorphous, recommended value	$FeCO_3$•n(H_2O), as $FeCO_3$	-664.84		Mel'nik (1972)
		-679.5	Woods and Garrels (1987)	Mel'nik (1972)
		-768.26	Fosbøl et al. (2010)	Barin et al. (1973)

Table 4a. Thermodynamic properties of Iron Carbonate Minerals and Synthetic Solid Carbonates: Gibbs Free Energies of Formation (Continued)

Mineral		$\Delta G^0_{f,P_r,T_r}$ kJ/gfw $^{-1}$	Secondary Reference	Primary Reference
Name	Formula			
		-680.3	Woods and Garrels (1987)	Naumov et al. (1974)
		-665.5	Dobrydiev et al. (2005)	Ryabin et al. (1977)
		-679.4	Woods and Garrels (1987)	Helgeson et al. (1978)
		-679.54	BSC (2007)	Helgeson et al. (1978)
		-679.440	Fosbøl et al. (2010)	Helgeson et al. (1978)
		-666.7	Woods and Garrels (1987)	Robie et al. (1978)
		-666.698	Fosbøl et al. (2010)	Robie et al. (1978)
		-666.70 ± 2.09	Radha and Navrotsky (2013)	Robie et al. (1978)
		-669.02	Fosbøl et al. (2010)	Reiterer (1980)
		-662.91 ± 0.46	At 50°C	Reiterer et al. (1981)
		-669.02 ± 0.46		Reiterer et al. (1981)
		-665.67	Bénézeth et al.	Wagman et al. (1982)
		-666.67	Fosbøl et al. (2010)	Wagman et al. (1982)
recommended value		-665.16	Fosbøl et al. (2010)	Wagman et al., 1982
		-679.5	Woods and Garrels (1987)	Helgeson (1983, 1984)
		-679.4	Woods and Garrels (1987)	Sangameshwar and Barnes (1983)
		-682.8 ± 5.5		Robie et al. (1984)
		-680.03 ± 0.6	from solubility data, cited by Bénézeth et al. (2009) and by Chai and Navrotsky (1994)	Robie et al. (1984),
		-682.8 ± 5.5	Robie and Hemingway (1995)	Robie et al. (1984)
		-680.03	Fosbøl et al. (2010)	Robie et al. (1984)
recommended value		-676.88	Fosbøl et al. (2010)	Cox et al. (1989), Parker and Khodakovskii (1995)
		-688.04	Fosbøl et al. (2010)	Holland and Powell (1990)
		-682.8		Robie and Hemingway (1995)
		-682.80	Bénézeth et al. (2009)	Robie and Hemingway (1995)
		-682.8	Fosbøl et al. (2010)	Robie and Hemingway (1995)
		-688.16		Holland and Powell (1998)

Table 4a. Thermodynamic properties of Iron Carbonate Minerals and Synthetic Solid Carbonates: Gibbs Free Energies of Formation (Continued)

Mineral		$\Delta G^0_{f,P_r,T_r}$ kJ/gfw $^{-1}$	Secondary Reference	Primary Reference
Name	Formula			
		-668.978		NAGRA
		-678.9 ± 1.2		Preis and Gamsjäger (2002)
		-678.9	Fosbøl et al. (2010)	Preis and Gamsjäger (2002)
		-680.71 ± 2.		Bénézeth et al. (2009)
Fe(II)/Fe(III)				
Fougèrite ($GR(CO_3^{2-})$) sp.				
$GR1(CO_3^{2-})$	$[Fe^{II}_4Fe^{III}_2(OH)_{12}][CO_3^{2-} \cdot 2(H_2O)]$	-4042.79	Génin et al. (1998)	Drissi et al. (1994)
$GR1(CO_3^{2-})$	$[Fe^{II}_4Fe^{III}_2(OH)_{12}][CO_3^{2-} \cdot 2(H_2O)]$	-4042.28 ± 0.84		Drissi et al. (1995)
$GR1(CO_3^{2-})_{anhyd}$	$Fe^{II}_4Fe^{III}_2(OH)_{12}(CO_3^{2-})$	-3568.41		Drissi et al. (1995)
$GR1(CO_3^{2-})_{anhyd}$	$Fe^{II}_4Fe^{III}_2(OH)_{12}(CO_3)$	- 3588.0 ± 11	Bourrié et al. (1999)	Drissi et al. (1995)
$GR(CO_3^{2-})$	$Fe^{II}_4Fe^{III}_2(OH)_{12}CO_3 \cdot 2(H_2O)$	-4076	Refait et al. (2006)	Drissi et al. (1995)
Fougèrite ($GR(CO_3^{2-})$)	$Fe^{II}_4Fe^{III}_2(OH)_{12}CO_3 \cdot 2(H_2O)$	−4064 ± 10	Bourdoiseau et al. (2012)	Drissi et al. (1995), Génin et al. (1998)
$GR(CO_3^{2-})$	$[Fe^{II}_4Fe^{III}_2(OH)_{12}]^{2+}[CO_3^{2-} \cdot n(H_2O)]^{2-}$	-3590 ± 5	Bourrié et al. (2004)	Bourrié et al. (1999)
$GR(CO_3^{2-})$ *calculated*	$[Fe^{II}_4Fe^{III}_2(OH)_{12}]^{2+}[CO_3^{2-} \cdot n(H_2O)]^{2-}$	-3872		Bourrié et al. (2004)
$GR(CO_3^{2-})$	$Fe^{II}_4Fe^{III}_2O_{12}H_{12}CO_3$	-3601.62		Génin et al. (2006), Ruby et al. (2006)
$GR(CO_3^{2-})$	$Fe^{II}_2Fe^{III}_4O_{12}H_{10}CO_3$	-3488.76		Génin et al. (2006), Ruby et al. (2006)
$GR(CO_3)$*	$Fe^{III}_6O_{12}H_8CO_3$	-3345.18		Génin et al. (2006), Ruby et al. (2006)
Fougèrite ($GR(CO_3^{2-})$)		−4070 ± 15		Bourdoiseau et al. (2012)
$GR1(CO_3^{2-})_{anhyd}$	$Fe^{II}_4Fe^{III}_2(OH)_{12}CO_3$	-3588.00		Trolard and Bourrié (2012)
Fe(III)				
Hydrotalcite-CO_3 (-Pyroaurite)	$Mg_3Al_{0.896}Fe_{0.097}(CO_3)_{0.336}(OH)_{8.305} \cdot 2.51(H_2O)$	−3671.87 ± 112.49		Rozov et al. (2010)
	$Mg_3Al_{0.827}Fe_{0.192}(CO_3)_{0.536}(OH)_{7.987} \cdot 2.62(H_2O)$	−3690.29 ± 112.49		Rozov et al. (2010)

Table 4a. Thermodynamic properties of Iron Carbonate Minerals and Synthetic Solid Carbonates: Gibbs Free Energies of Formation (Continued)

Mineral		$\Delta G^0_{f,P_r,T_r}$ kJ/gfw $^{-1}$	Secondary Reference	Primary Reference
Name	Formula			
	$Mg_3Al_{0.802}Fe_{0.205}(CO_3)_{0.537}(OH)_{7.946}$•2.67($H_2O$)	−3701.77 ± 111.44		Rozov et al. (2010)
	$Mg_3Al_{0.695}Fe_{0.304}(CO_3)_{0.481}(OH)_{8.034}$•2.52($H_2O$)	−3623.89 ± 104.99		Rozov et al. (2010)
	$Mg_3Al_{0.625}Fe_{0.394}(CO_3)_{0.553}OH)_{7.95}$•2.50($H_2O$)	−3604.44 ± 103.58		Rozov et al. (2010)
	$Mg_3Al_{0.502}Fe_{0.496}(CO_3)_{0.361}(OH)_{8.276}$•2.45($H_2O$)	−3499.21 ± 95.95		Rozov et al. (2010)
	$Mg_3Al_{0.415}Fe_{0.619}(CO_3)_{0.531}(OH)_{8.039}$•2.47($H_2O$)	−3513.97 ± 95.17		Rozov et al. (2010)
	$Mg_3Al_{0.299}Fe_{0.703}(CO_3)_{0.248}(OH)_{8.509}$•2.55($H_2O$)	−3387.14 ± 85.67		Rozov et al. (2010)
	$Mg_3Al_{0.207}Fe_{0.839}(CO_3)_{0.491}OH)_{8.157}$•2.55($H_2O$)	−3418.14 ± 86.37		Rozov et al. (2010)
	$Mg_3Al_{0.108}Fe_{0.902}(CO_3)_{0.342}(OH)_{8.344}$•2.64($H_2O$)	−3323.14 ± 71.95		Rozov et al. (2010)
	$Mg_3Fe_{1.086}(CO_3)_{0.343}(OH)_{8.570}$•2.15($H_2O$)	−3321.52 ± 78.70		Rozov et al. (2010)
Synthetic Phases				
Fe(II)				
Fe(III)				
Fe–monocarbonate	$Ca_4[Fe(OH)_6]_2(CO_3)$•6(H_2O)	-6679.20 ± 1.71	-	Moschner et al. (2008)
	$Ca_4Fe_2(CO_3)(OH)_{12}$•6(H_2O)	-6674.0		Dilnesa et al. (2011)
Fe–hemicarbonate	$Ca_4Fe_2O_{6.5}(CO_3)_{0.5}$•11.5($H_2O$)	-6440.19	-	Lothenbach et al. (2008)
	$Ca_4Fe_2(CO_3)_{0.5}(OH)_{12}$•4($H_2O$)	-5952.9	-	Dilnesa et al. (2011)

(1) Formation from the oxides

Table 4b. Thermodynamic properties of Iron Carbonate Minerals and Synthetic Solid Carbonates: Enthalpies of Formation

Mineral		$\Delta H^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
Minerals				
Fe(II)				
Ankerite	$Ca(Fe_{0.1583}Mg_{0.8417})(CO_3)_2$	–1964.65 ± 3.59	Radha and Navrotsky (2013)	Chai and Navrotsky (1996 a,b), Robie et al. (1978)
	$Ca(Fe_{0.2990}Mg_{0.7010})(CO_3)_2$	-1914.73 ± 2.87	Radha and Navrotsky (2013)	Chai and Navrotsky (1996 a,b), Robie et al. (1978)
	$Ca(Fe_{0.4996}Mg_{0.5004})(CO_3)_2$	–1842.80 ± 5.00	Radha and Navrotsky (2013)	Chai and Navrotsky (1996 a,b), Robie et al. (1978)
	$Ca(Fe_{0.6482}Mg_{0.3518})(CO_3)_2$	−1793.51 ± 2.66	Radha and Navrotsky (2013)	Chai and Navrotsky (1996 a,b), Robie et al. (1978)
	$CaFe(CO_3)_2$	–1687.17 ± 3.09	Radha and Navrotsky (2013)	Chai and Navrotsky (1996 a,b), Robie et al. (1978)
		-1971.50 ± 1.48		Holland and Powell (1998)
Fe Dolomite	$CaFe(CO_3)_2$	-1969.30 ± 1.97		Holland and Powell (1990)
		-1969.3	La Iglesia and Felix (1994)	Holland and Powell (1990)
predicted		-1959.6 ± 2.5		La Iglesia and Felix (1994)
Siderite *crystalline, at constant volume*	$Fe^{II}CO_3$	-718.4 ± 0.5%		Roth (1929)
crystalline, at constant pressure		-722.2 ± 0.5%		Roth (1929)
synthetic		-748.48		Kelley and Anderson (1935)
		-747.6	Chai and Navrotsky (1994)	Kelley and Anderson (1935)
		-747.6	Preis and Gamsjäger (2002)	Kelly and Anderson (1935)
		-747.60	Fosbøl et al. (2010)	Kelley and Anderson (1935)
		-744.8	Fosbøl et al. (2010)	Latimer (1952)
		-744.75	Latimer (1952)	Rossini et al. (1952)?
		-747.68	Zhuk (1954)	Rossini et al. (1952), Karapet'yants (1953)

Table 4b. Thermodynamic properties of Iron Carbonate Minerals and Synthetic Solid Carbonates: Enthalpies of Formation (Continued)

Mineral		$\Delta H^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
		-745.59 ± 5.02	Robie (1962, 1966) Data from Kelley and King (1961).corrected for magnetic contribution to entropy	Rossini et al. (1952), Kelley and King (1961)
		-744.75	Karpov et al. (1968)	Rossini et al. (1952)
		-747.68	Mel'nik (1972)	Rossini et al. (1952), Latimer (1952), Krestovnikov et al. (1963), Nikolaev and Dolivo-Dobovolskii (1961)
		-88.07(1)	Mel'nik (1972)	Rossini et al. (1952), Latimer (1952), Krestovnikov et al. (1963), Nikolaev and Dolivo-Dobovolskii (1961)
		-747.7	Woods and Garrels (1987)	Rossini et al. (1952)
		-740.6	Stern (2000)	Kubaschevski and Evans (1958)
		-745.59 ± 5.02	Karpov et al. (1968)	Robie (1962)
		-753.12	Karapet'yants and Karapet'yants (1970)	Egorev and Titova (1962)
		-748.94 ± 62.76	Estimated value	Wilcox and Bromley (1963)
		-748.94	Karapet'yants and Karapet'yants (1970)	Wilcox and Bromley (1963)
		-748.9	Fosbøl et al. (2010)	Wilcox and Bromley (1963)
		-91.63(1)	Karpov et al. (1968)	Kireev (1964)
		-752.07	Mel'nik (1972)	Karpov et al. (1968)
		-91.63(1)	Mel'nik (1972)	Karpov et al. (1968)
		-743.97 ± 2.26	Langmuir (1969)	Robie and Waldbaum (1968)
		-743.97 ± 2.26	Mel'nik (1972)	Robie and Waldbaum (1968)
		-84.18(1)	Mel'nik (1972)	Robie and Waldbaum (1968)
		-743.965	Fosbøl et al. (2010)	Robie and Waldbaum (1968)
		-753.12	Naumov et al. (1974)	Langmuir (1969)
		-740.57	Mel'nik (1972)	Wagman et al. (1969)
		-80.79(1)	Mel'nik (1972)	Wagman et al. (1969)
		-740.57		Wagman et al. (1969)
		-736.985 ± 2.259	Robie et al. (1979)	Wagman et al. (1969), Kelley and Anderson (1935)
		-740.57	Fosbøl et al. (2010)	Wagman et al. (1969)

Table 4b. Thermodynamic properties of Iron Carbonate Minerals and Synthetic Solid Carbonates: Enthalpies of Formation (Continued)

Mineral		$\Delta H^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
		-775.71	Fosbøl et al. (2010)	French (1971)
		-753.12	Mel'nik (1972)	Naumov et al. (1971)
		-93.30[(1)]	Mel'nik (1972)	Naumov et al. (1971)
recommended value		-752.20		Mel'nik (1972)
recommended value		-93.43[(1)]		Mel'nik (1972)
		-752.2	Woods and Garrels (1987)	Mel'nik (1972)
		-740.6	Preis and Gamsjäger (2002)	Barin and Knacke (1973)
		-740.57	Fosbøl et al. (2010)	Barin et al. (1973)
		-753.1	Woods and Garrels (1987)	Naumov et al. (1974)
		-738.6	Dobrydiev et al. (2005)	Ryabin et al. (1977)
		-749.6	Woods and Garrels (1987)	Helgeson et al. (1978)
solubility data		-749.70	Chai and Navrotsky (1994)	Helgeson et al. (1978) after Langmuir (1969)
		-749.70	Bénézeth et al. (2009)	Helgeson et al. (1978)
		-749.656	Fosbøl et al. (2010)	Helgeson et al. (1978)
		-737.0	Woods and Garrels (1987)	Robie et al. (1978)
		-736.985	Fosbøl et al. (2010)	Robie et al. (1978)
		-740.6	Woods and Garrels (1987)	Robie et al. (1978)
solubility data		-737.0 ± 2.3	Chai and Navrotsky (1994)	Robie et al. (1978)
		-736.98 ± 2.26	Radha and Navrotsky (2013)	Robie et al. (1978)
solubility data		-741.90	Chai and Navrotsky (1994)	Reiterer et al. (1981)
		-741.90	Bénézeth et al. (2009)	Reiterer et al. (1981)
		-740.6	Chai and Navrotsky (1994)	Wagman et al. (1982)
		-740.57	Bénézeth et al.	Wagman et al. (1982)
		-740.6	Preis and Gamsjäger (2002)	Wagman et al. (1982)
		-740.57	Fosbøl et al. (2010)	Wagman et al. (1982)
		-749.6	Woods and Garrels (1987)	Helgeson (1983, 1984)
		-737.0	Woods and Garrels (1987)	Sangameshwar and Barnes (1983)

Table 4b. Thermodynamic properties of Iron Carbonate Minerals and Synthetic Solid Carbonates: Enthalpies of Formation (Continued)

Mineral		$\Delta H^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
		-755.9 ± 5.5		Robie et al. (1984)
solubility data		-753.2	Chai and Navrotsky (1994)	Robie et al. (1984),
phase equilibrium		-758.6	Chai and Navrotsky (1994)	Robie et al. (1984)
		-755.9 ± 5.5	Robie and Hemingway (1995)	Robie et al. (1984)
		753.22 ± 0.6	Bénézeth et al. (2009)	Robie et al. (1984)
		-753.22	Fosbøl et al. (2010)	Robie et al. (1984)
phase equilibrium		-749		Stubina and Toguri (1989)
		-749.21	Chai and Navrotsky (1994)	Stubina and Toguri (1989),
		-749.0	Preis and Gamsjäger (2002)	Stubina and Toguri (1989)
		-749	Fosbøl et al. (2010)	Stubina and Toguri (1989)
		-761.18 ± 0.91		Holland and Powell (1990)
phase equilibrium		-761.2 ± 0.9	Chai and Navrotsky (1994)	Holland and Powell (1990)
phase equilibrium		-760.6 ± 0.5	Chai and Navrotsky (1994)	Holland and Powell (1990, updated)
		-761.20 ± 0.9	Bénézeth et al. (2009)	Holland and Powell (1990)
		-761.18	Fosbøl et al. (2010)	Holland and Powell (1990)
		-740.5	Preis and Gamsjäger (2002)	Knacke et al. (1991)
average of 2 values		-750.6 ± 1.1		Chai and Navrotsky (1994)
		-750.6 ± 1.1	Preis and Gamsjäger (2002)	Chai and Navrotsky (1994)
		-750.6	Fosbøl et al. (2010)	Chai and Navrotsky (1994)
		-750.5 ± 0.8	Radha and Navrotsky (2013)	Chai and Navrotsky (1994), Robie et al. (1978)
		-755.9		Robie and Hemingway (1995)
		-755.000		Matas et al. (2000)
		-752 ± 1.2		Preis and Gamsjäger (2002)
		-752	Fosbøl et al. (2010)	Preis and Gamsja¨ger (2002)
		-755.9 ± 5.5	Preis and Gamsjäger (2002)	Robie and Hemingway (1995)
		-755.9	Fosbøl et al. (2010)	Robie and Hemingway (1995)
		-761.50 ± 0.51		Holland and Powell (1998)

Table 4b. Thermodynamic properties of Iron Carbonate Minerals and Synthetic Solid Carbonates: Enthalpies of Formation (Continued)

Mineral		$\Delta H^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
		-740.6		Stern (2000)
		-752.00 ± 1.2		Preis and Gamsjäger (2002)
		-755.90 ± 5.5		Bénézeth et al. (2009)
		-749.59 ± 2.		Bénézeth et al. (2009)
		-738.28	Recommended value (Wagman et al., 1982)	Fosbøl et al. (2010)
		-750.01	Recommended value (Cox et al., 1989; Parker and Khodakovskii, 1995)	Fosbøl et al. (2010)
		-749.66		EQ3/6
		-754.037		NAGRA
Fe(II)/Fe(III)				
Fe(III)				
Synthetic Phases				
Fe(II)				
$Fe(HCO_3)_2$ *Undetermined ΔH*	$Fe(HCO_3)_2$	-870 ± 8		Yatsimirskii (1958)
Estimated value of fictive compound		-1481.14 ± 62.76		Wilcox and Bromley (1963)
		-1481.14	Karapet'yants and Karapet'yants (1970)	Wilcox and Bromley (1963)
Fe(III)				
Fe–Monocarbonate	$Ca_4[Fe(OH)_6]_2(CO_3)•6(H_2O)$	-7637	-	Moschner et al. (2008)
	$Ca_4Fe_2(CO_3)(OH)_{12}•6(H_2O)$	-7485	-	Dilnesa et al. (2011)
Fe–Hemicarbonate	$Ca_4Fe_2O_{6.5}(CO_3)_{0.5}•11.5(H_2O)$	-7363	-	Lothenbach et al. (2008)
	$Ca_4Fe_2(CO_3)_{0.5}(OH)_{12}•4(H_2O)$	-6581	-	Dilnesa et al. (2011)

(1) Formation from the oxides

Table 4c. Thermodynamic properties of Iron Carbonate Minerals and Synthetic Solid Carbonates: Entropies

Mineral		$S^0_{P_r,T_r}$	Secondary Reference	Primary Reference
Name	Formula	J K^{-1} gfw^{-1}		
Minerals				
Fe(II)				
Ankerite		187.00		Holland and Powell (1998)
Fe Dolomite	$CaFe(CO_3)_2$	185.60		Holland and Powell (1990)
Siderite *synthetic*	$Fe^{II}CO_3$	74.06	Kelley and Anderson (1935)	Smith (1918)
graphical		92.9 ± 1.7		Anderson (1934)
calculated		90.8		Anderson (1934)
		92.88 ± 1.67	Kelley and King (1961)	Anderson (1934)
		92.9	Fosbøl et al. (2010)	Anderson (1934)
		92.9	Fosbøl et al. (2010)	Kelley and Anderson (1935)
		92.9	Fosbøl et al. (2010)	Latimer (1952)
		92.88	Latimer (1952)	Rossini et al. (1952)?
		92.88	Zhuk (1954)	Rossini et al. (1952), Karapet'yants (1953)
		92.88 ± 1.67	Mel'nik (1972)	Rossini et al. (1952), Krestovnikov et al. (1963), Nikolaev and Dolivo-Dobovolskii (1961)
		92.88	Karpov et al. (1968)	Rossini et al. (1952)
		92.9	Woods and Garrels (1987)	Rossini et al. (1952)
calculated		93.30		Zhuk (1954)
		93.30	Karpov et al. (1968)	Zhuk (1954)
		93.30	Karapet'yants and Karapet'yants (1970)	Zhuk (1954)
		93.30	Mel'nik (1972)	Zhuk (1954)
		92.9	Stern (2000)	Kubaschevski and Evans (1958)
		100.00 ± 2.51	Robie (1962, 1966), corrected for magnetic contribution	Kelley and King (1961)
		100.00 ± 2.51	Karpov et al. (1968)	Robie (1962)
		92.88 ± 1.67	Karpov et al. (1968)	Kelley and King (1961)

Table 4c. Thermodynamic properties of Iron Carbonate Minerals and Synthetic Solid Carbonates: Entropies (Continued)

Mineral		$S^0_{P_r,T_r}$ J K^{-1} gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
		96.1		Kostryukov and Kalinkina (1964)
		96.1	Karapet'yants and Karapet'yants (1970)	Kostryukov and Kalinkina (1964)
		96.11 ± 0.42	Mel'nik (1972)	Kostryukov and Kalinkina (1964), Naumov et al. (1974)
		96.11 ± 0.4	Naumov et al. (1974)	Kostryukov and Kalinkina (1964)
		96.1	Fosbøl et al. (2010)	Kostryukov and Kalinkina (1964)
		105.02 ± 2.51	Mel'nik (1972)	Robie (1965), Robie and Waldbaum (1968)
		105.0 ± 2.5	Robie et al. (1979)	Robie (1965)
		105.0	Fosbøl et al. (2010)	Robie (1965)
		105.0	Fosbøl et al. (2010)	Robie and Waldbaum (1968)
		92.88		Wagman et al. (1969)
		92.9	Fosbøl et al. (2010)	Wagman et al. (1969)
		74.1	Fosbøl et al. (2010)	French (1971)
recommended value		96.11		Mel'nik (1972)
		96.1	Woods and Garrels (1987)	Mel'nik (1972)
		92.9	Fosbøl et al. (2010)	Barin et al. (1973)
		96.1	Woods and Garrels (1987)	Naumov et al. (1974)
		105.0	Fosbøl et al. (2010)	Helgeson et al. (1978)
		105.0	Woods and Garrels (1987)	Helgeson et al. (1978)
		105.0	Woods and Garrels (1987)	Robie et al. (1978)
		105.0	Fosbøl et al. (2010)	Robie et al. (1978)
		92.9	Woods and Garrels (1987)	Robie et al. (1978)
		92.90	Bénézeth et al. (2009)	Wagman et al. (1982)
		92.9	Fosbøl et al. (2010)	Wagman et al. (1982)
		95.5 ± 0.2		Robie et al. (1984)
natural	$(Fe_{0.965}Mn_{0.042}Mg_{0.002})CO_3$	95.5	Woods and Garrels (1987)	Robie et al. (1984)
		95.5 ± 0.2	Robie and Hemingway (1995)	Robie et al. (1984)
		95.47 ± 0.15	Preis and Gamsjäger (2002)	Robie et al. (1984)
		95.47 ± 0.15	Bénézeth et al. (2009), Chai and Navrotsky (1994)	Robie et al. (1984), from solubility data,

Table 4c. Thermodynamic properties of Iron Carbonate Minerals and Synthetic Solid Carbonates: Entropies (Continued)

Mineral		$S^0_{P_r,T_r}$	Secondary Reference	Primary Reference
Name	Formula	J K^{-1} gfw^{-1}		
		95.47	Fosbøl et al. (2010)	Robie et al. (1984)
		95.47	Fosbøl et al. (2010)	Robie et al. (1984)
		95.50		Holland and Powell (1990)
		95.50	Bénézeth et al. (2009)	Holland and Powell (1990),
		95.50	Fosbøl et al. (2010)	Holland and Powell (1990)
		95.47		Robie and Hemingway (1995)
		95.47	Fosbøl et al. (2010)	Robie and Hemingway (1995)
		95.47		Matas et al. (2000)
		92.9		Stern (2000)
		95.47	Fosbøl et al. (2010)	Preis and Gamsja¨ger (2002)
		109.54 ± 2.		Bénézeth et al. (2009)
		95.47	Recommended value (Wagman et al., 1982)	Fosbøl et al. (2010)
		95.47	Recommended value (C Cox et al., 1989; Parker and Khodakovskii, 1995)	Fosbøl et al. (2010)
		105.02		BSC (2007)
				NAGRA
Fe(II)/Fe(III)				
Fe(III)				
Synthetic Phases				
Fe(II)				
Fe(III)				
Fe–Monocarbonate	$Ca_4[Fe(OH)_6]_2(CO_3)•6(H_2O)$	737	-	Möschner et al. (2008)
	$Ca_4Fe_2(CO_3)(OH)_{12}•6(H_2O)$	1230	-	Dilnesa et al. (2011)
Fe–Hemicarbonate	$Ca_4Fe_2O_{6.5}(CO_3)_{0.5}•11.5(H_2O)$	749	-	Lothenbach et al. (2008)
	$Ca_4Fe_2(CO_3)_{0.5}(OH)_{12}•4(H_2O)$	1270	-	Dilnesa et al. (2011)

Table 5. Crystallographic Properties of Iron Carbonate Minerals and Synthetic Solid Carbonates

	Name	Formula	Reference
	Minerals		
	Fe(II)		
1	Biraite-(Ce)	$Ce_2Fe^{II}(CO_3)(Si_2O_7)$	Mineralogy Database (http://webmineral.com/)
2	Bonshtedtite	$Na_3Fe^{II}(PO_4)(CO_3)$	Gaines et al. (1997)
3	Caresite	$Fe^{II}_4Al_2(OH)_{12}CO_3 \cdot 3(H_2O)$	Chao and Gault (1997)
4	Caresite	$Fe^{II}_4Al_2(OH)_{12}CO_3 \cdot 3(H_2O)$	Gaines et al. (1997)
5	Chukanovite	$Fe^{II}_2(CO_3)(OH)_2$	Gaines et al. (1997)
6	Chukanovite	$Fe^{II}_2(CO_3)(OH)_2$	Pekov et al. (2007)
7	$Fe_2(CO_3)(OH)_2$	$Fe^{II}_2(CO_3)(OH)_2$	Erdös and Altorfer (1976)
8	Ferrotychite	$Na_6Fe^{II}_2(SO_4)(CO_3)_4$	Malinovskii et al. (1979)
9	Ferrotychite	$Na_6Fe^{II}_2(SO_4)(CO_3)_4$	Gaines et al. (1997)
10	Siderite	$Fe^{II}CO_3$	Graf (1961)

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
	Minerals									
	Fe(II)									
1	Biraite-(Ce)	6.505	6.744	18.561		108.75		4	$P2_1/c$	116.09
2	Bonshtedtite	8.921	6.631	5.151		90.42		2	$P2_1/m$	91.747
3	Caresite	10.805		22.48				6	$P3_1$ or $P3_212$	228.13
4	Caresite	10.805		22.48				6	$P3_122$ or $P3_212$	228.13
5	Chukanovite	12.396	9.407	3.2152		97.78		4	$P2_1/a$	55.927
6	Chukanovite	12.396	9.407	3.2152		97.78		4	$P2_1/a$	55.927
7	$Fe_2(CO_3)(OH)_2$	9.390	24.53	3.212					orthorh	55.693
8	Ferrotychite	13.962						8	Fd3	204.88
9	Ferrotychite	13.962						8	Fd3	204.88
10	Siderite	4.6887		15.373				4	R3c	29.376

	Name	Formula	Reference
11	Siderite	$Fe^{II}CO_3$	Gaines et al. (1997)
12	Siderite	$Fe^{II}CO_3$	Mineralogy Database (http://webmineral.com/)
	Fe(II)/Fe(III)		
13	Fougèrite	$Fe^{II}_4Fe^{III}_2(OH)_{12}CO_3 \cdot 3(H_2O)$	Génin et al. (2014)
14	Trébeurdenite	$Fe^{II}_2Fe^{III}_4O_2(OH)_{10}CO_3 \cdot 3(H_2O)$	Génin et al. (2014)
	Fe(III)		
15	Brugnatellite	$Mg_6Fe^{III}(CO_3)(OH)_{13} \cdot 4(H_2O)$	Gaines et al. (1997)
16	Brugnatellite	$Mg_6Fe^{III}(CO_3)(OH)_{13} \cdot 4(H_2O)$	[not found]
17	Coalingite	$Mg_{10}Fe^{III}_2(CO_3)(OH)_{24} \cdot 2(H_2O)$	Pastor-Rodriguez and Taylor (1971)
18	Coalingite	$Mg_{10}Fe^{III}_2(CO_3)(OH)_{24} \cdot 2(H_2O)$	Gaines et al. (1997)
19	Coalingite	$Mg_{10}Fe^{III}_2(CO_3)(OH)_{24} \cdot 2(H_2O)$	Mineralogy Database (http://webmineral.com/)

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
11	Siderite	4.6916		15.3796				6	R3c	29.425
12	Siderite	4.72		15.46				6	R3c	29.938
	Fe(II)/Fe(III)									
13	Fougèrite	3.182		22.896					R-3m	
14	Trébeurdenite	3.173		22.695					R-3m	
	Fe(III)									
15	Brugnatellite	5.48		16.00				1	$P6_3/mmc$	250.59
16	Brugnatellite	8.629	5.805	7.654.		103.17		2	$P2_1/m$ or $P2_1$	224.82
17	Coalingite	3.12		37.4				0.5	R3c	379.75
18	Coalingite	6.24		74.8				4	R3c	379.75
19	Coalingite	3.12		37.4				0.5	R3c	379.75

	Name	Formula	Reference
20	Fencooperite	$Ba_6Fe^{III}_3Si_8O_{23}(CO_3)_2Cl_3•(H_2O)$	Gaines et al. (1997)
21	Fencooperite	$Ba_6Fe^{III}_3Si_8O_{23}(CO_3)_2Cl_3•(H_2O)$	Grice (2001)
22	Mössbauerite	$Fe^{III}_6O_4(OH)_8CO_3•(3H_2O)$	Génin et al. (2014)
23	Pyroaurite	$Mg_6Fe^{III}_2(CO_3)(OH)_{16}•4(H_2O)$	Ingram and Taylor (1967)
24	Pyroaurite	$Mg_6Fe^{III}_2(CO_3)(OH)_{16}•4(H_2O)$	Gaines et al. (1997)
25	Pyroaurite	$Mg_6Fe^{III}_2(CO_3)(OH)_{16}•4(H_2O)$	Mineralogy Database (http://webmineral.com/)
26	Reevesite	$Ni_6Fe^{III}_2(CO_3)(OH)_{16}•4(H_2O)$	de Waal and Viljoen (1971)
27	Reevesite	$Ni_6Fe^{III}_2(CO_3)(OH)_{16}•4(H_2O)$	Gaines et al. (1997)
28	Sjogrenite	$Mg_6Fe^{III}_2(CO_3)(OH)_{16}•4(H_2O)$	Ivanov et al. (1986)
29	Sjogrenite	$Mg_6Fe^{III}_2(CO_3)(OH)_{16}•4(H_2O)$	Gaines et al. (1997)

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
20	Fencooperite	10.727		7.085				1	P3m1	425.19
21	Fencooperite	10.7409		7.0955				1	P3m1	426.92
22	Mössbauerite	(≈3.16)		≈22.02					R-3m	
23	Pyroaurite	3.13		23.49				3	R3m	320.05
24	Pyroaurite	6.219		46.83				3	R-3m	314.87
25	Pyroaurite	6.19		46.54				3	R-3m	310.00
26	Reevesite	6.614(3)		45.54(2)				3	R-3m	346.32
27	Reevesite	6.614		45.54				3	R-3m	346.32
28	Sjogrenite	3.113		15.61				0.25	$P6_3/mmc$	315.58
29	Sjogrenite	6.22		15.61				1	$P6_3/mmc$	314.97

	Name	Formula	Reference
	Synthetic Phases		
	Fe(II)		
30			
	Fe(III)		
31			

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
	Synthetic Phases									
	Fe(II)									
30										
	Fe(III)									
31										

[#]Calculated from cell constants, this work

Table 6. Carbonate Minerals containing greater than 10 wt.% Iron*

Name	Formula	Iron, wt.%	gfw	Thermodynamic Data	
				Est.	Meas.
Fe(II)					
Ankerite	$Ca(Fe^{II},Mg,Mn)(CO_3)_2$	16.24	206.39	no	yes
Bonshtedtite	$Na_3Fe^{II}(PO_4)(CO_3)$	19.96	279.80	no	no
Caresite	$Fe^{II}{}_4Al_2(OH)_{12}CO_3{\bullet}3(H_2O)$	37.51	595.49	no	no
Chukanovite	$Fe_2(CO_3)(OH)_2$	53.18	206.88	no	no
Ferrotychite	$Na_6Fe^{II}{}_2(SO_4)(CO_3)_4$	19.07	585.73	no	no
IMA2009-010	$Ba_6(PO_4)_2(CO_3)][Fe^{II}{}_7(OH)_4Fe^{III}{}_2O_2(SiO_3)_8$	21.99	2285.23	no	no
Siderite	$Fe^{II}CO_3$	48.20	115.86	no	yes
Fe(II)/Fe(III)					
Fougèrite	$Fe^{II}{}_4Fe^{III}{}_2(OH)_{12}CO_3{\bullet}3(H_2O)$			no	yes
Trébeurdenite	$Fe^{II}{}_2Fe^{III}{}_4O_2(OH)_{10}CO_3{\bullet}3(H_2O)$			no	no
Fe(III)					
Mössbauerite	$Fe^{III}{}_6O_4(OH)_8CO_3{\bullet}(3H_2O)$			no	no
Brugnatellite	$Mg_6Fe^{III}(CO_3)(OH)_{13}{\bullet}4(H_2O)$	10.07	554.84	no	no
Coalingite	$Mg_{10}Fe^{III}{}_2(CO_3)(OH)_{24}{\bullet}2(H_2O)$	13.00	858.96	no	no
IMA2009-010	$Ba_6(PO_4)_2(CO_3)][Fe^{II}{}_7(OH)_4Fe^{III}{}_2O_2(SiO_3)_8$	21.99	2285.23	no	no
Pyroaurite	$Mg_6Fe^{III}{}_2(CO_3)(OH)_{16}{\bullet}4(H_2O)$	16.88	661.71	no	yes
Reevesite	$Ni_6Fe^{III}{}_2(CO_3)(OH)_{16}{\bullet}4(H_2O)$	12.87	868.02	no	no
Sjogrenite	$Mg_6Fe^{III}{}_2(CO_3)(OH)_{16}{\bullet}4(H_2O)$	16.88	661.71	no	no

*Data taken primarily from a compilation given by the Mineralogy Database (http://webmineral.com).

References

Adams, C.D., Garber, J.D., Singh, R.K. and. Jangama, V.R. (1996). Computer modeling to predict rates in gas condensate wells containing CO_2. CORROSION/96, paper no. 176 (Houston, TX, NACE, 1996).

Anderson, C.T. (1934). The heat capacities of magnesium, zinc, lead, manganese and iron carbonates at low temperatures1. Journal of the American Chemical Society, 56(4), 849-851.

Bardy, J. and Péré, C. (1976). Détermination expérimental du coefficient de solubilité du carbonate ferreux en mileux aqueux. Tribune du CEBEDEAU, 29(387), 75-81.

Barin, I. and Knacke, O. (1973). Thermochemical Properties of InorganicSubstances, 2nd edn. Springer-Verlag, Berlin.

Barin, I., Knacke, O. and Kubaschewski, O. (1977). Thermochemical Properties of Inorganic Substances. Berlin: Springer-Verlag. 1973. Supplementum 1977.

Bénézeth, P., Dandurand, J.L. and Harrichoury, J.C. (2009). Solubility product of siderite ($FeCO_3$) as a function of temperature (25-250°C). Chemical Geology, 265, 3-12.

Berner. A. (1967). Thermodynamic stability of sedimentary iron sulfides. American Journal of Science, 265, 773-785.

Bourdoiseau, J.A., Sabot, R., Jeannin, M., Termemil, F. and Refait, Ph. (2012). Determination of standard Gibbs free energy of formation of green rusts and its application to the Fe(II-III) hydroxy-oxalate. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 410, 72-80.

Bourrié, G., Trolard, F., Génin, J.-M.R., Jaffrezic, A., Maître, V. and Abdelmoula, M. (1999). Iron control by equilibria between hydroxy-green rusts and solutions in hydromorphic soils. Geochimica et Cosmochimica Acta, 63, 3417-3427.

Bourrié, G., Trolard, F., Philippe Refait, P. and Feder, F. (2004). A solid-solution model for Fe(II)-Fe(III)-Mg(II) green rusts and fougerite and estimation of their gibbs free energies of formation. Clays and Clay Minerals, 52(3), 382-394.

Braun, R.D. (1991). Solubility of iron(II) carbonate at temperatures between 30 and 80°. Talanta, 38(2), 205-211.

Bruno, J. (1990). Personal communication to Millero and Hawke (1992).

Bruno, J., Wersin, P. and Stumm, W. (1992). On the influence of carbonate in mineral dissolution: II. The solubility of FeCO3 (s) at 25°C and 1 atm total pressure. Geochimica et Cosmochimica Acta, 56(3), 1149–1155.

BSC (Bechtel SAIC Company) (2007). Qualification of Thermodynamic Data for Geochemical Modeling of Mineral–Water Interactions in Dilute Systems. ANL-WIS-GS-000003 REV 01. Las Vegas, Nevada: Bechtel SAIC Company.DOC.20070619.0007. [EQ3/6 Data0.YMP.R5 database]

Chai, L. and Navrotsky, A. (1994). Enthalpy of formation of siderite and its application in phase equilibrium calculation. American Mineralogist, 79, 921–929.

Chai, L. and Navrotsky, A. (1996a). Synthesis, characterization, and energetics of solid solution along the dolomite ankerite join, and implications for the stability of ordered $CaFe(CO_3)_2$. American Mineralogist, 81, 1141-1147

Chai, L. and Navrotsky, A. (1996b). Synthesis, characterization, and enthalpy of mixing of the (Fe,Mg)CO_3 solid solution. Geochimica et Cosmochimica Acta, 60, 4377-4383.

Chao, G.Y. and Gault, R.A. (1997). Quintinite-2H, quintinite-3T, charmarite-2H, charmarite-3T and caresite-3T, a new group of carbonate minerals related to the hydrotalcite-manasseite group. Canadian Mineralogist, 35, 1541-1549.

Cox, J. D. Wagman, D.D. and V. A. Medvedev, V.A. (1989). CODATA key values for thermodynamics. New York, Hemisphere Publishing Corp.

de Waal, S.A. and Viljoen, E.A. (1971). Nickel minerals from Barberton, South Africa: IV. Reevesite, a member of the hydrotalcite group. American Mineralogist, 56, 1077-1081.

Dilnesa, B.Z., Lothenbach, B., Le Saout, G., Renaudin, G., Mesbah, A., Filinchuk, Y., Wichser, A. and Wieland, E. (2011). Iron in carbonate containing AFm phases. Cement and Concrete Research, 41, 311-323.

Dobrydiev, S.V., Nilova, E.V. and Beskov, V.S. (2005). Calculation of $\Delta_f G^0(298)$ and $\Delta_f H^0(298)$ for sparingly soluble metal carbonates and oxalates in the solid state. Zhurnal Neorganicheskoi Khimii, 50(12), 2015-2018. [In Russian].

Drissi, H., Refait, P. and Génin, J.M.R. (1994). The oxidation of $Fe(OH)_2$ in the presence of carbonate ions: Structure of carbonate green rust one. Hyperfine Interactions, 90, 395-400.

Drissi, S.H., Refait, Ph., Abdelmoula, M. and Génin, J.M. (1995). Preparation and thermodynamic properties of Fe(II)-Fe(III) hydroxide–carbonate (green rust one), Pourbaix diagram of iron in carbonate-containing aqueous media. Corrosion Science, 37, 2025-2041.

Egorov, A.M. and Titova, Z.P. (1962). Solubility products of salts with polyatomic ions as a function of the temperature. Zhurnal Neorganicheskoi Khimii, 7, 275-278, English translation. p. 141-142.

Ehlert, H. and Hempel, W. (1913). Solubility of Certain Salts. Zeitschrift für Elektrochemie und angewandte physikalische Chemie, 18, 727-729.

Emerson, S. (1976). EarIy diagenesis in anaerobic lake sediments: chemical equilibria in interstitial waters. Geochimica et Cosmochimica Acta, 40, 925-934.

Erdös, V.E. and Altorfer, H. (1976). Ein dem Malachit ähnliches basisches Eisen-karbonat als Korrosionprodukt von Stahl. Werkstöffe und Korrosion, 27, 304-312.

Fosbøl, P.L., Thomsen, F. and Stenby, E.H. (2010). Review and recommended thermodynamic properties of $FeCO_3$. Corrosion Engineering, Science and Technology, 45(2), 115-135.

Fouillac, A. and Criaud, A. (1984). Carbonate and bicarbonate trace metal complexes: Critical reevaluation of stability constants. Geochemical Journal, 18, 297-303.

French, B.M. (1971). Stability relations of siderite ($FeCO_3$) in the system Fe-CO. American Journal of Science, 271(1), 37-78.

Gaines, R.V., Skinner, H.C.W., Foord, E.E., Mason, B., Rosenzweig, A. King, V.T. and Dowty, E. (1997). Dana's New Mineralogy (Eighth edition). John Wiley and Sons, Inc., New York. 1819 p.

Gamsjäger, H. (1974). Wechselwirkung von Metalloxiden, -hydroxiden, -carbonaten und -sulfiden mit Wasser. Radex-Rundschau, 4, 274-285.

Gamsjäger, H. (1985). Solid state chemical model for the solubility behavior of homogeneous solid cobalt manganese carbonate mixtures. Berichte der Bunsen-Gesellschaft, 89(12), 1318-22.

Garber, J.D., Perkins, R.S., Vamshidhar, R.J. and Rama, R.A. (1996). Proc. Conf. CORROSION/96, Paper 176; 1996, Houston, TX, NACE. [As cited by Fosbol et al. (2010). See Adams et al. (1996)]

Génin, J.M., Bourrié, G., Trolard, F., Abdelmoula, M., Jaffrezic, A., Refait, Ph., Maître, V., Humbert, B. and Herbillon, A. (1998). Thermodynamic equilibria in aqueous solutions of synthetic and natural Fe(II)–Fe(III) green rusts; occurrences of the mineral in hydromorphic soils. Environmental Science and Technology, 32, 1058-1068.

Génin, J.-M.R., Refait, P., Simon, L. and Drissi, S.H. (1998). Preparation and Eh–pH diagrams of Fe(II)–Fe(III) green rust compounds; hyperfine interaction characteristics and stoichiometry of hydroxy-chloride, -sulphate and –carbonate. Hyperfine Interactions, 111, 313-318.

Génin, J.-M.R., Ruby, C. and Upadhyay, C. (2006). Structure and thermodynamics of ferrous, stoichiometric and ferric oxyhydroxycarbonate green rusts; redox flexibility and fougerite mineral. Solid State Sciences, 8, 1330-1343.

Génin, J.-M.R., Christy, A., Kuzmann, E., Mills, S. and Ruby, C. (2014). Structure and occurrences of <<green rust>> related new minerals of the <<fougèrite>> group, trébeurdenite and mössbauerite, belonging to the <<hydrotalcite>> supergroup; how Mössbauer spectroscopy helps XRD. Hyperfine Interactions, 226, 459-482.

Goskhimizdat. (1952). Chemical Reference, vol. 3. [In Russian]. (As cited in Zhuk, 1954).

Graf, D.L. (1961). Crystallographic tables for the rhombohedral carbonates. American Mineralogist, 46, 1283-1316.

Grauer, R. (1999). Solubility products of M(II)-Carbonates [edited and translated by U. Berner]. Paul Scherrer Institute, Waste Management Laboratory, PSI Bericht Nr. 99-04, ISSN 1019-0643, 24 p.

Greenberg, J. and Tomson, M. (1992). Precipitation and dissolution kinetics and equilibria of aqueous ferrous carbonate vs temperature. Applied Geochemistry, 7, 185-190.

Grice, J D. (2001). The crystal structure of fencooperite: Unique [Fe_3O_{13}] pinwheels cross-connected by [Si_8O_{22}] islands. Canadian Mineralogist, vol. 39, p. 1065-1071.

Haarberg, T., Jakobsen, J.E. and Oestvold, T, (1990). The effect of ferrous iron on mineral scaling during oil recovery. Acta Chemica Scandinavica, 44(9), 907-15.

Haehnel, O. (1924). Über die Löslichkeit der Carbonate des Strontiums, des Bariums und der Schwermetalle in Wasser unter hohen Kohlendioxyddrucken sowie über die Eigenschaften solcher Lösungen. Journal für praktische Chemie (Leipzig), 108, 187-193.

Helgeson, H.C. (1969). Thermodynamics of hydrothermal systems at elevated temperatures and pressures. American Journal of Science, 267, 729-804.

Helgeson, H.C., Delany, J.M., Nesbitt, H.W. and Bird, D.K. (1978). Summary and critique of the thermodynamic properties of rock forming minerals. American Journal of Science, 278-A. 229 p.

Helgeson, H.C. (1993, 1994). SUPCRT update notices, (Cited in Woods and Garrels, 1987.)

Helgeson, H.C. (1985). Errata II. Thermodynamics of minerals, reactions, and aqueous solutions at high pressures and temperatures. American Journal of Science, 285, (9), 845-855.

Holland, T.J.B. and Powell, R. (1990). An enlarged and updated internally consistent thermodynamic dataset with uncertainties and correlations: the system Na2O–K_2O–CaO–MgO–MnO–FeO–Fe_2O_3–Al_2O_3–TiO_2–SiO_2–C–H_2–O_2. Journal of Metamorphic Geology, 8, 89-124.

Holland, T.J.B. and Powell, R. (1998). An internally consistent thermodynamic dataset for phases of petrological interest. Journal of Metamorphic Geology, 16, 309-343**.**

Ingram, L. and Taylor, H.F.W. (1967). The crystal structures of sjoegrenite and pyroaurite. Mineralogical Magazine, 36, 465–479.

Ivanov, O.K., Mozzherin, Y.V. and Vilisov, V.I. (1986). New data on sjögrenite. Izvestiya Akad. Nauk Kazakh. SSR, Geol. Ser. 1, 40–45. [in Russian]. See also American Mineralogist, 73(6) (1988), 199 (abs. ref. 5).

Jensen, D.L., Boddum, J.K., Tjell, J.C. and Christensen, T.H. (2002). The solubility of rhodochrosite ($MnCO_3$) and siderite ($FeCO_3$) in anaerobic aquatic environments. Applied Geochemistry, 17, 503–511.

Johnson, G.K. and Bauman, J.E., Jr. (1978). Equilibrium constants for the aquated iron(II) cation. Inorganic Chemistry, 17(10), 2774-2779.

Karapet'yants, M. Kh. (1953). Khimicheskaya Termodinamika (Chemical Thermodynamics). 2nd Edition. Goshkhimizdat. 611 p. [In Russian].

Karapet'yants, M.Kh. and Karapet'yants, M.L. (1970). Thermodynamic constants of Inorganic and Organic Compounds (trans. By J. Schmorak). Humphrey Science Publishers, Ann Arbor, Michigan. 461 p.

Karpov, I.K., Kashik, S.A. and Pampura, V.D. (1968). Thermodynamic Constants for Calculations in Geochemistry and Petrology. Izdva, Nauka, 143 p. [In Russian]

Kelley, K.K. and Anderson, C.T. (1935). Theoretical metallurgy. IV. Metal carbonates-correlations and applications of thermodynamic properties. In Contributions to the data on theoretical metallurgy IV, U.S. Bureau of Mines Bulletin No. 384, 73 p.

Kelley, K.K. and King. E.G. (1961). Contribution to the Data on Theoretical Metallurgy. XIV. Entropies of the Elements and Inorganic Compounds. U.S. Bureau of Mines Bulletin No. 592, 149 p.

King D.W. (1998). Role of carbonate speciation on the oxidation rate of Fe(II) in aquatic systems. Environmental Science and Technology, 32(19), 2997-3003.

Kireev, V.A. (1964). Acid-base properties of oxides. Zhurnal Fizicheskoi Khimii, 38(8), 1881-1894. [In Russian].

Kostryukov, V.N. and Kalinkina, I.N. (1964). Heat capacity and entropy for manganese, iron, cobalt, and nickel carbonates at low temperatures. Zhurnal Fizicheskoi Khimii, 38, 780-781.

Krestovnikov, A.N. et al. (1963). Spravochnik po Raschetam Ravnovesii Metallurgicheskikh Reaktsii (Uskorennye Metody) (Handbook for Calculation of Equilibrium in Metallurgical Reactions (Accelerated Method)) 416 p. Metallyurgizdat. [In Russian]. As cited by Mel'nik (1972).

Krishnamurti, K.V., Harris, G.M. and Sastrp, V.S. (1970). The chemistry of the metal carbonato complexes. Chemical Reviews, 70(2), 171-197

Kubaschewski, O. and Evans, K. (1991). Thermochemical Properties of Inorganic Substances, 2nd edn. Springer-Verlag, Berlin,

La Iglesia, A. and Félix, J.F. (1994). Estimation of thermodynamic properties of mineral carbonates at high and low temperatures from the sum of polyhedral contributions. Geochimica et Cosmochimica Acta, 58(19), 3983-3991.

Langmuir, D. (1969). The Gibbs free energies of substances in the system Fe–O_2–H_2O–CO_2 at 25°C. U. S. Geological Survey Professional Paper 650-B.

Larson, J.W., Cerutti, P., Garber, H.K. and Hepler, L.G. (1968). Electrode potentials and thermodynamic data for aqueous ions. Copper, zinc, cadmium, iron, cobalt, and nickel. Journal of Physical Chemistry, 72(8), 2902-2907

Latimer, W.M. (1952). The Oxidation States of the Elements and their Potentials in Aqueous Solutions. Second edition. Prentice Hall, New York, 392 p.

Lothenbach, B., Matschei, T., Möschner, G. and Glasser, F.P. (2008). Thermodynamic modelling of the effect of temperature on the hydration and porosity of Portland cement. Cement and Concrete Research, 38(1), 1-18.

Lothenbach, B. (2010). Thermodynamic equilibrium calculations in cementitious systems. Materials and Structures, 43, 1413-1433.

Malinovskii, Yu A, Baturin, S.V. and Belov, N.V. (1979). The crystal structure of Fe-tychite. Doklady Akademii Nauk SSSR 249, p. 1365-1368. [In Russian].

Marion, G.M., Catling, D.C. and Kargel, J.S. (2003). Modeling aqueous ferrous iron chemistry at low temperatures with application to Mars. Geochimica et Cosmochimica Acta, *67*(22), 4251-4266.

Martell, A.E. and Smith, R.M. (1976). Critical Stability Constants 4: Inorganic Complexes. New York, Plenum Press.

Matas, J., Gillet, P., Ricard, Y. and Martinez, I. (2000). Thermodynamic properties of carbonates at high pressures from vibrational modelling. European Journal of Mineralogy, 12(4), 703-720.

Mattigod, S.V. and Sposito, G. (1977). Estimated association constants for some complexes of trace metals with inorganic ligands. Soil Science Society of America Journal, 41(6), 1092-1097.

Mel'nik, Y.P. (1972). Thermodynamic Constants for the Analysis of Conditions of Formation of Iron Ores., Naukova Dumka, Kiev, 196 p. [In Russian].

Millero, F.J. and Hawke, D.J. (1992). Ionic interactions of divalent metals in natural waters. Marine Chemistry, 40(1-2), 19-48.

Millero, F.J., Yao, W. and Aicher, J. (1995). The speciation of Fe(II) and Fe(III) in natural waters. Marine Chemistry, 50, 21-39. [Amsterdam, The Netherlands]: Elsevier.

Moore, P.B. and Araki, T. (1979). Armangite, $Mn_{26}[As_6(OH)_4O1_4][As_6O_{18}]_2[CO_3]$, a fluorite derivative structure. American Mineralogist, 64, 748-757.

Möschner, G., Lothenbach, B., Rose, J., Ulrich, A., Figi, R. and Kretschmar, R. (2008). Solubility of Fe-ettringite ($Ca_6[Fe(OH)_6]_2(SO_4).26H_2O$). Geochimica et Cosmochimica Acta. 72, 1-18.

Murray J.W., Grundmanis V. and Smethie W.M. Jr. (1978). Interstitial water chemistry in sediments of Saanich Inlet. Geochimica et Cosmochimica Acta, 42, 1011-1026.

Naumov, G.B., Ryzhenko, B.N., and Khodakovsky, I.L. (1974). Handbook of Thermodynamic Data. National Technical Information Service, 722176A, U.S. Dept. Commerce. 328 p.

Naumov, G.B., Ryzhenko, B.N., and Khodakovskii, I.L. (1971). Handbook of Thermodynamic Values. Atomizdat, Moscow. [In Russian].

Nikolaev, V.A. and Dolivo-Dobrovolskii, V.V. (1961). Osnovy teorii protsessov magmatizma i metamorfizma (Fundamentals of the Theory of Processes of Magmatism and Metamorphism), Moscow. [In Russian].

Nordstrom, D.K., Plummer, L.N., Langmuir, D., Busenberg, E., May, H.M., Jones, B.F. and Parkhurst, D.L. (1990). Revised chemical equilibrium data for major water-mineral reactions and their limitations, Chapter 31 in: Chemical Modelling of Aqueous Systems II, (Melchoir D.C., Basset R.L., eds.) p. 398-413, ACS Symp. Ser. 146, American Chemical Society, Washington, DC.

Palmer, D.A. and van Eldik, R. (1983). The chemistry of metal carbonato and carbon dioxide complexes. Chemical Reviews, 83, 651-731.

Parker, V.B. and Khodakovskii, I.L. (1995). Thermodynamic properties of the aqueous ions (2+ and 3+) of iron and the key compounds of iron. Journal of Physical and Chemical Reference Data, 24(5), 1699-1745.

Pastor-Rodriguez, J. and Taylor, H.F.W. (1971). Crystal structure of coalingite. Mineralogical Magazine, 38, 286-294.

Pekov, I.V., Perchiazzi, N., Merlino, S, Kalachev, V.N., Merlini, M., and Zadov, A.E. (2007). Chukanovite, $Fe_2(CO_3)(OH)_2$, a new mineral from the weathered iron meteorite Dronino. European Journal of Mineralogy, 19, 891-898.

Ptacek, C.J. (1992). Experimental determination of siderite solubility in high ionic-strength aqueous solutions. Ph.D thesis, University of Waterloo, Ontario, Canada.

Ptacek, C.J., and Reardon, E.J. (1992). Solubility of siderite ($FeCO_3$) in concentrated NaCl and Na_2SO_4 solutions at 25°C. Water–Rock Interaction, Proc. Int. Symp., 7th, (Y.K. Kharaka and A.S. Meast, Eds.) p. 181-183. Balkema, Rotterdam, Netherlands.

Ptacek, C.J. and Blowes, D.W. (1994). Influence of siderite on the pore-water chemistry of inactive mine-tailings impoundments. In: Alpers, C.N., Blowes, D.W. (Eds.), Environmental Geochemistry of Sulfide Oxidation. American Chemical Society, Washington, DC, p. 172-189.

Preis, W. and Gamsjäger, H. (2001). Thermodynamic investigation of phase equilibria in metal carbonate-water-carbon dioxide systems (Invited Review). Monatshefte für Chemie, 132, 1327-1346.

Preis, W. and Gamsjäger, H. (2002). Critical evaluation of solubility data: enthalpy of formation of siderite. Physical Chemistry and Chemical Physics, 4(16), 4014-4019.

Radha, A.V. and Navrotsky, A. (2013). Thermodynamics of carbonates. Reviews in Mineralogy and Geochemistry, 77(1), 73-121.

Randall, M. and Frandsen, M. (1932). Determination of the free energy of ferrous hydroxide from measurements of electromotive force. Journal of the American Chemical Society, 54, 40-47.

Refait, P., Abdelmoula, M., Génin, J.M.R. and Sabot, R. (2006). Green rusts in electrochemical and microbially influenced corrosion of steel. C. R. Geoscience, 338, 476-487.

Reiterer, F. (1980). Lös1ichkeitskonstanten und freie Bildungsenthalpien neutraler Übergangsmetallcarbonate: $MnCO_3$, $FeCO_3$, $CoCO_3$, $NiCO_3$, $CuCO_3$, $ZnCO_3$. PhD thesis, Montanuniversität, Leoben, Austria.

Reiterer, F., Johannes, W. and Gamsjäger, H. (1981). Semi~microdetermination of solubility constants of copper(II) carbonate and iron(II) carbonate. Microchimica Acta, 1(1-2), 63-72.

Robie, R.A. (1962). Thermodynamic properties of minerals. U.S. Geological Survey Open File Report TEI-816. 31 p.

Robie, R.A. (1965). Heat and free energy of formation of herzenbergite, troilite, magnesite, and rhodochrosite calculated from equilibrium data U.S. Geological Survey Professional Paper, 525-D, p. D65-D72.

Robie, R.A. (1966). Section 20: Thermodynamic properties of minerals. Handbook of Physical Constants, Geological Society of America Memoirs, 97, 437-458.

Robie, R.A. and Waldbaum, D.R. (1968). Thermodynamic properties of minerals and related substances at 29S.15°K and one atmosphere pressure and at higher temperatures: U.S. Geological Survey Bulletin No. 1259, 256 p.

Robie, R.A., Haselton, H.T. and Hemingway, B.S. (1984). Heat capacities and entropies of rhodochrosite ($MnCO_3$) and siderite ($FeCO_3$) between 5 and 600 K. American Mineralogist, 69, 349-357.

Robie, R.A., Hemingway, B.S. and Fisher, J.R. (1978) Thermodynamic properties of minerals and related subslances at 298.15 K and I bar (10^5 Pascals) pressure and at higher temperatures. U.S. Geological Survey Bulletin No. 1452. U.S. Government Printing Office, Washington, DC. 456 p.

Robie, R.A., Hemingway, B.S. and Fisher, J.R. (1979). Thermodynamic properties of minerals and related subslances at 298.15 K and I bar (10^5 Pascals) pressure and at higher temperatures. U.S. Geological Survey Bulletin No. 1452. (Reprinted with corrections). U.S. Government Printing Office, Washington, DC. 456 p.

Robie, R.A., and Hemingway, B.S. (1995). Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 Pascals) pressure and at higher temperatures. U.S. Geological Survey Bulletin No. 2131, 461 p.

Rossini, F.D., Wagman, D.D., Evans, W.H., Levine, S. and Jaffe, I. (1952). Selected values of chemical thermodynamical properties. NBS Circular 500. 1268 p., Washington, D.C.

Roth, W.A. (1929). Zur Thermochemie des Eisens, Mangans und Nickels. Zeitschrift für angewandte Chemie, 42, 981-84.

Rozov, K., Berner, U., Taviot-Gueho, C., Leroux, F., Renaudin, G., Kulika, D., and Diamond, L.W. (2010). Synthesis and characterization of the LDH hydrotalcite–pyroaurite solid-solution series. Cement and Concrete Research, 40(8), 1248-1254.

Ruby, C., Upadhyay, C., Géhin, A., Ona-Nguema, G. and Génin, J.M.R. (2006). In situ redox flexibility of Fe^{II-III} oxyhydroxycarbonate green rust and fougerite. Environmental Science and Technology, 40, 4696-4702.

Serebrennikov, V.S. (1977). Redox conditions in the low Caucasus carbonated mineral springs. Geochemstry International, 14(3), 141-149.

Ryabin, V.A., Ostroumov, M.A. and Svit, T.F. (1977). Thermodynamic Properties of Substances: Handbook (Termodinamicheskie Svoistva Veshchestv: Spravochnik). Khimiya, Leningr. Otd. Leningrad, USSR 389 p. [In Russian].

Sangameshwar, S.R. and Barnes, H.L. (1983). Supergene processes in zinc-lead-silver sulfide ores in carbonates. Economic Geology, 78, 1379-1397.

Shock, E.L. and Koretsky, C.M. (1995). Metal-organic complexes in geochemical pr ocesses: Estimation of standard partial molal thermodynamic properties of aqueous complexes between metal cations and monovalent organic acid ligands at high pressures and temperatures. Geochimica et Cosmochimica Acta, 59, 1497-1532.

Silva, C.A.R., Liu, X. and Millero, F.J. (2002). Solubility of siderite ($FeCO_3$) in NaCl solutions. Journal of Solution Chemistry, 31, 97-108.

Singer, P.C. and Stumm, W. (1970). The Solubility of Ferrous Iron in Carbonate-Bearing Waters. Journal of the American Water Works Association, 62, 198-202.

Smith, H.J. (1918). On equilibrium in the system: Ferrous carbonate, carbon dioxide and water. Journal of the American Chemical Society, 40, 879-883.

Smith, R.M. and Martell, A.E. (1976). Critical Stability Constants, Volume 4, Inorganic Complexes. Plenum Press, New York.

Stern, K.H. (2000). High Temperature Properties and Thermal Decomposition of Inorganic Salts with Oxyanions. 256 p. CRC Press LLC, 2000 N.W. Corporate Blvd., Boca Raton Florida 33431.

Stubina, N.M. and Toguri, J.M. (1989). The decomposition pressure of synthetic siderite ($FeCO_3$). Transactions of the Iron and Steel Society, 10, 87-90.

Stull, D.R. and H. Prophet, H. (1971). JANAF Thermochemical Tables, 2nd Ed., Washington, DC. U. S. Government Printing Office.

Sverjensky, D.A., Shock, E.L. and Helgeson, H.C. (1997). Prediction of the thermo dynamic properties of aqueous metal complexes to 1000 C and 5 kb. Geochimica et Cosmochimica Acta, 61(7), 1359-1412.

Sun, Y. and Nesic, S. (2004). A parametric study and modeling on localized CO_2 corrosion in horizontal wet gas flow. Proc. Conf. CORROSION/04, Paper 380; 2004, Houston, TX, NACE.

Sun, W., Nesic, S. and Woollam, R.C. (2009). The effect of temperature and ionic strength on iron carbonate ($FeCO_3$) solubility limit. Corrosion Science, 51(6), 1273-1276.

Tillmans, J. and Klarmann, B. (1924). The solution of iron by oxygen-free natural waters. Angewandte Chemie, 36, 94-97. [In German]

Trolard, F. and Bourrié, G. (2012). Fougerite a natural layered double hydroxide in gley soil: habitus, structure, and some properties. Chapter 9 in Clay minerals in nature-their characterization, modification and application, (M. Valaškova and G.S. Martynkova, Eds.). InTech, Rijeka, Croatia, 171-188.

Turner, D.R., Whitfield, M. and Dickson, A.G. (1981). The equilibrium speciation of dissolved components in freshwater and sea water at 25 C and 1 atm pressure. Geochimica et Cosmochimica Acta, 45(6), 855-881.

Wagman, D.D., Evans, W.H., Parker, V.B., Halow, I., Bailey, S.M. and Schumm, R.H. (1969). Selected Values of Chemical Thermodynamic Properties. Tables for elements 35 through 53 in the standard order of arrangement. NBS Technical Note 270-4, U.S. Department of Commerce, National Bureau of Standards, 141 p.

Wagman, D.D., Evans, W.H., Parker, V.B., Schumm, R.H., Halow, I., Bailey, S.M., Churney, K.L. and Nuttall, R.L. (1982). The NBS Tables of Chemical Thermodynamic Properties: Selected Values for Inorganic and C1 and C2 Organic Substances in SI Units: American Chemical Society and the American Institute of Physics for the National Bureau of Standards (Journal of Physical Chemical Reference Data, 11, supplement 2, 392 p.).

Wersin, P., Charlet, L., Karthein, R. and Stumm, W. (1989). From adsorption to precipitation: Sorption of Mn^{2+} on $FeCO_3$(s). Geochimica et Cosmochimica Acta, 53(11), 2787-2796.

Wilcox. D.E. and Bromley, L.A. (1963). Computer Estimation of heat and free energy for simple inorganic compounds. Industrial and Engineering Chemistry, 55(7), 32-39.

Woods, T.L. and Garrels, R.M. (1987). Thermodynamic Values at Low Temperature for Natural Inorganic Materials. An Uncritical Summary. Oxford University Press. 242 p. plus references.

Zhuk, N.P. (1954). Thermodynamic constants of sulfates, carbonates, chromates, bromates, iodates, oxalates, and other salts slightly soluble in water. Zhurnal Fizicheskoi Khimii, 28, 1690–1697. [In Russian].

Zvyagintsev, O.E. and Lopatto, Yu.S. (1962). Tetracarbonate complexes of trivalent iron. Zhurnal Neorganicheskoi Khimii, 7(6), 1272-1276. [In Russian].

LEAD

Table 1. Association Constants for Aqueous Carbonate Complexes in the System $PbO-CO_2-H_2O$

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
$Pb^{2+} + CO_3^{2-} = PbCO_3(aq)$	7.0 ± 0.08	-	Sol. 1.0 *M* Na_2CO_3 + $NaClO_4$		Baranova (1969)
	7.0	-	Sol. 1.0 *M* $NaClO_4$	Bilinski et al. (1976)	Baranova (1969)
	7.0	-	Sol., 1.0 *M* $NaClO_4$	Clever and Johnston (1980)	Baranova (1969)
	7	-		Palmer and Van Eldik (1983)	Baranova (1969)
	10.9	-	200°C	Palmer and Van Eldik (1983)	Baranova (1969)
	7.5	-	Estimate		Zirino and Yamamoto (1972)
	7.5	-	*I* = 0	Bilinski et al. (1976)	Zirino and Yamamoto (1972)
	6.51	-	*I* = 0.72	Whitfield and Turner (1980)	Zirino and Yamamoto (1972)
	7.5	-	*I* = 0	Palmer and Van Eldik (1983)	Zirino and Yamamoto (1972)
	3.0		*I* = 0.72	Whitfield and Turner (1980)	Dyrssen and Wedborg (1975)
	6.2 ± 0.2	-	DPP, = 0.1 *M* KNO_3		Ernst et al. (1975)
	6.3 ± 0.4	-	DPASV, = 0.1 *M* KNO_3		Ernst et al. (1975)
	6.3	-	DPP/DPASV, 0.1 *M* KNO_3	Bilinski et al. (1976)	Ernst et al. (1975)
	6.3	-		Long and Angino (1977)	Ernst et al. (1975)
	6.3	-	DPP, 0.1 *M* KNO_3	Clever and Johnston (1980)	Ernst et al. (1975)
	6.2	-	*I* = 0.72	Whitfield and Turner (1980)	Stumm and Brauner (1975)
	5.31	-	*I* = 0.72	Whitfield and Turner (1980)	Long and Angino (1977)
	7.4	-	*I* = 0.72	Whitfield and Turner (1980)	Lu and Chen (1977)
	6.4	-	*I* = 0.1 – 1.0	Palmer and Van Eldik (1983)	Clever and Johnston (1980)
	5.36	-	*I* = 0.7	Palmer and Van Eldik (1983)	Laddha et al. (1981)?
	5.59	-	*I* = 0	Palmer and Van Eldik (1983)	Laddha et al. (1981)?

Table 1. Association Constants for Aqueous Carbonate Complexes in the System $PbO-CO_2-H_2O$ (Continued)

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	5.62	-	seawater	Palmer and Van Eldik (1983)	Laddha et al. (1981)?
	5.4 ± 0.1	-	I = 0.3	Palmer and Van Eldik (1983)	Bilinski and Schindler (1982)
	5.75	-	Sol. 0.3 M $NaClO_4$	Bilinski et al. (1976)	Bilinski and Schindler (to be published)
	5.62	-	See Bilinski et al. (1976) 0.7 M $NaClO_4$	Bilinski et al. (1976)	L Sipos, private communication.
	5.62	-	ASV, 0.7 M $NaClO_4$	Clever and Johnston (1980)	Sipos, cited in Bilinski et al. (1976)
	6.4	-	ASV, 0.1 M KNO_3		Bilinski et al. (1976)
	6.1	-	DPP, 0.1 M KNO_3		Bilinski et al. (1976)
	6.3	-	ASV, 0.1 M KNO_3	Clever and Johnston (1980)	Bilinski et al. (1976)
	6.40	-	ASV, 0.1 M KNO_3	Clever and Johnston (1980)	Bilinski et al. (1976)
	6.11	-	DPP, 0.1 M KNO_3	Clever and Johnston (1980)	Bilinski et al. (1976)
	7.24				Hem (1976)
	5.62	-	ASV, 0.7 M $NaClO_4$		Sipos (1976)
	6.20	-	I = seawater, estimate		Sipos et al. (1980)
	7.00	-		Millero and Hawke (1992)	Turner et al. (1981)
	7.0	-	Estimated value	Woosley and Millero (2013)	Turner et al. (1981)
	6.60†	-			Bilinski and Schindler (1982)
	5.40 ± 0.10	-	Sol. 0.3 M $NaClO_4$		Bilinski and Schindler (1982)
	5.75	-	Sol., 0.3 M $NaClO_4$	Clever and Johnston (1980)	Bilinski and Schindler (1982), cited in Bilinski et al. (1976)
	7.20	-17.15	Estimate		Fouillac and Criaud (1984)
	7.14				Taylor and Lopata (1984)
	6.45 ± 0.72	-	Review, indicative value		Powell et al. (2009)
	6.789 ± 0.022	-	I = 0	Woosley and Millero (2013)	Easley and Byrne (2011)
	6.87 ± 0.09	-	I = 0, NaCl and $NaClO_4$ media		Woosley and Millero (2013)

Table 1. Association Constants for Aqueous Carbonate Complexes in the System $PbO-CO_2-H_2O$ (Continued)

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
$Pb^{2+} + 2CO_3^{2-} = Pb(CO_3)_2^{2-}$	8.2	-	18ºC. Pol., 1.7 *M* KNO_3 (+ K_2CO_3 + $KHCO_3$)		Faucherre and Bonnaire (1959)
	8.2	-	18ºC. Pol., 1.7 *M* KNO_3	Krishnamurty et al. (1970)	Faucherre and Bonnaire (1959)
	8.2		Pol., 1.7 *M* KNO_3,	Bilinski et al. (1976)	Faucherre and Bonnaire (1959)
	8.20	-	18ºC. Pol., 1.7 *M* KNO_3	Clever and Johnston (1980)	Faucherre and Bonnaire (1959)
	10.8	-	Re-interpreted. *I* = 0	Bilinski et al. (1976)	Baranova and Barsukov (1965)
	9.09 ± 0.04	-	Sol. 1.0 *M* $NaClO_4$		Baranova (1968)
	9.0 ± 0.08	-	Sol. 1.0 *M* Na_2CO_3 + $NaClO_4$		Baranova (1969)
	9.0	-	Sol. 1.0 *M* $NaClO_4$	Bilinski et al. (1976)	Baranova (1969)
	9.0	-	Sol., 1.0 *M* $NaClO_4$	Clever and Johnston (1980)	Baranova (1969)
	9.0	-		Palmer and Van Eldik (1983)	Baranova (1969)
	12.3	-	200°C	Palmer and Van Eldik (1983)	Baranova (1969)
	10.5	-	Sol. *I* = 0	Ferri et al. (1987)	Baranova (1969)
	10.64	-		Long and Angino (1977)	Ernst et al. (1875)
	9.1		DPP, 0.1 *M* KNO_3		Bilinski et al. (1976)
	9.8		ASV, 0.1 *M* KNO_3		Bilinski et al. (1976)
	9.8	-	0.1 *M* KNO_3	Clever and Johnston (1980)	Bilinski et al. (1976)
	9.80	-	ASV, 0.1 *M* KNO_3	Clever and Johnston (1980)	Bilinski et al. (1976)
	9.11	-	DPP, 0.1 *M* KNO_3	Clever and Johnston (1980)	Bilinski et al. (1976)
	9.15	-	Sol., 0.3 *M* $NaClO_4$	Clever and Johnston (1980)	Bilinski and Schindler (to be published) cited in Bilinski et al. (1976)
	10.6		ASV, *I* = 0	Ferri et al. (1987)	Bilinski et al. (1976)
	9.9		DPP, *I* = 0	Ferri et al. (1987)	Bilinski et al. (1976)
	10.64				Hem (1976)

Table 1. Association Constants for Aqueous Carbonate Complexes in the System $PbO-CO_2-H_2O$ (Continued)

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	8.2	-	18°C, *I* = 1.7	Palmer and Van Eldik (1983)	Smith and Martell (1976)
	9.65		*I* = 0.72	Whitfield and Turner (1980)	Long and Angino (1977)
	9.89		*I* = 0.72	Whitfield and Turner (1980)	Lu and Chen (1977)
	9.4	-	*I* = 0.1 – 1.0	Palmer and Van Eldik (1983)	Clever and Johnston (1980)
	9.96	-	*I* = seawater, estimate		Sipos et al. (1980)
	8.8	-	seawater	Palmer and Van Eldik (1983)	Balko et al. (1981)?
	8.6	-	*I* = 0.7	Palmer and Van Eldik (1983)	Laddha et al. (1981)?
	9.08	-	*I* = 0	Palmer and Van Eldik (1983)	Laddha et al. (1981)?
	10.29	-		Millero and Hawke (1992)	Turner et al. (1981)
	8.86 ± 0.04	-	*I* = 0.3	Palmer and Van Eldik (1983)	Bilinski and Schindler (1982)
	9.15	-	Sol. 0.3 *M* $NaClO_4$	Bilinski et al. (1976)	Bilinski and Schindler (to be published)
	10.06†				Bilinski and Schindler (1982)
	8.86 ± 0.10	-	Sol. 0.3 *M* $NaClO_4$		Bilinski and Schindler (1982)
	10.1	-	Sol. *I* = 0	Ferri et al. (1987)	Bilinski and Schindler (1982)
	8.9 ± 0.10	-	Sol. 3 *M* $NaClO_4$		Ferri et al. (1987)
	10.4	-	Sol. *I* = 0		Ferri et al. (1987)
	10.13 ± 0.24	-	Review, provisional value		Powell et al. (2009)
$2Pb^{2+} + H_2O + CO_2(g) = Pb_2CO_3^{2+} + 2H^+$	-10.51 ± 0.37	-	EMF, 3 *M* $NaClO_4$		Neher-Neumann (1992)
$2Pb^{2+} + CO_3^{2-} = Pb_2CO_3^{2+}$	8.28 ± 0.37*	-	EMF, *I* = 0		Neher-Neumann (1992)
$3Pb^{2+} + H_2O + CO_2(g) = Pb_3CO_3^{4+} + 2H^+$	-9.20 ± 0.01	-	EMF, 3 *M* $NaClO_4$		Neher-Neumann (1992)

Table 1. Association Constants for Aqueous Carbonate Complexes in the System $PbO-CO_2-H_2O$ (Continued)

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
$3Pb^{2+} + CO_3^{2-} = Pb_3CO_3^{4+}$	7.19 ± 0.05*	-	EMF, I = 0		Neher-Neumann (1992)
$Pb^{2+} + CO_3^{2-} + OH^- = PbCO_3OH^-$	10.9 ± 0.3	-	Sol. 3 M $NaClO_4$		Ferri et al. (1987)
$Pb^{2+} + CO_3^{2-} + H^+ = PbHCO_3^+$	13.2	-	Estimate		Zirino and Yamamoto (1972)
	12.23*	-11.26*	Estimate		Fouillac and Criaud (1984)
	12.38*	-			Millero and Hawke (1992)
	12.72* ± 0.1	-	EMF, I = 0		Neher-Neumann (1992)
$Pb^{2+} + H_2O + CO_2(g) = PbHCO_3^+ + H^+$	-6.09 ± 0.04	-	EMF, 3 M $NaClO_4$		Neher-Neumann (1992)
$Pb^{2+} + HCO_3^{2-} = PbHCO_3^+$	2.9	-		Long and Angino (1977)	Zirino and Yamamoto (1972)
	2.40	-	I = 0.72	Whitfield and Turner (1980)	Zirino and Yamamoto (1972)
	2.9	-	I = 0	Palmer and Van Eldik (1983)	Zirino and Yamamoto (1972)
	2.2	-	I = 0.72	Whitfield and Turner (1980)	Dyrssen and Wedborg (1975)
	1.86 ± 0.1	-	Review, provisional value 3.5 M $NaClO_4$		Powell et al. (2009)
$Pb^{2+} + 3CO_3^{2-} + 3H^+ = Pb(HCO_3)_3^-$	36.18	-	20ºC, I = ?		Baranova and Barsukov (1965)
$Pb^{2+} + 2HCO_3^- = Pb(HCO_3)_2(aq)$	4.77	-	20ºC. Pol. 1. M $NaHCO_3$ + $NaNO_3$		Baranova and Barsukov (1965)
	4.77	-	18 ± 0.5°C. Pol., 1 M $NaHCO_3$		Baranova (1967)
	4.78 ± 0.07	-	I = 1.	Baranova (1969)	Baranova (1967)

Table 1. Association Constants for Aqueous Carbonate Complexes in the System $PbO-CO_2-H_2O$ (Continued)

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
$Pb^{2+} + 3HCO_3^- = Pb(HCO_3)_3^-$	5.19	-	20ºC. Pol., 1. *M* $NaHCO_3$ + $NaNO_3$	Baranova and Barsukov (1965)	
	5.21 ± 0.06		18 ± 0.5°C. Pol., 1 *M* $NaHCO_3$		Baranova (1967)
	6.20 ± 0.05		*I* = 1.	Baranova (1969)	Baranova (1967)
$Cu^{2+} + 2CO_3^{2-} + 2H_2O = [Cu(OH)_2(HCO_3)_2]^{2-}$	-	-	0.5 – 1.0 *M* $KHCO_3$. Evidence for complex. Incurrectly specified charge on complex.		Shirai (1961)
$Pb^{2+} + CO_3^{2-} + Cl^- = PbCO_3Cl^-$	7.23 ± 0.74	-	*I* = 0		Woosley and Millero (2013)

(1) At standard state (25°C, 1 atm, *I* = 0), unless otherwise noted.

* Corrected using bicarbonate dissociation equation from PHREEQC

† Corrected to 0 ionic strength using the extended Debye-Hückel equation

Table 2. Solubility Constants of Solid Carbonates in the System $PbO-CO_2-H_2O$

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
Minerals					
Caledonite					
$Pb_5Cu_2CO_3(SO_4)_3(OH)_6 + 6H^+ = 5Pb^{2+} + 2Cu^{2+} + CO_3^{2-} + 3SO_4^{2-} + 6H_2O$	-26.6		See note		Abdul-Samad et al. (1982)
Cerussite					
$PbCO_3(s) = Pb^{2+} + CO_3^{2-}$	≈ -14.		16°C		Johnston (1915)
	≈ -14.		16°C	Kelley and Anderson (1935)	Johnston (1915)
			18°C. Solubility = 0.014% and 0.015% at $P(CO_2)$ = 1 and 56 atm., respectively		Haehnel (1924)
	-11.87		18°C	Kelley and Anderson (1935)	Haehnel (1924)
	-13.140	-	Review. No correction for activity coefficients		Kelley and Anderson (1935)
	-12.82	-	Literature Review	Latimer (1952)	Kelley and Anderson (1935)
	-13.66	-	Based on electrochemical cell measurements		Saegusa (1950)
	-12.89	-		Zhuk (1954)	Goskhimizdat (1952)
	-13.24	-	Cond. measurements		Uggla (1959)
	-13.13	-			Näsänen et al. (1961)
	-13.13	-		Clever and Johnston (1980)	Näsänen et al. (1961)
	-12.96	-		Clever and Johnston (1980)	Egorev and Titova (1962)
	-12.83	-	From thermodynamic data	Clever and Johnston (1980)	Wagman et al. (1968)
	-13.45	23.89	Thermodynamic calculations		Helgeson (1969)
	-13.45	-		Clever and Johnston (1980)	Helgeson (1969)
	-13.13				Hem (1976)
	-13.1	-	I = 0	Palmer and Van Eldik (1983)	Smith and Martell (1976)
	-11.0	-	I = 1	Palmer and Van Eldik (1983)	Smith and Martell (1976)

Table 2. Solubility Constants of Solid Carbonates in the System PbO-CO2-H2O (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	-13.1	-	I = 0	Palmer and Van Eldik (1983)	Clever and Johnston (1980)
	-12.15 ± 0.05	-	Sol. 0.3 M $NaClO_4$		Bilinski and Schindler (1982)
	-13.35†				Bilinski and Schindler (1982)
	-12.1	-	I = 0.3	Palmer and Van Eldik (1983)	Bilinski and Schindler (1982)
	-12.8				Wagman et al. (1982)
	-13.21				Taylor and Lopata (1984)
	-13.2 ± 0.2	-	Literature Review		Grauer (1999)
	-13.18 ± 0.07	-	Review, recommended value		Powell et al. (2009)
	-11.70		Estimated		Yoder et al. (2010)
$PbCO_3(s) = PbCO_3(aq)$	6.4 ± 0.1		I = 0.3	Palmer and Van Eldik (1983)	Bilinski and Schindler (1982)
Hydrocerussite					
$Pb_3(CO_3)_2(OH)_2 + 2H^+ = 3Pb^{2+} + 2CO_3^{2-} + 2H_2O$	-		Soly in distilled water and various salts		Ruchhoft and Kachmar (1942)
	-17.64				Taylor and Lopata (1984)
	-16.91		**[not found in ref]**		Mercy et al. (1998)
	-9.70		Estimated		Yoder and Rowand (2006)
	-14.30		Estimated		Yoder et al. (2010)
$Pb_3(CO_3)_2(OH)_2 = 3Pb^{2+} + 2CO_3^{2-} + 2OH^-$	-46.78	-	Sol. I = 0. Calc from Gibbs free energy of formation		Schrock (1980)
	-44.08 ± 0.06	-	Sol. 0.3 M $NaClO_4$, uncorrected for complex formation		Bilinski and Schindler (1982)
	-44.81 ± 0.20	-	Sol. 0.1 M $NaClO_4$, uncorrected for complex formation		Bilinski and Schindler (1982)
	-43.77 ± 0.30	-	Sol. 0.3 M $NaClO_4$, corrected for complex formation		Bilinski and Schindler (1982)

Table 2. Solubility Constants of Solid Carbonates in the System PbO-CO2-H2O (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	-44.1 ± 0.1		I = 0.3	Palmer and Van Eldik (1983)	Bilinski and Schindler (1982)
	-44.8 ± 0.2		I = 0.1	Palmer and Van Eldik (1983)	Bilinski and Schindler (1982)
$Pb_3(CO_3)_2(OH)_2 + 7OH^- = 3HPbO_2^- + 2CO_3^{2-} + 3H_2O$	-5.10	-	Corrections for ionic strength approximate		Randall and Spencer (1928)
	-5.10			Naumov et al. (1974)	Randall and Spencer (1928)
Leadhillite					
$Pb_4SO_4(CO_3)_2(OH)_2 + 2H^+ = 4Pb^{2+} + 3SO_4^{2-} + 2CO_3^{2-} + 2H_2O$	-26.7				Abdul-Samad et al. (1982)
Phosgenite					
$Pb_2(CO_3)Cl_2 = 2Pb^{2+} + CO_3^{2-} + 2Cl^-$	-9.90	-		Naumov et al. (1974)	Näsänen et al. (1963)
	-9.93 ± 0.08	-	Review, recommended value		Powell et al. (2009)
$Pb_2(CO_3)Cl_2 + 2H^+ + 2Cl^- = 2PbCl_2(s) + CO_2(g) + H_2O$	19.78	-	25°C, I = 0		Näsänen et al. (1962)
$Pb_2(CO_3)Cl_2 + CO_2(g) + H_2O = PbCO_3 + 2H^+ 2Cl^-$	-19.68	-	25°C, I = 0		Näsänen et al. (1962)
Synthetic Phases					
$Pb_2CO_3(OH)_2$					
$Pb_2CO_3(OH)_2 + 2H^+ = 2Pb^{2+} + CO_3^{2-} + 2H_2O$	-2.70	-	Estimated		Yoder et al. (2010)
$Pb_3CO_3(OH)_4$					
$Pb_3CO_3(OH)_4 + 4H^+ = 3Pb^{2+} + CO_3^{2-} + 4H_2O$	6.30	-	Estimated		Yoder et al. (2010)
$Pb_4CO_3(OH)_6$					

Table 2. Solubility Constants of Solid Carbonates in the System PbO-CO2-H2O (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
$Pb_4CO_3(OH)_6 + 6H^+ = 4Pb^{2+} + CO_3^{2-} + 6H_2O$	15.30	-	Estimated		Yoder et al. (2010)
$\underline{Pb_5CO_3(OH)_8}$					
$Pb_5CO_3(OH)_8 + 8H^+ = 5Pb^{2+} + CO_3^{2-} + 8H_2O$	24.30	-	Estimated		Yoder et al. (2010)
$\underline{Pb_5(CO_3)_2(OH)_6}$					
$Pb_5(CO_3)_2(OH)_6 + 6H^+ = 5Pb^{2+} + 2CO_3^{2-} + 6H_2O$	3.60	-	Estimated		Yoder et al. (2010)

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

† Corrected to 0 ionic strength using the extended Debye-Hückel equation

Note: Abdul-Samad et al. (1982) also determined the solubility of wherryite with an assumed formula: $PbCuCO_3(SO_4)_2O(OH,Cl)_2$. However, a subsequent crystallographic structure determination by Cooper and Hawthorne (1994) indicated that its composition is actually $Pb_7Cu_2(SO_4)_4(SiO_4)_2(OH)_2$.

Table 3a. Association Constants of Aqueous Carbonate Complexes in the System PbO-CO_2-H_2O extracted from Databases of Distribution-of-Species Codes

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Database	Source
$Pb^{2+} + CO_3^{2-} = PbCO_3(aq)$	6.53		MinteqA2	
	7.24		Wateq4f	
	6.58		V8.R6+	
	7.24	0	Minteq (2009)	
	6.478	0.	Minteq (2006)	NIST46.4, MTQ3.11
	7.240	-	Phreeqc (2009)	
	7.24	-	Wateq4f (2005)	
	7.	-3.015	ThermoChimie v.7.b	Blanc et al. (2006)
	-	-	NAGRA/PSI (2001)	
	-	-	Data0.YMP.R5	
	7.0568	-	Thermoddem (2009)	Blanc et al. (2006)
$Pb^{2+} + 2CO_3^{2-} = Pb(CO_3)_2^{2-}$	9.94		MinteqA2	
	10.64		Wateq4f	
	9.40		V8.R6+	
	10.64	0	Minteq (2009)	
	9.938	0.	Minteq (2006)	NIST46.4, MTQ3.11
	10.64	-	Phreeqc (2009)	
	10.64	-	Wateq4f (2005)	
	10.13	-	ThermoChimie v.7.b	Lothenbach et al. (1999)
	-	-	NAGRA/PSI (2001)	
	-	-	Data0.YMP.R5	
	10.1296	-	Thermoddem (2009)	Blanc et al. (2006)
$Pb^{2+} + CO_3^{2-} + H^+ = PbHCO_3^+$	13.23		MinteqA2	
	13.36		Wateq4f	
	-		V8.R6+	
	13.2	0	Minteq (2009)	
	13.2	0.	Minteq (2006)	NIST46.4, MTQ3.11
	13.229	-	Phreeqc (2009)	
	13.229	-	Wateq4f (2005)	
	-	-	ThermoChimie v.7.b	
	-	-	NAGRA/PSI (2001)	
	-	-	Data0.YMP.R5	
	13.7698	-	Thermoddem (2009)	Martell and Smith (1989)

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Table 3b. Solubility Constants of Solid Carbonates in the System $PbO-CO_2-H_2O$ extracted from Databases of Distribution-of-Species Codes

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Database	Source
Cerussite				
$PbCO_3(s) = Pb^{2+} + CO_3^{2-}$	-13.39		MinteqA2	
	-13.29		Wateq4f	
	-13.54		V8.R6+	
	-13.13	20.33	Minteq (2009)	
	-13.13	24.79	Minteq (2006)	
	-13.13	20.33	Phreeqc (2009)	
	-13.13	20.33	Wateq4f (2005)	
	-13.29	27.414	ThermoChimie v.7.b	Not cited.
	-	-	NAGRA/PSI (2001)	
	-13.5379	-	Data0.YMP.R5	Helgeson et al. (1978)
	-13.2898	-	Thermoddem (2009)	Taylor and Lopata (1984)
Hydrocerussite				
$Pb_3(CO_3)_2(OH)_2 + 2H^+ = 3Pb^{2+} + 2CO_3^{2-} + 2H_2O$	-18.76		MinteqA2	
	-17.46		Wateq4f	
	-18.81		V8.R6+	
	-17.46	-0	Minteq (2009)	
	-18.7705	-0	Minteq (2006)	
	-	-	Phreeqc (2009)	
	-17.460	-	Wateq4f (2005)	
	-17.91	-5.16	ThermoChimie v.7.b	Sangameshwar and Barnes (1983)
	-	-	NAGRA/PSI (2001)	
	-	-	Data0.YMP.R5	
	-17.9040	-	Thermoddem (2009)	Taylor and Lopata (1984)
Pb_2OCO_3				
$Pb_2OCO_3 + 2H^+ = 2Pb^{+2} + H_2O + CO_3^{-2}$	-0.5	-47.95	Minteq (2009)	
	-0.5578	-40.8199	Minteq (2006)	
	-	-	Phreeqc (2009)	
	-0.5	-47.95	Wateq4f (2005)	
	-	-	ThermoChimie v.7.b	
	-	-	NAGRA/PSI (2001)	
	-0.6577	-	Data0.YMP.R5	Wagman et al. (1982)
	-	-	Thermoddem (2009)	
$Pb_3O_2CO_3$				
$Pb_3O_2CO_3 + 4H^+ = 3Pb^{+2} + CO_3^{-2} + 2H_2O$	11.02	-110.58	Minteq (2009)	
	11.02	-110.583	Minteq (2006)	
	-	-	Phreeqc (2009)	
	11.020	-110.58	Wateq4f (2005)	
	-	-	ThermoChimie v.7.b	

Table 3b. Solubility Constants of Solid Carbonates in the System PbO-CO_2-H_2O extracted from Databases of Distribution-of-Species Codes (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Database	Source
	-	-	NAGRA/PSI (2001)	
	-	-	Data0.YMP.R5	
	-	-	Thermoddem (2009)	
Phosgenite				
$PbCl_2$:$PbCO_3$ = $2Pb^{+2}$ + $2Cl^-$ + CO_3^{-2}	-19.81	-0	Minteq (2009)	
	-19.81	-0	Minteq (2006)	
	-	-	Phreeqc (2009)	
	-19.810	-	Wateq4f (2005)	
	-19.9	-163.291	ThermoChimie v.7.b	Naumov et al. (1974)
	-	-	NAGRA/PSI (2001)	
	-19.9643	-	Data0.YMP.R5	Wagman et al. (1982)
	-19.8998	-	Thermoddem (2009)	Rickard and Nriagu (1978)
Plumbonacrite				
$Pb_{10}(OH)_6O(CO_3)_6$ + $8H^+$ = $10Pb^{+2}$ + $6CO_3^{-2}$ + $7H_2O$	-	-	Minteq (2009)	
	-8.76	-0	Minteq (2006)	
	-	-	Phreeqc (2009)	
	-	-	Wateq4f (2005)	
	-42.09	-	ThermoChimie v.7.b	Not cited.
	-	-	NAGRA/PSI (2001)	
	-	-	Data0.YMP.R5	
	-42.0891	-	Thermoddem (2009)	Taylor and Lopata (1984)

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Table 3c. Distribution-of-Species Codes: Database References

Database	Reference
Data0.com.V8.R6+	Wolery, T.J. (1994). EQ3NR, Letter report: EQ3/6 version 8.0. Differences from version 7. UCRL-ID-129749. Lawrence Livermore National Laboratory, Livermore, California. USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/LLNL.DAT
Data0.YMP.R5	BSC (Bechtel SAIC Company) (2007). Qualification of Thermodynamic Data for Geochemical Modeling of Mineral–Water Interactions in Dilute Systems. ANL-WIS-GS-000003 REV 01. Las Vegas, Nevada: Bechtel SAIC Company.DOC.20070619.0007.
MinteqA2	HydroGeoLogic, Inc. and Allison Geoscience Consultants, Inc. (1999). MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: User Manual Supplement for Version 4.0, Appendix A: thermodynamic database for MINTEQA2 V4.0, p. 44-74.
Minteq (2009)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/MINTEQ.DAT
Minteq (2006)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/minteq.v4.dat
NAGRA/PSI (2001)	Hummel, W., Berner, U., Curti, E., Pearson, F.J. and Thoenen, T. (2002). Nagra/PSI Chemical Thermodynamic Data Base 01/01. Universal Publishers/uPublish.com, Parkland, Florida. 565 p.
Phreeqc (2009)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/PHREEQC.DAT
ThermoChimie v.7.b	Duro, L., Grivém M. and Giffaut, E. (2010). ThermoChimie, the ANDRA thermodynamic database In Buckau G, Kienzler B, Duro L, Grivé M, Montoya V (eds). 2nd Annual Workshop Proceedings of the Collaborative Project “Redox Phenomena Controlling Systems” (7th EC FP CP Recosy) Larnaca (Cyprus) 16–19 March 2010. Karlsruhe: KIT Scientific Publishing, 275–283.
Thermoddem (2009)	Blanc P., Lassin A. and Piantone P. (2007) THERMODDEM a database devoted to waste minerals. BRGM (Orléans, France). For updates: http://thermoddem.brgm.fr
Wateq4f	Ball, J. W., & Nordstrom, D. K. (1991). User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters. U.S. GEOLOGICAL SURVEY, Open-File Report 91-183, Revised and reprinted - April, 2001. p. 81-94
Wateq4f (2005)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/WATEQ4F.DAT

Table 4a. Thermodynamic properties of Lead Carbonate Minerals and Synthetic Solid Carbonates: Gibbs Free Energies of Formation

Mineral		$\Delta G^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
Minerals				
Caledonite	$Pb_5Cu_2(CO_3)(SO_4)_3(OH)_6$	-4328 ± 2		Abdul-Samad et al. (1982)
Cerussite	$PbCO_3$	-626.39		Kelley and Anderson (1935)
		-627.60	Karpov et al. (1968)	Saegusa (1950)
		-627.60	Karapet'yants and Karapet'yants (1970)	Saegusa (1950)
		-627.60		Saegusa (1950)
		-626.34	Latimer (1952)	Rossini et al. (1952)?
		-626.34	Zhuk (1954)	Rossini et al. (1952), Karapet'yants (1953)
		-626.30 ± 4.18	Robie (1962, 1966)	Rossini et al. (1952)
		-626.34	Karpov et al. (1968)	Rossini et al. (1952)
		-626.3	Woods and Garrels (1987)	Rossini et al. (1952)
		-626.3	La Iglesia and Felix (1994)	Rossini et al. (1952)
calculated		-625.59		Zhuk (1954)
		-625.59	Karpov et al. (1968)	Zhuk (1954)
		-627.60	Karapet'yants and Karapet'yants (1970)	Zhuk (1954)
		-628.0		Uggla (1959)
		-626.3	Woods and Garrels (1987)	Pourbaix (1960)
		-626.39	Karpov et al. (1968)	Gerasimov (1961)
		-	Phase equilibria	Grisafe and White (1964)
		-49.79[(1)]	Karpov et al. (1968)	Kireev (1964)
		-625.337 ± 1.548	Robie et al. (1979)	Adami and Conway (1966), Parker et al. (1971)
		-629.02	Naumov et al. (1974)	Adami and Conway (1966)
		-625.5 ± 1.6	Robie and Hemingway (1995),	Wagman et al. (1982)
		-629.0	Woods and Garrels (1987)	Naumov et al. (1974)
		-629.0	La Iglesia and Felix (1994)	Naumov et al. (1974)
		-626.3	Dobrydiev et al. (2005)	Ryabin et al. (1977)
		-629.1	Woods and Garrels (1987)	Helgeson et al. (1978)

Table 4a. Thermodynamic properties of Lead Carbonate Minerals and Synthetic Solid Carbonates: Gibbs Free Energies of Formation (Continued)

Mineral		$\Delta G^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
		-628.8	Woods and Garrels (1987)	Hem (1978)
		-625.5	Woods and Garrels (1987)	Rickard and Nriagu (1978)
		-625.3	Woods and Garrels (1987)	Robie et al. (1978)
		-625.3	La Iglesia and Felix (1994)	Robie et al. (1979)
		-625.5	Woods and Garrels (1987)	Wagman et al. (1982)
		-625.5	La Iglesia and Felix (1994)	Wagman et al. (1982)
		-738.16	Stern (2000)	Barin (1993)
predicted		-626.3 ± 1.5		La Iglesia and Felix (1994)
Hydrocerussite	$Pb_3(CO_3)_2(OH)_2$	-1711.00 ± 4.18	Naumov et al. (1974)	Randall and Spencer (1928)
		-1712.		Latimer (1952)
		-1711.67	Karpov et al. (1968)	Latimer (1952)
		-1711.67	Karapet'yants and Karapet'yants (1970)	Latimer (1952)
estimated		-1699.		Garrels (1957)
		-1699.	Woods and Garrels (1987)	Garrels (1957)
		-1698.70	Karpov et al. (1968)	Garrels (1960)
		-1711.0	Woods and Garrels (1987)	Naumov et al. (1974)
		-1711.0	Mercy et al. (1998)	Naumov et al. (1974) after Randall and Spencer (1928)
			TGA, phase transformation	Ball and Casson (1977b)
		-1714.2	Woods and Garrels (1987)	Hem (1978)
		-1700.4	Woods and Garrels (1987)	Rickard and Nriagu (1978)
		-1709.6		Schrock (1980)
		-1705 ± 11.	Mercy et al. (1998)	Taylor and Lopata (1984),
Synthetic		-1699.8 ± 1.6		Mercy et al. (1998)
Leadhillite	$Pb_4(SO_4)(CO_3)_2(OH)_2$	-2525 ± 4		Abdul-Samad et al. (1982)

Table 4a. Thermodynamic properties of Lead Carbonate Minerals and Synthetic Solid Carbonates: Gibbs Free Energies of Formation (Continued)

Mineral		$\Delta G^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
Phosgenite	$Pb_2(CO_3)Cl_2$	-952.28 ± 4.18	Naumov et al. (1974)	Näsänen et al. (1963)
Plumbonacrite	$Pb_{10}(CO_3)_6O(OH)_6$			
Shannonite	Pb_2OCO_3	818.10	Saegusa (1950), based in part on:	Marshall and Bruzs (1925)
		-816.88		Kelley and Anderson (1935)
		-818.4	Woods and Garrels (1987)	Rossini et al. (1952)
		-	Phase equilibria	Grisafe and White (1964)
		-	TGA, phase transformation	Ball and Casson (1975, 1977b)
		-	DTA-TG, high-pressure DTA and PXRD	Yamaguchi et al. (1980)
		-816.7	Woods and Garrels (1987)	Wagman et al. (1982)
Widenmannite	$Pb_2(UO_2)(CO_3)_3$	-2818.0 ± 10.0		Van Genderen and Van der Weijden (1984)
Synthetic Phases				
$2PbO.PbCO_3$	$2PbO.PbCO_3$	-1012.	Woods and Garrels (1987)	Rossini et al. (1952)
		-	Phase equilibria	Grisafe and White (1964)
		-	TGA, phase transformation	Ball and Casson (1975, 1977a)
		-	DTA-TG, high-pressure DTA and PXRD	Yamaguchi et al. (1980)
$\underline{PbO.2PbCO_3}$	$PbO.2PbCO_3$	-	Phase equilibria	Grisafe and White (1964)
			TGA, phase transformation	Ball and Casson (1977b)
		-	DTA-TG, high-pressure DTA and PXRD	Yamaguchi et al. (1980)
$\underline{3PbO.4PbCO_3}$	$3PbO.4PbCO_3$	-	Phase equilibria	Grisafe and White (1964)

(1) Formation from the oxides

Table 4b. Thermodynamic properties of Lead Carbonate Minerals and Synthetic Solid Carbonates: Enthalpies of Formation

Mineral		$\Delta H^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
Minerals				
Cerussite	$PbCO_3$	-708.31	Kelley and Anderson (1935)	Gunther, cited, but not referenced
		-700.23		Kelley and Anderson (1935)
		-700.04		Saegusa (1950)
		-700.04	Karpov et al. (1968)	Saegusa (1950)
		-700.04	Karapet'yants and Karapet'yants (1970)	Saegusa (1950)
		-699.98	Zhuk (1954)	Rossini et al. (1952), Karapet'yants (1953)
		-699.98	Latimer (1952)	Rossini et al. (1952)?
		-699.98 ± 2.93	Robie (1962, 1966)	Rossini et al. (1952)
		-699.98	Karpov et al. (1968)	Rossini et al. (1952)
		-700.0	Woods and Garrels (1987)	Rossini et al. (1952)
		-7000.0	La Iglesia and Felix (1994)	Rossini et al. (1952)
		-722.6		Uggla (1959)
		-	Phase equilibria	Grisafe and White (1964)
		-83.26[(1)]	Karpov et al. (1968)	Kireev (1964)
		-702.70 ± 1.26	Naumov et al. (1974)	Adami and Conway (1966)
		-699.150 ± 1.172	Robie et al. (1979)	Adami and Conway (1966), Parker et al. (1971)
		-702.7	Woods and Garrels (1987)	Naumov et al. (1974)
		-702.7	La Iglesia and Felix (1994)	Naumov et al. (1974)
		-690 ± 40	CO_2 atm	Ball and Casson (1977a)
		-689 ± 40	N_2 atm	Ball and Casson (1977a)
		-700.0	Dobrydiev et al. (2005)	Ryabin et al. (1977)
		-702.9	Woods and Garrels (1987)	Helgeson et al. (1978)
		-699.2	Woods and Garrels (1987)	Robie et al. (1978)
		-699.2	La Iglesia and Felix (1994)	Robie et al. (1978)
		-699.1	Woods and Garrels (1987)	Wagman et al. (1982)
		-699.1	La Iglesia and Felix (1994)	Wagman et al. (1982)
		-699.2 ± 1.2	Robie and Hemingway (1995)	Wagman et al. (1982)

Table 4b. Thermodynamic properties of Lead Carbonate Minerals and Synthetic Solid Carbonates: Enthalpies of Formation (Continued)

Mineral		$\Delta H^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
		-699.10	Stern (2000)	Barin (1993)
predicted		-700.0 ± 1.5		La Iglesia and Felix (1994)
amorphous	$PbCO_3$	-697.47	Kelley and Anderson (1935)	Berthelot in Landolt-Bornstein (1923)
Hydrocerussite *CO_2 atm*	$Pb_3(CO_3)_2(OH)_2$	-1906 ± 80		Ball and Casson (1977a)
N_2 atm		-1939 ± 81		Ball and Casson (1977a)
		-1914.2	Woods and Garrels (1987)	Sangameshwar and Barnes (1983)
Plumbonacrite	$Pb_{10}(CO_3)_6O(OH)_6$			
Shannonite	$PbO.PbCO_3$	-919.11	Saegusa (1950), based in part on:	Marshall and Bruzs (1925)
		-919.31		Kelley and Anderson (1935)
		-920.5	Woods and Garrels (1987)	Rossini et al. (1952)
Phase equilibria		-		Grisafe and White (1964)
Thermal transformation		-		Ball and Casson (1975, 1977a)
CO_2 atm		-934 ± 30		Ball and Casson (1977a)
N_2 atm		-917 ± 30		Ball and Casson (1977a)
		-918.4	Woods and Garrels (1987)	Wagman et al. (1982)
Widenmannite	$Pb_2(UO_2)(CO_3)_3$	-3102.0		Van Genderen and Van der Weijden (1984)
Synthetic Phases				
$\underline{2PbO.PbCO_3}$	$2PbO.PbCO_3$	-1142.	Woods and Garrels (1987)	Rossini et al. (1952)
Phase equilibria		-		Grisafe and White (1964)

Table 4b. Thermodynamic properties of Lead Carbonate Minerals and Synthetic Solid Carbonates: Enthalpies of Formation (Continued)

Mineral		$\Delta H^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
Thermal transformation		-		Ball and Casson (1975, 1977a)
CO_2 atm		-1127 ± 40		Ball and Casson (1977a)
N_2 atm		-1131 ± 35		Ball and Casson (1977a)
$\underline{PbO.2PbCO_3}$ *Phase equilibria*	$PbO.2PbCO_3$	-		Grisafe and White (1964)
CO_2 atm		-1624 ± 60		Ball and Casson (1977a)
$\underline{3PbO.4PbCO_3}$	$3PbO.4PbCO_3$	-710.61	Kelley and Anderson (1935)	Thompsen, cited, but not referenced
Phase equilibria		-		Grisafe and White (1964)
$Pb(HCO_3)_2$	$Pb(HCO_3)_2$	-837.22	Karpov et al. (1968)	Rossini et al. (1952)
Estimated value of fictive compound		-1456.03 ± 62.76		Wilcox and Bromley (1963)
		-1456.03	Karapet'yants and Karapet'yants (1970)	Wilcox and Bromley (1963)

(1) Formation from the oxides

Table 4c. Thermodynamic properties of Lead Carbonate Minerals and Synthetic Solid Carbonates: Entropies

Mineral		$S^0_{P_r,T_r}$ J K^{-1} gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
Minerals				
Cerussite *graphical*	$PbCO_3$	131. 0 ± 3.3		Anderson (1934)
calculated		131.4		Anderson (1934)
		130.96 ± 3.35	Kelley and King (1961)	Anderson (1934)
		130.96 ± 3.35	Naumov et al. (1974)	Anderson (1934)
		135.56		Saegusa (1950)
		135.56	Karpov et al. (1968)	Saegusa (1950)
		135.56	Karapet'yants and Karapet'yants (1970)	Saegusa (1950)
		130.96	Karpov et al. (1968)	Latimer (1952)
		130.96	Latimer (1952)	Rossini et al. (1952)?
		130.96	Zhuk (1954)	Rossini et al. (1952), Karapet'yants (1953)
		131.0	Woods and Garrels (1987)	Rossini et al. (1952)
calculated		128.45		Zhuk (1954)
		128.45	Karpov et al. (1968)	Zhuk (1954)
		128.45	Karapet'yants and Karapet'yants (1970)	Zhuk (1954)
		131.0 ± 3.4	Robie and Hemingway (1995)	Kelley (1960)
		130.96 ± 3.35	Robie (1962, 1966)	Kelley and King (1961)
		130.96 ± 3.35	Robie et al. (1978)	Kelley and King (1961)
Phase equilibria, 200-900°C. and 15-1400 bars $P(CO_2)$		-		Grisafe and White (1964)
		131.0	Woods and Garrels (1987)	Naumov et al. (1974)
		131.0	Woods and Garrels (1987)	Helgeson et al. (1978)
		131.0	Woods and Garrels (1987)	Robie et al. (1978)
		131.0	Woods and Garrels (1987)	Wagman et al. (1982)
		131.00	Stern (2000)	Barin (1993)
Hydrocerussite	$Pb_3(CO_3)_2(OH)_2$			

Table 4c. Thermodynamic properties of Lead Carbonate Minerals and Synthetic Solid Carbonates: Entropies (Continued)

Mineral		$S^0_{P_r,T_r}$ J K^{-1} gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
Plumbonacrite	$Pb_{10}(CO_3)_6O(OH)_6$			
Shannonite	$PbO.PbCO_3$	202.92		Kelley and Anderson (1935)
		202.9	Woods and Garrels (1987)	Rossini et al. (1952)
Phase equilibria		-		Grisafe and White (1964)
		204.2	Woods and Garrels (1987)	Wagman et al. (1982)
Synthetic Phases				
$2PbO.PbCO_3$	$2PbO.PbCO_3$	272.	Woods and Garrels (1987)	Rossini et al. (1952)
Phase equilibria		-		Grisafe and White (1964)
$PbO.2PbCO_3$ *Phase equilibria*	$PbO.2PbCO_3$	-		Grisafe and White (1964)
$3PbO.4PbCO_3$ *Phase equilibria*	$3PbO.4PbCO_3$	-		Grisafe and White (1964)
$Pb(HCO_3)_2$	$Pb(HCO_3)_2$	152.72	Karpov et al. (1968)	Latimer (1952)

Table 5. Crystallographic Properties of Lead Carbonate Minerals and Synthetic Solid Carbonates

	Name	Formula	Reference
	Minerals		
1	Barstowite	$Pb_4(CO_3)Cl_6 \bullet (H_2O)$	Steele et al. (1999b)
2	Barstowite	$Pb_4(CO_3)Cl_6 \bullet (H_2O)$	Gaines et al. (1997)
3	Caledonite	$Pb_5Cu_2(CO_3)(SO_4)_3(OH)_6$	Gaines et al. (1997)
4	Caledonite	$Pb_5Cu_2(CO_3)(SO_4)_3(OH)_6$	Mineralogy Database (http://webmineral.com/)
5	Caledonite	$Pb_5Cu_2(CO_3)(SO_4)_3(OH)_6$	Schofield et al. (2009)
6	Cerussite	$PbCO_3$	Colby and LaCoste (1933)
7	Cerussite	$PbCO_3$	Chevrier et al. (1992)
8	Cerussite	$PbCO_3$	Antao and Hassan (2009)
9	Cerussite	$PbCO_3$	Gaines et al. (1997)
10	Cerussite	$PbCO_3$	Mineralogy Database (http://webmineral.com/)

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
	Minerals									
1	Barstowite	4.2043	9.199	16.663		91.82		2	$P2_1m$	193.97
2	Barstowite	4.218	9.180	16.673		91.48		2	$P2_1$ or $P2_1m$	194.33
3	Caledonite	20.089	7.146	6.560				2	$Pmn2_1$	5.689
4	Caledonite	20.088	7.143	6.564				2	$Pmn2_1$	283.60
5	Caledonite	20.085	7.141	6.563				2	$Pmn2_1$	286.44
6	Cerussite	5.16_8	8.46_8	6.14_6				4	Pmcn	40.494
7	Cerussite	5.179(1)	8.492(3)	6.141(2)				4	Pmcn	40.662
8	Cerussite	5.18324(2)	8.49920(3)	6.14746(3)				4	Pmcn	40.773
9	Cerussite	5.180	8.492	6.134				4	Pmcn	40.623
10	Cerussite	5.195	8.436	6.152				4	Pmcn	40.591

	Name	Formula	Reference
11	Dundasite	$PbAl_2(CO_3)_2(OH)_4 \bullet (H_2O)$	Birch et al. (2000)
12	Dundasite	$PbAl_2(CO_3)_2(OH)_4 \bullet (H_2O)$	Gaines et al. (1997), Cocco et al. (1972)
13	Hydrocerussite	$Pb_3(CO_3)_2(OH)_2$	Gaines et al. (1997)
14	Hydrocerussite	$Pb_3(CO_3)_2(OH)_2$	Cowley (1956)
15	Hydrocerussite	$Pb_3(CO_3)_2(OH)_2$	Martinetto et al. (2002)
16	Kegelite	$Pb_8Al_4Si_8O_{20}(SO_4)_2(CO_3)_4(OH)_8$	Gaines et al. (1997), Dunn et al. (1990)
17	Leadhillite	$Pb_4(SO_4)(CO_3)_2(OH)_2$	Gaines et al. (1997)
18	Leadhillite	$Pb_4(SO_4)(CO_3)_2(OH)_2$	Mineralogy Database (http://webmineral.com/)
19	Leadhillite	$Pb_4(SO_4)(CO_3)_2(OH)_2$	Bindi and Menchetti (2005)
20	Leadhillite	$Pb_4(SO_4)(CO_3)_2(OH)_2$	Giuseppetti et al. (1990)

	Name	Cell Constants							Space Group	$V^{o\#}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		$cm^3\ gfw^{-1}$
11	Dundasite	9.05	16.35	5.61				4	Pbmm	126.35
12	Dundasite	9.08	16.37	5.62				4	Pbmm	125.77
13	Hydrocerussite	5.24		23.74				3	$P3_1m$	113.32
14	Hydrocerussite	9.06		8.27				3	$P3_1m$	118.01
15	Hydrocerussite	5.2465		23.702				3	R-3m	113.42
16	Kegelite	21.04(1)	15.55(1)	8.986(6)		91.0(1)		3	$A2/m_1$ A2, Am	590.07
17	Leadhillite	9.09	11.57	20.74		90.5		8	$P2_1/a$	164.19
18	Leadhillite	9.08	20.76	11.56		89.8		8	$P2_1/a$	164.03
19	Leadhillite	9.0104	20.792	11.59		90.50		8	$P2_1/a$	163.44
20	Leadhillite	9.11	20.82	11.56		90.46		8	P2-1/a	165.05

	Name	Formula	Reference
21	Macphersonite	$Pb_4(SO_4)(CO_3)_2(OH)_2$	Gaines et al. (1997)
22	Macphersonite	$Pb_4(SO_4)(CO_3)_2(OH)_2$	Steele et al. (1998)
23	Nasledovite	$PbMn_3Al_4(CO_3)_4(SO_4)O_5•5(H_2O)$	Gaines et al. (1997)
24	Petterdite	$PbSr_{0.1}Cr_{1.5}Al_{0.4}(CO_3)_{2.1}(OH)_{3.6}•(H_2O)$	Gaines et al. (1997)
25	Petterdite	$PbCr^{III}_2(CO_3)_2(OH)_4•(H_2O)$	Birch et al. (2000)
26	Phosgenite	$Pb_2(CO_3)Cl_2$	Gaines et al. (1997)
27	Phosgenite	$Pb_2(CO_3)Cl_2$	Giuseppetti and Tadini (1974)
28	Plumbonacrite	$Pb_{10}(CO_3)_6O(OH)_6$	Gaines et al. (1997)
29	Plumbonacrite	$Pb_{10}(CO_3)_6O(OH)_6$	Krivovchev and Burns (2000a)
30	Sanromanite	$Na_2CaPb_3(CO_3)_5$	Mineralogy Database (http://webmineral.com/)

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
21	Macphersonite	10.37	23.10	9.35				8	Pcab	**171.85**
22	Macphersonite	9.242	23.050	10.383				8	Pbca	166.50
23	Nasledovite								Triclin	
24	Petterdite	9.079	16.321	5.786				4	Pbnm	129.08
25	Petterdite	9.079(3)	16.321(9)	5.786(7)				4	Pbnm	129.08
26	Phosgenite	8.112	8.112	8.814				4	P4/mbm	87.321
27	Phosgenite	8.160	8.160	8.883				4	P4/mbm	89.049
28	Plumbonacrite	9.076		24.96				3?	hex	357.43
29	Plumbonacrite	9.0921		24.932				3	P6-3cm	358.30
30	Sanromanite	10.5564		6.6446				2	$P6_3mc$	193.09

	Name	Formula	Reference
31	Sanromanite	$Na_2CaPb_3(CO_3)_5$	Schluter et al. (2007)
32	Shannonite	Pb_2OCO_3	Krivovichev and Burns (2000b)
33	Shannonite	Pb_2OCO_3	Roberts et al. (1995)
34	Susannite	$Pb_4(SO_4)(CO_3)_2(OH)_2$	Gaines et al. (1997)
35	Susannite	$Pb_4(SO_4)(CO_3)_2(OH)_2$	Mineralogy Database (http://webmineral.com/)
36	Susannite *	$Pb_4(SO_4)(CO_3)_2(OH)_2$	Bindi and Menchetti (2005)
37	Susannite	$Pb_4(SO_4)(CO_3)_2(OH)_2$	Steele et al. (1999a)
38	Widenmannite	$Pb_2(UO_2)(CO_3)_3$	Gaines et al. (1997)
39	Widenmannite	$Pb_2(UO_2)(CO_3)_3$	Plášil et al. (2010)

	Name	Cell Constants							Space Group	$V_o^{\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
31	Sanromanite	10.570(1)		6.651(1)				2	$P6_3mc$	193.77
32	Shannonite	5.1465	9.014	9.315				5	P2-12-12-1	52.047
33	Shannonite	9.294(3)	9.000(3)	5.133(2)				4	$P2_122_1$ or $P2_12_12_1$	51.713
34	Susannite	9.05		11.54				3	R-3	164.31
35	Susannite	9.05		11.54				3	R-3	164.31
36	Susannite *	9.077		11.611				3	P3	166.31
37	Susannite	9.0718		11.570				3	P3	165.53
38	Widenmannite	8.99	9.36	4.95				2	Pnnm, $Pnm2_1$ or $P22_12_1$	125.42
39	Widenmannite	8.964(4)	9.378(6)	5.007(4)				2	Pnnm, $Pnm2_1$ or $P22_12_1$	126.74

	Name	Formula	Reference
	Synthetic Phases		
40	$Pb_3O_2CO_3$	$Pb_3O_2CO_3$	Krivovichev and Burns (2000c)
41	$NaPb_2(CO_3)_2(OH)$	$NaPb_2(CO_3)_2(OH)$	Belokoneva et al. (2002)
42	$NaPb_2(CO_3)_2(OH)$	$NaPb_2(CO_3)_2(OH)$	Krivovichev and Burns (2000c)

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
	Synthetic Phases									
40	$Pb_3O_2CO_3$	22.194(3)	9.108(1)	5.7405(8)				8	Pnma	87.351
41	$NaPb_2(CO_3)_2(OH)$	5.268(4)		13.48(1)				2	P31c	97.551
42	$NaPb_2(CO_3)_2(OH)$	5.276(1)		13.474(4)				2	P63mc	97.804

*T = 82 C

#Calculated from cell constants, this work

Table 6. Carbonate Minerals containing greater than 10 wt.% Lead*

Name	Formula	Lead, wt.%	gfw	Thermodynamic Data	
				Est.	Meas.
Ashburtonite	$HPb_4Cu^{II}_4Si_4O_{12}(HCO_3)_4(OH)_4Cl$	47.75	1735.88	no	no
Barstowite	$Pb_4(CO_3)Cl_6•(H_2O)$	74.03	1119.54	no	no
Britvinite	$Pb_{7+x}Mg_{4-5}[(Si,Al)_5O_{14}](BO_3)(BO_3,AsO_4)(CO_3)(OH,O)_7(x<0.5)$	66.62	4587.29	no	no
Caledonite	$Pb_5Cu_2(CO_3)(SO_4)_3(OH)_6$	64.21	1613.34	yes	no
Cerussite	$PbCO_3$	77.54	267.21	no	yes
Dundasite	$PbAl_2(CO_3)_2(OH)_4•(H_2O)$	44.35	467.23	no	no
Ferrisurite	$(Pb,Cu)_{2-3}(CO_3)_{1.5-2}(OH,F)_{0.5-1}[(Fe,Al)_2Si_4O_{10}(OH)_2]•n(H_2O)$	38.50	914.93	no	no
Gartrellite	$Pb(Cu,Fe^{II})_2(AsO_4,SO_4)_2(CO_3,H_2O)_{0.7}$	33.39	620.46	no	no
Gysinite-(Nd)	$Pb(Nd,La)(CO_3)_2(OH)•(H_2O)$	41.02	505.15	no	no
Hydrocerussite	$Pb_3(CO_3)_2(OH)_2$	80.14	775.63	no	yes
Kegelite	$Pb_8Al_4Si_8O_{20}(SO_4)_2(CO_3)_4(OH)_8$	57.59	2878.42	no	no
Leadhillite	$Pb_4(SO_4)(CO_3)_2(OH)_2$	76.82	1078.90	yes	no
Macphersonite	$Pb_4(SO_4)(CO_3)_2(OH)_2$	76.82	1078.90	no	no
Nasledovite	$PbMn_3Al_4(CO_3)_4(SO_4)O_5•5(H_2O)$	21.01	986.11	no	no
Petterdite	$PbCr^{III}_2(CO_3)_2(OH)_4•(H_2O)$	40.63	510.01	no	no
Philolithite	$Pb_{12}O_6Mn(Mg,Mn)_2(Mn,Mg)_4(SO_4)(CO_3)_4Cl_4(OH)_{12}$	69.30	3587.70	no	no
Phosgenite	$Pb_2(CO_3)Cl_2$	75.99	545.31	yes	no
Plumbonacrite	$Pb_{10}(CO_3)_6O(OH)_6$	81.25	2550.10	no	yes
Sanromanite	$Na_2CaPb_3(CO_3)_5$	61.68	1007.70	no	no
Schuilingite-(Nd)	$PbCu(Nd,Gd,Sm,Y)(CO_3)_3(OH)•1.5(H_2O)$	29.76	696.16	no	no
Shannonite	Pb_2OCO_3	84.50	490.41	no	yes
Surite	$(Pb,Cu)_{2-3}(CO_3)_{1.52}(OH,F)_{0.51}[(Al,Fe^{III})_2(Si,Al)_4O_{10}(OH)_2]•n(H_2O)$	39.80	937.16	no	no
Susannite	$Pb_4(SO_4)(CO_3)_2(OH)_2$	76.82	1078.90	no	no
Widenmannite	$Pb_2(UO_2)(CO_3)_3$	47.94	864.46	no	no

*Data taken primarily from a compilation given by the Mineralogy Database (http://webmineral.com).

References

Abdul-Samad, F., Thomas, J.H., Williams, P.A., Bideaux, R.A. and Symes, R.F. (1982). Mode of formation of some rare copper(II) and lead(II) minerals from aqueous solution, with particular reference to deposits at Tiger, Arizona. Transition Metal Chemistry, 7, 32-37.

Adami, L.H. and Conway, K.C., 1966. Heats and free energies of formation of anhydrous carbonates of barium, strontium, and lead. U.S. Bureau of Mines Report of Investigations, 6822, 7 p.

Anderson, C.T. (1934). The heat capacities of magnesium, zinc, lead, manganese and iron carbonates at low temperatures1. Journal of the American Chemical Society, 56(4), 849-851.

Antao, S.M. and Hassan, I. (2009). The orthorhombic structure of $CaCO_3$, $SrCO_3$, $PbCO_3$ and $BaCO_3$: Linear structural trends. Canadian Mineralogist, 47, 1245-1255.

Balko, B., Bowen, P., Berger, R.L. and Anderson, K. (1981). Fast stopped-flow microcalorimeter. Journal of Biochemical and Biophysical methods, 4(1), 1-28.

Ball, M.C. and M.J. Casson (1975), Thermal studies on lead(II) salts-I. Stoicheiometry of lead carbonate deocomposition at 1 atm. pressure. Journal of Inorganic and Nuclear Chemistry, 37, p. 2253-2255.

Ball, M.C. and M.J. Casson (1977a), Thermal studies on lead(II) salts-V. Enthalpies of formation of lead(II) oxide carbonates by scanning calorimetry. Journal of Inorganic and Nuclear Chemistry, 39, 1456-1457.

Ball, M.C. and Casson, M.J. (1977b). Thermal studies on lead (II) salts – II: The decomposition of lead hydroxide carbonate, $Pb(OH)_2 \cdot 2PbCO_3$. Journal of Inorganic and Nuclear Chemistry, 39(11), 1949-1951.

Baranova, N.N. (1967). Polarographic study of lead bicarbonate complexes. Russian Journal of Inorganic Chemistry [English translation], 12(6), 1438-1441.

Baranova, N.N. (1968). Composition of lead carbonate complexes and their dissociation constants at *25*º, 250º and 300º C. Geochemistry International, 5(1), 13-20.

Baranova, N.N. (1969). Lead carbonate complexes at 25° and 200°C. Zhurnal Neorganicheskoi Khimii, 14(12), 3257-63. [In Russian]. Also in Russian Journal of Inorganic Chemistry [English translation], 14(12), 1717-1720.

Baranova, N.N. and Barsukov, V.L (1965). Transport of lead by hydrothermal solutions in the form of carbonate complexes. Geochemistry International, 2(5), 802-809.

Barin, I. (1993). Thermochemical Data of Pure Substances VCH Velagsgesellschaft, Weinheim, Germany.

Belokoneva, E.L., Al'-Ama, A.G., Dimitrova, O.V., Kurazhkovskaya, V.S. and Stefanovich, S.Yu. (2002). Synthesis and Crystal Structure of New Carbonate $NaPb_2(CO_3)_2(OH)$. Crystallography Reports, 47(2), 217–222. Translated from Kristallografiya, 47(2), 253-258.

Bilinski, H., Huston, R. and Stumm, W. (1976). Determination of the stability constants of some hydroxo and carbonato complexes of Pb(II), Cu(II), Cd(II), and Zn(II) in dilute solutions by anodic stripping voltammetry and differential pulse polarography. Analytica Chimica Acta, 84, 157-164.

Bilinski, H. and Schindler, P. (1982). Solubility and equilibrium constants of lead in carbonate solutions (25°C, I = 0.3 mol dm^{-3}). Geochimica et Cosmochimica Acta, 46, 921-928.

Bindi, L. and Menchetti, S. (2005). Structural changes accompanying the phase transformation between leadhillite and susannite: a structural study by means of in situ high-temperature single- crystal X-ray diffraction. American Mineralogist, 90, 1641-1647.

Birch, W.D., Kolitsch, U., Witzke, T., Nasdala, L. and Bottrill, R.S. (2000). Petterdite, the Cr-dominant analogue of dundasite, a new mineral species from Dundas, Tasmania, Australia and Callenberg, Saxony, Germany. Canadian Mineralogist, 38, 1467-1476.

Blanc, P., Piantone, P., Lassin, A. and Burnol, A. (2006). ThemoChimie: Selection de constantes thermodynamiques pour les elements majeurs, le plomb et le cadmium. ANDRA report C RP PSTR.07.0014 or BRGM 54902-FR.

Chevrier, G, Giester, G, Heger, G, Jarosch, D, Wildner, M. and Zemann, J. (1992). Neutron single-crystal refinement of cerussite, $PbCO_3$, and comparison with other aragonite-type carbonates. Zeitschrift für Kristallographie 199, 67-74.

Clever, H.L. and Johnston, F.J. (1980). The solubility of some sparingly soluble lead salts: An evaluation of the solubility in water and aqueous electrolyte solution. Journal of Physical and Chemical Reference Data, 9(3), 751-784.

Cocco, G, Fanfani, L, Nunzi, A, and Zanazzi, P.F. (1972). The crystal structure of dundasite. Mineralogical Magazine, 38, 564-569.

Colby, M. and LaCoste L. (1933). The crystal structure of Cerussite. Zeitschrift für Kristallographie, 84, 299-309.

Cooper, M. and Hawthorne, F.C. (1994). The crystal structure of wherryite, $Pb_7Cu_2(SO_4)_4(SiO_4)_2(OH)_2$, a mixed sulfate-silicate with $[^{[6]}M(TO_4)_2\ \phi]$chains. Canadian Mineralogist, 32, 373-380.

Cowley, J.M. (1956). Electron-diffraction study of the structure of basic lead carbonate, $2PbCO_3.Pb(OH)_2$. Acta Crystallographica, 9, 391-396.

Dobrydiev, S.V., Nilova, E.V. and Beskov, V.S. (2005). Calculation of $\Delta_f G^0(298)$ and $\Delta_f H^0(298)$ for sparingly soluble metal carbonates and oxalates in the solid state. Zhurnal Neorganicheskoi Khimii, 50(12), 2015-2018. [In Russian].

Dunn, P.J., Braithwaite, R.S.W. Roberts, A.C. and Ramik, R.A. (1990). Kegelite from Tsumeb, Namibia: A redefinition. American Mineralogist, 75, 702-704.

Dyrssen, D. and Wedborg, M, (1975). Equilibrium calculations of the speciation of elements in sea water. In The Sea (E.D. Goldberg, Ed.), Wiley Interscience, New York, 5, 181-195.

Easley, R.A. and Byrne, R.H. (2011). The ionic strength dependence of lead (II) carbonate complexation in perchlorate media. Geochimica et Cosmochimica Acta, 75(19), 5638-5647.

Ernst, R., Allen, H.E. and Mancy, K.H. (1975). Characterization of trace metal species and measurement of trace metal stability constants by electrochemical techniques. Water Research, 9, 969-979.

Egorov, A. M. and Titova, Z. P. (1962). Solubility products of salts with polyatomic ions as a function of the temperature. Zhurnal Neorganicheskoi Khimii, 7, 275-278. [In Russian]. Eng. trans. p. 141-142.

Faucherre, J. and Bonnaire, Y. (1959). Sur la constitution des carbonates complexes de cuivre et de plomb. Comptes Rendus de l'Academie des Sciences de Paris, 248, 3705-3707.

Ferri, D., Grenthe, I., Hietanen, S. and Salvatore, S. (1987). Studies on metal carbonate equilibria. 18. Lead(II) carbonate complexes in alkaline solutions. Acta Chemica Scandinavica, A 41, 349-354.

Fouillac, A. and Criaud, A. (1984). Carbonate and bicarbonate trace metal complexes: Critical reevaluation of stability constants. Geochemical Journal, 18, 297-303.

Gaines, R.V., Skinner, H.C.W., Foord, E.E., Mason, B., Rosenzweig, A. King, V.T. and Dowty, E. (1997). Dana's New Mineralogy (Eighth edition). John Wiley and Sons, Inc., New York. 1819 p.

Garrels, R.M. (1957). Some free energy values from geologic relations. American Mineralogist, 42(11-2), 780-791.

Garrels, R.M. (1960). Some free energy values from geologic correlations. In Thermodynamics of Geochemical Processes, 122-136. [In Russian]. See Garrels (1957).

Gerasimov, Ya.I., Krestovnikov, A.N. and Shakhov, A.S. (1961). Khimicheskaya termodinamika v tsvetnoi metallurgii. Spravochnoe rukovodstvo. Tom. 2. Termodinamika medi, svintsa, olova, serebra i ikh vazhneishikh soedinenii (Chemical Thermodynamics in Nonferrous Metallurgy. Volume 2. Thermodynamics of Copper, Lead, Tin, Silver, and their Most Important Compounds). 262 p. [In Russian].

Goskhimizdat. (1952). Chemical Reference, vol. 3. [In Russian]. (As cited in Zhuk, 1954).

Grauer, R. (1999). Solubility products of M(II) - carbonates [edited and translated by U. Berner]. Paul Scherrer Institute, Waste Management laboratory, PSI Bericht Nr. 99-04, ISSN 1019-0643, 24 p.

Grisafe, D.A. and White, W.B. (1964). Phase relations in the system PbO-CO_2 and the decomposition of cerussite. American Mineralogist, 49, 1184-1198.

Giuseppetti, G. and Tadini, C. (1974). Reexamination of the crystal structure of phosgenite, $Pb_2Cl_2(CO_3)$. Tschermaks mineralogische und petrographische Mitteilungen, 21, 101-109.

Giuseppetti, G, Mazzi, F. and Tadini, C. (1990). The crystal structure of leadhillite: $Pb_4(SO_4)(CO_3)_2(OH)_2$. Neues Jahrbuch für Mineralogie, Monatshefte 1990, 255-268.

Haehnel, O. (1924). Über die Löslichkeit der Carbonate des Strontiums, des Bariums und der Schwermetalle in Wasser unter hohen Kohlendioxyddrucken sowie über die Eigenschaften solcher Lösungen. Journal für praktische Chemie (Leipzig), 108, 187-193.

Helgeson, H.C. (1969). Thermodynamics of hydrothermal systems at elevated temperatures and pressures. American Journal of Science, 267, 729-804.

Helgeson, H.C., Delany, J.M., Nesbitt, H.W. and Bird, D.K. (1978). Summary and critique of the thermodynamic properties of rock forming minerals. American Journal of Science, 278-A, 229p.

Hem, J.D. (1976). Geochemical controls on lead concentrations in stream water and sediments. Geochimica et Cosmochimica Acta, 40, 599-609.

Hem, J.D. (1978). Redox processes at the surfaces of manganese oxide and their effects on aqueous metal ions. Chemical Geology, 21, 199-218.

Johnston, J. (1915). The solubility-product constant of calcium and magnesium carbonates. Journal of the American Chemical Society, 37(9), 2001-2020.

Karapet'yants, M. Kh. (1953). Khimicheskaya Termodinamika (Chemical Thermodynamics). 2nd Edition. Goshkhimizdat. 611 p. [In Russian].

Karapet'yants, M.Kh. and Karapet'yants, M.L. (1970). Thermodynamic constants of Inorganic and Organic Compounds (trans. by J. Schmorak). Humphrey Science Publishers, Ann Arbor, Michigan. 461 p.

Karpov, I.K., Kashik, S.A. and Pampura, V.D. (1968). Thermodynamic Constants for Calculations in Geochemistry and Petrology. Izdva, Nauka, 143 p. [In Russian].

Kelley, K.K. and Anderson, C.T. (1935). Theoretical metallurgy. IV. Metal carbonates-correlations and applications of thermodynamic properties. U.S Bureau of Mines Bulletin No. 384, 73 p.

Kelley, K.K. (1960). High-Temperature Heat-Content, Heat-Capacity, and Entropy Data for the Elements and Inorganic Compounds. Contributions to the Data on Theoretical Metallurgy XIII. U.S Bureau of Mines Bulletin No. 584. Washington, D.C. U.S Government Printing Office. 232 p.

Kelley, K.K. and King. E.G. (1961). Contribution to the Data on Theoretical Metallurgy. XIV. Entropies of the Elements and Inorganic Compounds. U.S Bureau of Mines Bulletin No. 592, 149 p.

Kireev, V.A. (1964). Acid-base properties of oxides. Zhurnal Fizicheskoi Khimii, 38(8), 1881-1894. [In Russian].

Krishnamurty, K.V. Harris, G.M. and Sastri, V.S. (1970). The chemistry of the metal carbonato complexes. Chemical Reviews, 70(2), 171-197.

Krivovichev, S.V. and Burns, P.C. (2000a). Crystal chemistry of basic lead carbonates. I. Crystal structure of synthetic shannonite, $Pb_2O(CO_3)$. Mineralogical Magazine, 64, 1063-1068.

Krivovichev, S.V. and Burns, P.C. (2000b). Crystal chemistry of basic lead carbonates II. Crystal structure of synthetic `plumbonacrite'. Mineralogical Magazine, 64, 1069-1075.

Krivovichev, S.V. and Burns, P.C. (2000c). Crystal chemistry of basic lead carbonates. III. Crystal structures of $Pb_3O_2(CO_3)$ and $NaPb_2(OH)(CO_3)_2$. Mineralogical Magazine, 64(6), 1077-1087.

Laddha, S.S., Diaz, J.M. and Danckwerts, P.V. (1981). The nitrous oxide analogy: the solubilities of carbon dioxide and nitrous oxide in aqueous solutions of organic compounds. Chemical Engineering Science, 36(1), 228-229. *[Note: This citation in Palmer and Van Eldik (1983) may be in error]*

Landolt-Bornstein. (1923). Physikalisch~chemische Tabellen. Julius Springer, Berlin, vol. 2.

Latimer, W.M. (1952). The Oxidation States of the Elements and their Potentials in Aqueous Solutions. Second edition. Prentice Hall, New York, 392 p.

Long, D.T. and Angino, E.E. (1977). Chemical speciation of Cd, Cu, Pb, and Zn in mixed freshwater, seawater, and brine solutions. Geochimica et Cosmochimica Acta, 41(9), 1183-1191.

Lothenbach B., Ochs M., Wanner H., and Yui M., 1999. Thermodynamic data for the speciation and solubility of Pd, Pb, Sn, Sb, Nb and Bi in aqueous solution. JNC TN8400 99 011.

Lu, J.C. and Chen, K.Y. (1977). Migration of trace metals in interfaces of sea water and polluted surficial sediments. Environmental Science and Technology, 11(2), 174-182.

Marshall, A.L. and Bruzs, B. (1925). Heat of formation of lead carbonate. Journal of Physical Chemistry, 29, 1184-1186.

Martell A.E. and Smith R.M. (1989). Critical Stability Constants, Vol. 3: Other Organic Ligands (2nd printing). Plenum, New York, 495 p.

Martinetto, P, Anne, M., Dooryhee, E., Walter, P. and Tsoucaris, G. (2002). Synthetic hydrocerussite, $2PbCO_3.Pb(OH)_2$ by X-ray powder diffraction. Acta Crystallographica, C58, i82-i84.

Mercy, M.A., Rock, P.A., Casey, W.H. and Mokarram, M.M. (1998). Gibbs energies of formation for hydrocerussite $[Pb(OH)_2 \cdot (PbCO_3)_2(s)]$ and hydrozincite $\{[Zn(OH)_2]_3 \cdot (ZnCO_2(s)\}$ at 298 K and 1 bar from electrochemical cell measurements. American Mineralogist, 83, 739-745.

Millero, F.J. and Hawke, D.J. (1992). Ionic interactions of divalent metals in natural waters. Marine Chemistry, 40, 19-48.

Näsänen, R., Meriläinen, P. and Leppänen, K. (1961). Potentiometric Determination of the solubility product of lead carbonate, Acta Chemica Scandinavica, 15, 913-918.

Näsänen, R., Meriläinen, P. and Havanka, R. (1962). Potentiometric study of a synthesis of phosgenite. Acta Chemica Scandinavica, 16, 1549-1552.

Näsänen, R., Merilainen, P. and Hyle, M. (1963). Solubility product of $Pb_2Cl_2CO_3$. Suomen Kemistilehti B, 36(4), 73-6.

Naumov, G.B., Ryzhenko, B.N. and Khodakovsky, I.L. (1974). Handbook of Thermodynamic Data. Natl. Tech. Inf. Service, 722176A, U.S. Dept. Commerce. 328 p.

Neher-Neumann, E. (1992). Studies on metal carbonate equilibria 24. The hydrogen carbonate and carbonate complexes of lead(II) and cadmium ions in acid solutions and a 3 M $(Na)ClO_4$ ionic medium at 25ºC. Acta Chemica Scandinavica, 46, 231-239.

Palmer, D.A. and van Eldik, R. (1983). The chemistry of metal carbonato and carbon dioxide complexes. Chemical Reviews, 83, 651-731.

Plášil, J., Cejka, J., Sejkora, J., Škácha, P., Goliáš, V., Jarka, P., Laufek, F., Jehlicka, J., Nemec, I. and Strnad, L. (2010). Widenmannite, a rare uranyl lead carbonate: occurrence, formation and characterization. Mineralogical Magazine, 74, 97-110.

Pourbaix, M. (1960). Standard free energies of formation at 25ºC. CEBELCOR Rapt. 684, Belgian Center for the Study of Corrosion, Brussels, 57 p.

Powell, K.J., Brown, P.L., Byrne, R.H., Gajda, T., Hefter, G., Leuz, A.-K., Sjöberg, S. and Wanner, H. (2009). Chemical speciation of environmentally significant metals with inorganic ligands. Part 3: The Pb^{2+} + OH^-, Cl^-, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-} systems (IUPAC Technical Report). Pure and Applied Chemistry, 81(12), 2425-2476.

Radha, A.V. and Navrotsky, A. (2013). Thermodynamics of carbonates. Reviews in Mineralogy and Geochemistry, 77(1), 73-121.

Randall, M. and Spencer, H.M. (1928). Solubility of lead monoxide and basic lead carbonate in alkaline solutions. Journal of the American Chemical Society, 50, 1572-1583.

Rickard D.T. and Nriagu J.O. (1978). Aqueous environmental chemistry of lead. In The biochemistry of lead in the environment. Part A. Ecological Cycles (J.O. Nriagu, Ed), Elsevier/North-Holland Biomedical Press, 219-284.

Roberts, A.C., Stirling, J.A.R., Carpenter, G.J.C., Criddle, A.J., Jones, G.C., Birkett, T.C. and Birch, W.D. (1995). Shannonite, Pb_2OCO_3, a new mineral from the Reef mine, Graham County, Arizona, USA. Mineralogical Magazine, 59, 305-310.

Robie, R.A. (1962). Thermodynamic properties of minerals. U.S. Geological Survey Open File Report TEI-816. 31 p.

Robie, R.A. (1966). Section 20: Thermodynamic properties of minerals. Handbook of Physical Constants, Geological Society of America Memoirs, 97, 437-458.

Robie, R.A. and Hemingway, B.S. (1995). Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 Pascals) pressure and at higher temperatures. U.S. Geological Survey Bulletin No. 2131, 461 p.

Robie, R.A., Hemingway B.S. and Fisher J.R. (1978). Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 Pa) pressure and at higher temperatures. U.S. Geological Survey Bulletin No. 1452. U.S. Government Printing Office, Washington, DC. 456 p.

Robie, R.A., Hemingway, B.S. and Fisher, J.R. (1979). Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 Pa) pressure and at higher temperatures. U.S. Geological Survey Bulletin No. 1452. (Reprinted with corrections). U.S. Government Printing Office, Washington, DC. 456 p.

Rossini F.D., Wagman D.D., Evans W.H., Levine S. and Jaffe I. (1952). Selected values of chemical tbermodynamical properties. National Bureau of Standards Circular 500. 1268 p., Washington, D.C.

Ruchhoft, C.C. and Kachmar, J.F. (1942). Study of solubility of two lead salts in dilute solutions with special reference to the lead hazard in drinking water. Journal of the American Water Works Association, 34(1), 85-93.

Ryabin, V.A., Ostroumov, M.A. and Svit, T.F. (1977). Thermodynamic Properties of Substances: Handbook (Termodinamicheskie Svoistva Veshchestv: Spravochnik). Khimiya, Leningr. Otd. Leningrad, USSR 389 p. [In Russian].

Saegusa, F. (1950). Thermodynamic studies on carbonates. Part I. Thermodynamic studies of cadmium, zinc, lead, mercurous, and thallous carbonates. Science Reports. Tohoku University, First Series, 34(1), 55-65.

Sangameshwar S.R. and Barnes H.L. (1983). Supergene processes in zinc lead silver sulfide ores in carbonates. Economic Geology, 78, 1379-1397.

Schluter, J., Malcherek, T. and Pohl, D. (2007). Sanromanite, from the Santa Rosa mine, Atacama desert, Chile, a new mineral of the burbankite group. Neues Jahrbuch für Mineralogie, Abhandlungen, 183, 117-121.

Schofield, P.F., Wilson, C.C., Knight, K.S. and Kirk, C.A. (2009). Proton location and hydrogen bonding in the hydrous lead copper sulfates linarite, $PbCu(SO_4)(OH)_2$, and caledonite, $Pb_5Cu_2(SO_4)_3CO_3(OH)_6$. Canadian Mineralogist, 47, 649-662.

Shirai, H. (1961). The reduction waves of copper and lead ions in potassium hydrogen carbonate solution. Nippon Kagaku Zasshi, 82, 1179-1182. [Cited in Chemical Abstracts].

Schrock, M.R. (1980). Response of lead solubility to dissolved carbonate in drinking water. Journal of the American Water Works Association, 72(12), 695-704.

Sipos, L. (1976). Private communication to Bilinski et al. (1976).

Sipos, L., Raspor, B., Nurnberg, H.W. and Pytkowicz, R.M. (1980). Interaction of metal complexes with coulombic ion-pairs in aqueous media of high salinity. Marine Chemistry, 9, 37-47.

Smith, R.M. and Martell, A.E. (1976). Critical Stability Constants, Volume 4, Inorganic Complexes. Plenum Press: New York.

Steele, I.M., Pluth, J.J. and Livingstone, A. (1998). Crystal structure of macphersonite ($Pb_4SO_4(CO_3)_2(OH)_2$): comparison with leadhillite. Mineralogical Magazine, 62, 451-459.

Steele, I.M., Pluth, J.J. and Livingstone, A. (1999a). Crystal structure of susannite, $Pb_4SO_4(CO_3)_2(OH)_2$: a trimorph with macphersonite and leadhillite. European Journal of Mineralogy, 11, 493-499.

Steele, I.M., Pluth, J.J. and Stanley, CJ. (1999b). Crystal structure of barstowite ($3PbCl_2PbCO_3H_2O$). Mineralogical Magazine, 63, 901-907.

Stumm, W. and Brauner, P.A. (1975). Chemical Oceanography, (J.P. Riley and G. Skirrow, Eds.). 1, 173-239.

Stern, K.H. (2000). High Temperature Properties and Thermal Decomposition of Inorganic Salts with Oxyanions. 256 p. CRC Press LLC, 2000 N.W. Corporate Blvd., Boca Raton Florida 33431.

Taylor, P. and Lopata, V.J. (1984). Stability and solubility relationships between some solids in the system $PbO-CO_2-H_2O$. Canadian Journal of Chemistry, 62, 395-402.

Turner, D.R., Whitfield, M. and Dickson, A.G. (1981). The equilibrium speciation of dissolved components in freshwater and seawater at 25°C and 1 atm pressure. Geochimica et Cosmochimica Acta, 45, 855-881.

Uggla, R. (1959). Corrosion and passive states of zinc, lead, and tin in the system water-oxygen-nitrogen-carbon dioxide. Annales Academiae Scientiarum Fennicae, Ser. A, 97(2), 74 p.

Van Genderen, A.C.G. and Van der Weijden, C.H. (1984). Prediction of Gibbs energies of formation and stability constants of some secondary uranium minerals containing the uranyl group. Uranium, 1(3), 249-256.

Wagman, D.D., Evans, W.H., Parker, V.B., Halow, L., Bailey, S.M. Schumm, R.H., and Churney, K.L. (1968). National Bureau of Standards Technical Note 270 Series, 270-3 January 1968.

Wagman, D.D., Evans, W.H., Parker, V.B., Schumm, R.H., Halow, I., Bailey, S.M., Churney, K.L. and Nuttall, R.L. (1982). The NBS Tables of Chemical Thermodynamic Properties: Selected Values for Inorganic and C1 and C2 Organic Substances in SI Units: American Chemical Society and the American Institute of Physics for the National Bureau of Standards (Journal of Physical Chemical Reference Data, 11, supp. 2, 392 p.).

Whitfield, M. and Turner, D.R. (1980). Theoretical studies of the chemical speciation of lead in seawater. In Lead in the Marine Environment, (M. Branica and Z. Konrad, Eds.), 109-148, Pergamon, New York.

Wilcox. D.E. and Bromley, L.A. (1963). Computer Estimation of heat and free energy for simple inorganic compounds. Industrial and Engineering Chemistry, 55(7), 32-39.

Woods, T.L. and Garrels, R.M. (1987). Thermodynamic Values at Low Temperature for Natural Inorganic Materials. An Uncritical Summary. Oxford University Press. 242 p. plus references.

Woosley, R.J. and Millero, F.J. (2013). Pitzer model for the speciation of lead chloride and carbonate complexes in natural waters. Marine Chemistry, 149, 1-7.

Yamaguchi, J., Sawada, Y., Sakurai, O., Uematsu, K., Mizutani, N. and Kato, M. (1980). Thermal decomposition of cerussite ($PbCO_3$) in carbon diosxide atmosphere (0-50 atm). Thermochimica Acta, 35, 307-313.

Yoder, C.H. and Rowand, J.P. (2006). Application of the simple salt lattice energy approximation to the solubility of minerals. American Mineralogist, 91(5-6), 747-752.

Yoder, C.H., Gotlieb, N.R. and Rowand, A.L. (2010). The relative stability of stoichiometrically related natural and synthetic double salts. American Mineralogist, 95(1), 47-51.

Zhuk, N.P. (1954). Thermodynamic constants of sulfates, carbonates, chromates, bromates, iodates, oxalates, and other salts slightly soluble in water. Zhurnal Fizicheskoi Khimii, 28, 1690-1697. [In Russian].

Zirino, A., and Yamamoto, S. (1972). A pH-dependent model for the chemical speciation of copper, zinc, cadmium, and lead in seawater. Limnology and Oceanography, 17, 661-671.

MANGANESE

Table 1. Association Constants for Aqueous Carbonate Complexes in the System MnO/Mn_2O_3 -CO_2-H_2O

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
$Mn^{2+} + CO_3^{2-} = MnCO_3(aq)$	4.90	-	$I = 0$	Palmer and van Eldik (1983)	Zirino and Yamamoto (1972)
	6.31		Estimate		Mattigod and Sposito (1977)
	4.4	-	Estimated rom linear free energy relationship with oxalate complexes	Morgan (2005)	Langmuir (1979)
	4.10	-		Millero and Hawke (1992)	Turner et al. (1981)
	4.90	-		Nordstrom et al. (1990),	Palmer and van Eldik (1983)
	4.10	1.88	Estimate		Fouillac and Criaud (1984)
	3.54 ± 0.19	-	EMF, 3 *M* $NaClO_4$		Neher-Neumann (1994)
	4.70 ± 0.03	-	EMF, $I = 0$		Neher-Neumann (1994)
	4.97 ± 0.32		$I = 0$		Wolfram and Krupp (1996)
$Mn^{2+} + 2CO_3^{2-} = Mn(CO_3)_2^{2-}$	8.99		Estimate		Mattigod and Sposito (1977)
	11.61*	-		Millero and Hawke (1992)	Lesht and Bauman (1978)
	5.7	-	Estimated from linear free energy relationship with oxalate complexes	Morgan (2005)	Langmuir (1979)
	5.7 ± 0.3	-	1 *M* K_2CO_3		Fattahi et al. (1999)
$Mn^{2+} + CO_3^{2-} + H^+ = MnHCO_3^+$	13.8*	-	EMF	Lesht and Bauman (1978)	Näsänen (1942)
	12.13*	-			Hem (1963a)
	12.11*	-		Michard and Faucherre (1964)	Hem (1963a)
	12.13 ± 0.12*	-	EMF	Lesht and Bauman (1978)	Hem (1963a)
	12.93 ± 0.2*	-	$I = 4 \times 10^{-3} – 8 \times 10^{-2}$ *M* $NaHCO_3$. T not given		Michard and Faucherre (1964)

Table 1. Association Constants for Aqueous Carbonate Complexes in the System MnO/Mn_2O_3-CO_2-H_2O (Continued)

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	12.26 ± 0.12*	-	EMF	Lesht and Bauman (1978)	Morgan (1967)
	12.28*	-		Nordstrom et al. (1990),	Morgan (1967)
	11.60 ± 0.05*	-	EMF.		Lesht and Bauman (1978)
	12.28	-8.21	Estimate		Fouillac and Criaud (1984)
	11.09 ± 0.08*	-	EMF, I = 0		Neher-Neumann (1994)
	11.6	-		Morgan (2005)	Stumm and Morgan (1996)
$Mn^{2+} + HCO_3^- = MnHCO_3^+$	3.52	-	I = 0.29		Näsänen (1942)
	3.52	-	I = 0.29	Michard and Faucherre (1964)	Näsänen (1942)
	3.48			Lesht and Bauman (1978)	Näsänen (1942)
	1.80	-	Sol.	Krishnamurty et al. (1970)	Hem (1963a)
	1.80			Lesht and Bauman (1978)	Hem (1963b)
	1.95			Mattigod and Sposito (1977)	Morgan (1967)
	1.93			Lesht and Bauman (1978)	Morgan (1967)
	0.45 ± 0.05		3 M $NaClO_4$		Gamsjäger et al. (1970)
	1.95		I = 0	Palmer and van Eldik (1983)	Zirino and Yamamoto (1972)
	1.80		I = 0	Palmer and van Eldik (1983)	Smith and Martell (1976)
	1.27 ± 0.03	-	I = ?	Johnson and Bauman (1978)	Lesht (1977)
	1.95			McBride (1979)	Mattigod and Sposito (1977)
	1.261 ± 0.019		5°C		Lesht and Bauman (1978)
	1.242 ± 0.010		10°C		Lesht and Bauman (1978)
	1.235 ± 0.003		15°C		Lesht and Bauman (1978)
	1.275 ± 0.004		25°C		Lesht and Bauman (1978)
	1.330 ± 0.009		40°C		Lesht and Bauman (1978)
	1.385 ± 0.015		55°C		Lesht and Bauman (1978)

Table 1. Association Constants for Aqueous Carbonate Complexes in the System MnO/Mn_2O_3-CO_2-H_2O (Continued)

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	1.27	4.1		Palmer and van Eldik (1983)	Lesht and Bauman (1978)
	1.28			Palmer and van Eldik (1983)	Bauman (1981)
	1.04				Sychev et al. (1981)
	1.04			Palmer and van Eldik (1983)	Sychev et al. (1981)
	0.32 ± 0.08	-	EMF, 3 *M* $NaClO_4$		Neher-Neumann (1994)
	2.2 ± 0.32		*I* = 0		Wolfram and Krupp (1996)
$MnHCO_3^+ + HCO_3^- = Mn(HCO_3)_2^{2+}$	0.57				Sychev et al. (1981)
	0.57			Palmer and van Eldik (1983)	Sychev et al. (1981)
$Mn^{2+} + CO_3^{2-} + OH^- = MnOHCO_3^-$	8.22 ± 0.41	-	90°C, *I* = 0		Wolfram and Krupp (1996)
$Mn^{2+} + CO_3^{2-} + H_2O = MnOHCO_3^- + H^+$	-6.1	-	Extrapolated from higher-temperature data	Morgan (2005)	Wolfram and Krupp (1996)

(1) At standard state (25°C, 1 atm, *I* = 0), unless otherwise noted.

* Corrected using bicarbonate dissociation equation from PHREEQC

Table 2. Solubility Constants of Solid Carbonates in the System MnO/Mn_2O_3-CO_2-H_2O

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
Minerals					
Mn(II)					
Kutnohorite					
$MnCa(CO_3)_2(cr) = Mn^{2+} + Ca^{2+} + CO_3^{2-}$	-19.36	-	From Fig. 3 in ref. Sol./pH, contains 2.21 wt.% Mg and 0.50 wt.% Fe.		Garrels et al. (1960)
	-19.52	-	Estimate		Yoder and Rowand (2006)
Rhodocrosite					
$MnCO_3(cr) = Mn^{2+} + CO_3^{2-}$ *precipitated*	-10.06			Latimer (1952)	Ageno and Valla (1911), Mellor (1932)
			18°C. Solubility = 0.04% and 0.08% at $P(CO_2)$ = 1 and 56 atm., respectively		Haehnel (1924)
	-10.056	-	Temperature not specified.		Ruff and Ascher (1930)
	-9.297	-	Review. No correction for activity coefficients		Kelley and Anderson (1935)
	-12.72	-	25°C, I = 0		Näsänen (1942)
	-9.30	-		Zhuk (1954)	Goskhimizdat (1952)
	-10.06		Not reported	Jensen et al. (2002)	Latimer (1952)
	-11.08		From Fig. 3 in ref. Sol./pH		Garrels et al. (1960)
	-10.34	-	From Fig. 3 in ref. Sol./pH		Garrels et al. (1960)
	-11.13	-5.98	See note	Nordstrom et al. (1990)	Garrels et al. (1960)
	-10.39	-	See note	Nordstrom et al. (1990),	Garrels et al. (1960)
	-10.30	-		Murray et al. (1978)	Morgan (1967)
	-10.42		Resuspension of dry crystals	Jensen et al. (2002)	Morgan (1967)
	-10.4		I = 0	Palmer and van Eldik (1983)	Sillen and Martell (1967)
	-9.3			Palmer and van Eldik (1983)	Smith and Martell (1976)
	-10.0	-	Calculated from DG data	Emerson (1976)	Berner (1967)
dried crystals	-8.99	-	Of $MnCO_3$ component in $(Mn_{0.89}Ca_{0.15}Mg_{0.05}CO_3$ in Baltic seawater. T not specified.		Suess (1979)

Table 2. Solubility Constants of Solid Carbonates in the System MnO/Mn_2O_3-CO_2-H_2O (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	-10.58 ± 0.01		I = 0		Johnson (1982)
	-10.60		Resuspension of dry crystals	Jensen et al. (2002)	Johnson (1982)
			Solubility in 5-8 *m* LiCl(aq), 250-400°C and 7 m (LiCl + NH_4Cl)(aq)		Egorov (1985)
	-11.24	6.1 ± 8.5	25°C, I = 0, based on soly in seawater		Wartel et al. (1990)
	-9.78 ± 0.04		Sol, 3 *M* $NaClO_4$		Néher-Neumann (1994)
	-10.76		Resuspension of crystals	Jensen et al. (2002)	Néher-Neumann (1994)
	-12.19 ± 0.26		I = 0		Wolfram and Krupp (1996)
	-12.19		Resuspension of crystal cleavages	Jensen et al. (2002)	Wolfram and Krupp (1996)
	-10.30		Resuspension of freeze dried crystals	Jensen et al. (2002)	Sternbeck (1997)
	-9.47		Precipitation from supersaturated solutions	Jensen et al. (2002)	McBeath et al. (1998)
	-9.68		Sol, I = 3		Fattahi et al. (1999)
	-11.0 ± 0.2	-	Literature review		Grauer (1999)
	-11.39 ± 0.14	-	Dried crystals		Jensen et al. (2002)
	-12.51 ± 0.07		Wet crystals		Jensen et al. (2002)
	-11.65 ± 0.14		From supersaturated solution		Jensen et al. (2002)
$MnCO_3(s) + 2H+ = Mn^{2+} + CO_2 + H_2O$	8.74		25°C, dilute solution	Gamsjäger et al. (1970)	Ageno et al. (1911)
	8.78		18°C, dilute solution	Gamsjäger et al. (1970)	Haehnel (1924)
	8.09		T = ?	Gamsjäger et al. (1970)	Ruff and Ascher (1930)
	7.81		ppt, 25°C, I = 0	Gamsjäger et al. (1970)	Garrels et al. (1960)
	7.07		Natural, 25°C, I = 0	Gamsjäger et al. (1970)	Garrels et al. (1960)
	7.97 ± 0.04		3 *M* $NaClO_4$,		Gamsjäger et al. (1970)
	8.32		25°C, I = 0	Gamsjäger (1974)	Gamsjäger et al. (1970)
	7.36 ± 0.06		50°C, 1 *M* $NaClO_4$,	Gamsjäger (1985)	Reiterer (1980)

Table 2. Solubility Constants of Solid Carbonates in the System MnO/Mn_2O_3-CO_2-H_2O (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
$MnCO_3(s) + H+ = Mn^{2+} + HCO_3^-$	0.08		25°C, *I* = 0	Wersin et al. (1989)	Stumm and Morgan (1981)
Mn(III)					
Synthetic Phases					
Mn(II)					
Mn(III)					

(1) At standard state (25°C, 1 atm, *I* = 0), unless otherwise noted.

Note: Dh0r from Wagman et al. (1982) and Robie et al. (1984) for solid.

Table 3a. Association Constants of Aqueous Carbonate Complexes in the System MnO/Mn_2O_3-CO_2-H_2O extracted from Databases of Distribution-of-Species Codes

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Database	Source
$Mn^{2+} + CO_3^{2-} = MnCO_3(aq)$	-	-	Minteq (2009)	
			Minteq (2006)	NIST46.4
	4.900	-	Phreeqc (2009)	not cited
	4.9	-	Wateq4f (2005)	not cited
	6.5	-	ThermoChimie v.7.b	#96FAL/REA
			NAGRA/PSI (2001)	
			Data0.YMP.R5	
			Thermoddem (2009)	Sverjensky et al. (1997)
$Mn^{2+} + 2CO_3^{2-} = Mn(CO_3)_2^{2-}$	-	-	Minteq (2009)	
	-	-	Minteq (2006)	
	-	-	Phreeqc (2009)	
	-	-	Wateq4f (2005)	
	-	-	ThermoChimie v.7.b	
	-	-	NAGRA/PSI (2001)	
	-	-	Data0.YMP.R5	
			Thermoddem (2009)	
$Mn^{2+} + CO_3^{2-} + H^+ = MnHCO_3^+$	11.6	0	Minteq (2009)	not cited
	11.629	-10.6	Minteq (2006)	NIST46.4; NIST46.4
	12.279	-	Phreeqc (2009)	not cited
	12.279	-	Wateq4f (2005)	not cited
	11.61	-	ThermoChimie v.7.b	#95CHI
			NAGRA/PSI (2001)	
	10.7706	-	Data0.YMP.R5	Wagman et al. (1982)
			Thermoddem (2009)	Shock and Koretsky (1995)

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Table 3b. Solubility Constants of Solid Carbonates in the System MnO/Mn_2O_3-CO_2-H_2O extracted from Databases of Distribution-of-Species Codes

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Database	Source
Alstonite				
$MnCa(CO_3)_2(s) = Mn^{2+} + Ca^{2+} + CO_3^{2-}$			Data0.YMP.R5	
Mnrytocalcite				
$MnCa(CO_3)_2(s) = Mn^{2+} + Ca^{2+} + CO_3^{2-}$			Data0.YMP.R5	
Rhodocrosite				
$MnCO_3(s) = Mn^{2+} + CO_3^{2-}$	-10.41	-8.699	Minteq (2009)	not cited
	-10.58	-1.98	Minteq (2006)	not cited
	-11.130	-5.983	Phreeqc (2009)	not cited
	-11.13	-5.983	Wateq4f (2005)	not cited
Rhodocrosite(d): $MnCO_3(s) = Mn^{2+} + CO_3^{2-}$	-10.390	-	Wateq4f (2005)	not cited
	-11.13	-5.899	ThermoChimie v.7.b	Pearson et al. (1992)
			NAGRA/PSI (2001)	
	-10.0818	-	Data0.YMP.R5	Helgeson et al. (1978)
	-	-	Thermoddem (2009)	

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Table 3c. Distribution-of-Species Codes: Database References

Database	Reference
Data0.com.VR.R6+	Wolery, T.J. (1994). EQ3NR, Letter report: EQ3/6 version 8.0. Differences from version 7. UCRL-ID-129749. Lawrence Livermore National Laboratory, Livermore, California. USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/LLNL.DAT
Data0.YMP.R5	BSC (Bechtel SAIC Company) (2007). Qualification of Thermodynamic Data for Geochemical Modeling of Mineral–Water Interactions in Dilute Systems. ANL-WIS-GS-000003 REV 01. Las Vegas, Nevada: Bechtel SAIC Company.DOC.20070619.0007.
MinteqA2	HydroGeoLogic, Inc. and Allison Geoscience Consultants, Inc. (1999). MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: User Manual Supplement for Version 4.0, Appendix A: thermodynamic database for MINTEQA2 V4.0, p. 44-74.
Minteq (2009)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/MINTEQ.DAT
Minteq (2006)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/minteq.v4.dat
NAGRA/PSI (2001)	Hummel, W., Berner, U., Curti, E., Pearson, F.J. and Thoenen, T. (2002). Nagra/PSI Chemical Thermodynamic Data Base 01/01. Universal Publishers/uPublish.com, Parkland, Florida. 565 p.
Phreeqc (2009)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/PHREEQC.DAT
ThermoChimie v.7.b	Duro, L., Grivém M. and Giffaut, E. (2010). ThermoChimie, the ANDRA thermodynamic database In Buckau G, Kienzler B, Duro L, Grivé M, Montoya V (eds). 2nd Annual Workshop Proceedings of the Collaborative Project “Redox Phenomena Controlling Systems” (7th EC FP CP Recosy) Larnaca (Cyprus) 16–19 March 2010. Karlsruhe: KIT Scientific Publishing, 275–283.
Thermoddem (2009)	Blanc P., Lassin A. and Piantone P. (2007) THERMODDEM a database devoted to waste minerals. BRGM (Orléans, France). For updates: http://thermoddem.brgm.fr
Wateq4f	Ball, J. W., & Nordstrom, D. K. (1991). User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters. U.S. GEOLOGICAL SURVEY, Open-File Report 91-183, Revised and reprinted - April, 2001. p. 81-94
Wateq4f (2005)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/WATEQ4F.DAT

Table 4a. Thermodynamic properties of Manganese Carbonate Minerals and Synthetic Solid Carbonates: Gibbs Free Energies of Formation

Mineral		$\Delta G^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
Minerals				
Mn(II)				
Holdawayite	$Mn^{II}_6(CO_3)_2(OH)_7(Cl,OH)$			
Kutnohorite	$Ca(Mn^{II},Mg,Fe^{II})(CO_3)_2$	-1950.58		Garrels et al. (1960)
		-1950.6	La Iglesia and Felix (1994)	Garrels et al. (1960)
		-1950.6	Radha and Navrotsky (2013)	Woods and Garrels (1987)
predicted		-1944.7 ± 1.8		La Iglesia and Felix (1994)
disordered	$Ca\ Mn^{II}(CO_3)_2$	-1944.80 ± 3.77		Tareen et al. (1992)
Rhodochrosite	$Mn^{II}CO_3$	-841.03		Kelley and Anderson (1935)
precipitate		-800.02		Kelley and Anderson (1935)
natural		-812.95	Karpov et al. (1968)	Latimer (1952)
precipitate		-812.95	Karapet'yants and Karapet'yants (1970)	Latimer (1952)
		-817.55	Latimer (1952)	Rossini et al. (1952)?
precipitate		-812.95	Latimer (1952)	Rossini et al. (1952)?
		-817.97	Zhuk (1954)	Rossini et al. (1952), Karapet'yants (1953)
natural	$Mn^{II}CO_3$	-817.55	Karpov et al. (1968)	Rossini et al. (1952)
		-817.6	Woods and Garrels (1987)	Rossini et al. (1952)
calculated		-804.58		Zhuk (1954)
natural		-804.58	Karpov et al. (1968)	Zhuk (1954)
		-804.58	Karapet'yants and Karapet'yants (1970)	Zhuk (1954)
precipitate		-811.28	Karapet'yants and Karapet'yants (1970)	Karapet'yants (1955)
		-812.49 ± 4.18	Robie (1962, 1966)	Goldsmith and Graff (1957)
		-866.09	Karapet'yants and Karapet'yants (1970)	Yatsimirskii (1958)
		-818.8		Garrels et al. (1960)

Table 4a. Thermodynamic properties of Manganese Carbonate Minerals and Synthetic Solid Carbonates: Gibbs Free Energies of Formation (Continued)

Mineral		$\Delta G^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
synthetic		-814.6		Garrels et al. (1960)
natural		-818.81		Garrels et al. (1960)
synthetic		-814.62		Garrels et al. (1960)
natural		-818.81	Karpov et al. (1968)	Garrels et al. (1960), (reference 359a not listed)
		-818.8	Woods and Garrels (1987)	Garrels et al. (1960)
		-818.8	La Iglesia and Felix (1994)	Garrels et al. (1960)
		-816.05	Robie (1965),	Kelley (1960)
natural		-59.83(1)	Karpov et al. (1968)	Kireev (1964)
		-58.84 ± 1.26(1)		Robie (1965)
		-816.047 ± 1.381	Robie et al. (1979)	Robie (1965), Garrels et al. (1960)
		-816.05 ± 1.38	Radha and Navrotsky (2013)	Robie (1965), Robie et al. (1978)
natural		-816.72		Wagman et al. (1969)
		-812.16 ± 0.14		Gamsjäger et al. (1970)
		-815.5	Woods and Garrels (1987)	Karpov et al. (1971)
		-815.5	La Iglesia and Felix (1994)	Karpov et al. (1971)
calculated		-816.72	Naumov et al. (1974)	Wagman et al. (1965-1969)
natural		-816.7	Woods and Garrels (1987)	Naumov et al. (1974)
		-817.8	La Iglesia and Felix (1994)	Naumov et al. (1974)
		-811.9	Dobrydiev et al. (2005)	Ryabin et al. (1977)
		-816.068	BSC (2007)	Helgeson et al. (1978)
		-816.1	Woods and Garrels (1987)	Helgeson et al. (1978)
		-816.1	La Iglesia and Felix (1994)	Helgeson et al. (1978)
		-816.0	Woods and Garrels (1987)	Robie et al. (1978)
natural		-816.0	La Iglesia and Felix (1994)	Robie et al. (1979)
		-816.7	Woods and Garrels (1987)	Wagman et al. (1982)
		-816.7	La Iglesia and Felix (1994)	Wagman et al. (1982)
		-815.0	Woods and Garrels (1987)	Sangameshwar and Barnes (1983)
		-815.0	La Iglesia and Felix (1994)	Sangameshwar and Barnes (1983)

Table 4a. Thermodynamic properties of Manganese Carbonate Minerals and Synthetic Solid Carbonates: Gibbs Free Energies of Formation (Continued)

Mineral		$\Delta G^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
natural	$(Mn^{II}_{0.994}Fe_{0.005}Mg_{0.001})CO_3$	-818.1	Woods and Garrels (1987)	Robie et al. (1984)
		-819.1 ± 0.6	Robie and Hemingway (1995),	Robie et al. (1984)
		-219.68	Stern (2000)	Barin (1989)
				Holland and Powell (1990)
		-822.170 ± 0.74		Fazeli et al. (1991)
predicted		-816.5 ± 1.6		La Iglesia and Felix (1994)
		-819.1		Robie and Hemingway (1995)
		-817.22		Holland and Powell (1998)
		-819.548		NAGRA
synthetic		-815.324		NAGRA
Mn(III)				
Synthetic Phases				
Mn(II)				
$CdMn^{II}(CO_3)_2$ *disordered*	$CdMn^{II}(CO_3)_2$	-1490.0 ± 3.0		Tareen et al. (1995)
$Mn(HCO_3)_2$	$Mn^{II}(HCO_3)_2$	-887.01	Karpov et al. (1968)	Latimer (1952)
Mn(III)				

(1) Formation from the oxides

Table 4b. Thermodynamic properties of Manganese Carbonate Minerals and Synthetic Solid Carbonates: Enthalpies of Formation

Mineral		$\Delta H^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
Minerals				
Mn(II)				
Holdawayite	$Mn^{II}_6(CO_3)_2(OH)_7(Cl,OH)$			
Kutnohorite *disordered*	$CaMn^{II}(CO_3)_2$	-2093.46 ± 3.77		Tareen et al. (1992)
Rhodochrosite *crystalline, at constant volume*	$Mn^{II}CO_3$	-920.1 ± 0.4%		Roth (1929)
crystalline, at constant pressure		-916.7 ± 0.4%		Roth (1929)
		-917.97		Kelley and Anderson (1935)
precipitate		-876.55		Kelley and Anderson (1935)
		???		See Roth et al. (1941)
		-894.96	Latimer (1952)	Rossini et al. (1952)?
precipitate		-887.01	Latimer (1952)	Rossini et al. (1952)?
		-894.96	Zhuk (1954)	Rossini et al. (1952), Karapet'yants (1953)
		-894.96	Karpov et al. (1968)	Rossini et al. (1952)
		-895	Woods and Garrels (1987)	Rossini et al. (1952)
		-894.1	La Iglesia and Felix (1994)	Wagman et al. (1982)
		-888.65 ± 3.35	Robie (1962, 1966)	Goldsmith and Graff (1957)
		-889.2 ± 1.3		10???
		-869.4		Yatsimirskii (1958)
		-869.44	Karpov et al. (1968)	Yatsimirskii (1958)
		-869.44	Karapet'yants and Karapet'yants (1970)	Yatsimirskii (1958)
		-916.7	Robie (1965),	Kelley (1960)
		-116.32[(1)]	Karpov et al. (1968)	Kireev (1964)
		-110.54 ± 0.63 [(1)]		Robie (1965)
		-110.54[(1)]	Karpov et al. (1968)	Robie (1965)
		-889.270 ± 1.213	Robie et al. (1979)	Robie (1965), Garrels et al. (1960)

Table 4b. Thermodynamic properties of Manganese Carbonate Minerals and Synthetic Solid Carbonates: Enthalpies of Formation (Continued)

Mineral		$\Delta H^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
		-889.27 ± 1.21	Radha and Navrotsky (2013)	Robie (1965), Garrels et al. (1960)
natural		-894.12		Wagman et al. (1969)
synthetic		-883.24		Wagman et al. (1969)
		-894.12	Naumov et al. (1974)	Wagman et al. (1965-1969)
		-888.6	Woods and Garrels (1987)	Karpov et al. (1971)
		-894.1	Woods and Garrels (1987)	Naumov et al. (1974)
		-894.1	La Iglesia and Felix (1994)	Naumov et al. (1974), Sangameshwar and Barnes (1983)
		-916.7	Dobrydiev et al. (2005)	Ryabin et al. (1977)
synthetic				
		-889.3	Woods and Garrels (1987)	Robie et al. (1978)
		-889.3	La Iglesia and Felix (1994)	Robie et al. (1978),
		-889.2	Woods and Garrels (1987)	Helgeson et al. (1978)
		-889.2	La Iglesia and Felix (1994)	Helgeson et al. (1978)
		-894.1	Woods and Garrels (1987)	Wagman et al. (1982)
		-889.3	Woods and Garrels (1987)	Sangameshwar and Barnes (1983)
	$(Mn^{II}_{0.994}Fe_{0.005}Mg_{0.001})CO_3$	-891.9	Woods and Garrels (1987)	Robie et al. (1984)
		-892.9 ± 0.5	Robie and Hemingway (1995),	Robie et al. (1984)
		-894.10	Stern (2000)	Barin (1989)
		-891.38 ± 1.07		Holland and Powell (1990)
		-894.382 ± 0.74		Fazeli et al. (1991)
predicted		-891.7 ± 2.3		La Iglesia and Felix (1994)
		-892.9		Robie and Hemingway (1995)
		-891.06 ± 0.66		Holland and Powell (1998)
		-889.188		BSC (2007)
		-890.081		NAGRA
		-896.064		NAGRA

Table 4b. Thermodynamic properties of Manganese Carbonate Minerals and Synthetic Solid Carbonates: Enthalpies of Formation (Continued)

Mineral		$\Delta H^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
Mn(III)				
Synthetic Phases				
Mn(II)				
$CdMn^{II}(CO_3)_2$ *disordered*	$CdMn^{II}(CO_3)_2$	-1641.5 ± 3.0		Tareen et al. (1995)
$Mn(HCO_3)_2$	$Mn^{II}(HCO_3)_2$	-1013.36	Karpov et al. (1968)	Rossini et al. (1952)
		-1615.02 ± 62.76	Estimated value of fictive compound	Wilcox and Bromley (1963)
		-1615.02	Karapet'yants and Karapet'yants (1970)	Wilcox and Bromley (1963)
Mn(III)				

(1) Formation from the oxides

Table 4c. Thermodynamic properties of Manganese Carbonate Minerals and Synthetic Solid Carbonates: Entropies

Mineral		$S^0_{P_r,T_r}$ J K^{-1} gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
Minerals				
Mn(II)				
Holdawayite	$Mn^{II}_6(CO_3)_2(OH)_7(Cl,OH)$			
Kutnohorite *disordered*	$Ca\ Mn^{II}(CO_3)_2$			Tareen et al. (1992)
Rhodochrosite *graphical*	$Mn^{II}CO_3$	85.8 ± 1.3		Anderson (1934)
calculated		84.9		Anderson (1934)
		85.77 ± 1.26	Kelley and King (1961)	Anderson (1934)
		100.00	Karpov et al. (1968)	Latimer (1952)
precipitate		99.58	Karapet'yants and Karapet'yants (1970)	Latimer (1952)
		85.77	Latimer (1952)	Rossini et al. (1952)?
precipitate		99.58	Latimer (1952)	Rossini et al. (1952)?
		85.77	Karpov et al. (1968)	Rossini et al. (1952)
		85.77	Zhuk (1954)	Rossini et al. (1952), Karapet'yants (1953)
calculated		41.84		Zhuk (1954)
		100.00 ± 2.1	Robie (1965),	Kelley (1960)
		100.00 ± 2.09	Robie (1962, 1966), corrected for magnetic contribution	Kelley and King (1961)
		85.77 ± 1.26	Karpov et al. (1968)	Kelley and King (1961)
		112.9		Kostryukov and Kalinkina (1964)
		112.9	Karapet'yants and Karapet'yants (1970)	Kostryukov and Kalinkina (1964)
		100.0 ± 2.09		Robie (1965)
		100.0 ± 2.1	Robie et al. (1979)	Robie (1965)
natural		85.77		Wagman et al. (1969)
		85.77	Naumov et al. (1974)	Wagman et al. (1965-1969)
		85.8	Woods and Garrels (1987)	Naumov et al. (1974)
		100.0	Woods and Garrels (1987)	Robie et al. (1978)
		100.0	Woods and Garrels (1987)	Helgeson et al. (1978)

4c. Thermodynamic properties of Manganese Carbonate Minerals and Synthetic Solid Carbonates: Entropies (Continued)

Mineral		$S^0_{P_r,T_r}$ J/gfw.K^{-1}	Secondary Reference	Primary Reference
Name	Formula			
		85.8	Woods and Garrels (1987)	Wagman et al. (1982)
	$(Mn^{II}_{0.994}Fe_{0.005}Mg_{0.001})CO_3$	98.03	Woods and Garrels (1987)	Robie et al. (1984)
		98.0 ± 0.1	Robie and Hemingway (1995),	Robie et al. (1984)
		85.80	Stern (2000)	Barin (1989)
		98.00		Holland and Powell (1990)
		98.03		Robie and Hemingway (1995)
		98.00		Holland and Powell (1998)
		99.998		EQ3/6
				NAGRA
				NAGRA
Mn(III)				
Synthetic Phases				
Mn(II)				
$Mn(HCO_3)_2$	$Mn^{II}(HCO_3)_2$	160.25	Karpov et al. (1968)	Latimer (1952)
Mn(III)				

Table 5. Crystallographic Properties of Manganese Carbonate Minerals and Synthetic Solid Carbonates

	Name	Formula	Reference
	Minerals		
	Mn(II)		
1	Armangite	$Mn^{II}_{26}[As_6(OH)_4O_{14}][As_6O_{18}]_2[CO_3]$	Gaines et al. (1997), Moore and Araki (1979)
2	Armangite	$Mn^{II}_{26}[As_6(OH)_4O_{14}][As_6O_{18}]_2[CO_3]$	Gaines et al. (1997)
3	Charmarite-2H	$Mn^{II}_4Al_2(CO_3)(OH)_{12}•3(H_2O)$	Gaines et al. (1997)
4	Charmarite-2H	$Mn^{II}_4Al_2(CO_3)(OH)_{12}•3(H_2O)$	Chao and Gault (1997)
5	Charmarite-3T	$Mn^{II}_4Al_2(CO_3)(OH)_{12}•3(H_2O)$	Gaines et al. (1997)
6	Charmarite-3T	$Mn^{II}_4Al_2(CO_3)(OH)_{12}•3(H_2O)$	Chao and Gault (1997)
7	Hauckite	$Mg_{14}Mn^{II}_{10}Zn_{18}Fe^{III}_3(SO_4)_4(CO_3)_2(OH)_{81}$	Gaines et al. (1997)
8	Hauckite	$(Mg,Mn^{II})_{24}Zn_{18}Fe^{III}_3(SO_4)_4(CO_3)_2(OH)_{81}$	Dunn et al. (1980)
9	Holdawayite	$Mn^{II}_6(CO_3)_2(OH)_7(Cl,OH)$	Gaines et al. (1997), Peacor and Rouse (1988)
10	Kutnohorite	$Ca(Mn^{II}_{0.6}Mg_{0.3}Fe^{II}_{0.1})(CO_3)_2$	Mineralogy Database (http://webmineral.com/)

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
	Minerals									
	Mn(II)									
1	Armangite	13.491(2)		8.855(1)				1	P-3	840.54
2	Armangite	13.491		8.855				1	P-3	840.54
3	Charmarite-2H	10.985		15.10				4	$P6_322$	237.57
4	Charmarite-2H	10.985(5)		15.10(2)				4	$P6_322$	237.57
5	Charmarite-3T	10.9885(?)		22.63				6	$P3_112$ or $P3_212$	237.36
6	Charmarite-3T	10.985(3)		22.63(3)				6	$P3_112$ or $P3_212$	237.36
7	Hauckite	9.17		30.21				1	P6/mmm	1324.9
8	Hauckite	9.17(4)		30.21(9)				1	P6/mmm	1324.9
9	Holdawayite	23.437	3.314	16.618		111.15		4	C2/m	181.24
10	Kutnohorite	4.85		16.34				3	R-3	66.818

	Name	Formula	Reference
11	Kutnohorite	$CaMn^{II}(CO_3)_2$	Gaines et al. (1997)
12	Kutnohorite (ord)	$CaMn^{II}(CO_3)_2$	Peacor et al,. (1987)
13	Kutnohorite (disord)	$(Ca_{0.8}Mg_{0.2})(Mn^{II}_{0.7}Ca_{0.3})(CO_3)_2$	Peacor et al,. (1987)
14	Loseyite	$(Mn^{II}_{3.5}Zn_{3.0}Mg_{0.5})(CO_3)_2(OH)_{10}$	Hill (1981)
15	Loseyite	$(Mn^{II}_{0.75}Zn_{0.25})_7(CO_3)_2(OH)_{10}$	Gaines et al. (1997)
16	Nasledovite	$PbMn^{II}_3Al_4(CO_3)_4(SO_4)O_5•5(H_2O)$	Gaines et al. (1997)
17	Rhodochrosite	$Mn^{II}CO_3$	Graf (1961)
18	Rhodochrosite	$Mn^{II}CO_3$	Mineralogy Database (http://webmineral.com/)
19	Rhodochrosite	$Mn^{II}CO_3$	Maslen et al. (1995)
20	Rhodochrosite	$Mn^{II}CO_3$	Maslen et al. (1995)
21	Sidorenkite	$Na_3Mn^{II}(PO_4)(CO_3)$	Gaines et al. (1997)
22	Sidorenkite	$Na_3Mn^{II}(PO_4)(CO_3)$	Kurova et al. (1987)

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
11	Kutnohorite	4.915		16.639				3	R-3	69.877
12	Kutnohorite (ord)	4.8732(8)		16.349(6)				3	R-3	67.496
13	Kutnohorite (disord)	4.894(1)		16.50(2)				3	R-3	68.702
14	Loseyite	16.408(7)	5.540(3)	15.150(4)		95.48(3)		4	A2/a	206.39
15	Loseyite	16.23	5.51	14.95		95.37		4	A2/a	200.40
16	Nasledovite									
17	Rhodochrosite	4.7771		15.664				6	R3c	31.071
18	Rhodochrosite	4.777		15.67				6	R3c	31.082
19	Rhodochrosite	4.773		15.642				6	R3c	30.975
20	Rhodochrosite	4.772		15.637				6	R3c	30.952
21	Sidorenkite	8.979	6.729	5.150		90.10		2	P21/m	93.693
22	Sidorenkite	8.997	6.741	5.163		90.16		2	P21/m	94.285

	Name	Formula	Reference
	Mn(III)		
23	Desautelsite	$Mg_6Mn^{III}_2(CO_3)(OH)_{16}•4(H_2O)$	Dunn et al. (1979)
24	Desautelsite	$Mg_6Mn^{III}_2(CO_3)(OH)_{16}•4(H_2O)$	Rmiths ID: R060303.9 Mineralogy Database (http://webmineral.com/)
25	Desautelsite	$Mg_6Mn^{III}_2(CO_3)(OH)_{16}•4(H_2O)$	Gaines et al. (1997)
26	Gaudefroyite	$Ca_4Mn^{III}_{2.5}(BO_3)_3(CO_3)O_{2.25}(OH)_{0.75}$	Gaines et al. (1997)
27	Gaudefroyite	$Ca_8Mn^{III}_6[(BO_3)_6(CO_3)_2O_6$	Antao and Hassan (2008)
28	Sailaufite	$Ca_2Mn^{III}_3O_2(AsO_4)_2(CO_3)•3(H_2O)$	Gaines et al. (1997)
29	Sailaufite	$Ca_2Mn^{III}_3O_2(AsO_4)_2(CO_3)•3(H_2O)$	Wildner et al. (2003)

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
	Mn(III)									
23	Desautelsite	3.II4(I)		23.39(2)				3/8	R3m or R-3m	315.44
24	Desautelsite	3.124(4)		23.54(2)				3/8	hexag	319.51
25	Desautelsite	6.23		46.78				3	R-3m	315.64
26	Gaudefroyite	10.589		5.891				2	$P6_3$	172.25
27	Gaudefroyite	10.60791(2)		5.88603(1)				1	$P6_3m$	345.43
28	Sailaufite	11.253	19.628	8.932		100.05		6	Cm	194.26
29	Sailaufite	11.253	19.628	8.932		100.05		6	Cm	194.26

	Name	Formula	Reference
	Synthetic Phases		
	Mn(II)		
30	$CaMn(CO_3)_2$	$CaMn^{II}(CO_3)_2$	Graf (1961)
	Mn(III)		
31			

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
	Synthetic Phases									
	Mn(II)									
30	$CaMn(CO_3)_2$	4.8797		16.367				3	R3c	67.751
	Mn(III)									
31										

[#]Calculated from cell constants, this work

Table 6. Carbonate Minerals containing greater than 10 wt.% Manganese*

Name	Formula	Manganese, wt.%	gfw	Thermodynamic Data	
				Est.	Meas.
Mn(II)					
Armangite	$Mn_{26}As^{III}_{18}O_{50}(OH)_4(CO_3)$	38.55	3704.99	no	no
Charmarite-2H	$Mn^{II}_4Al_2(CO_3)(OH)_{12}•3(H_2O)$	37.13	591.86	no	no
Charmarite-3T	$Mn^{II}_4Al_2(CO_3)(OH)_{12}•3(H_2O)$	37.13	591.86	no	no
Holdawayite	$Mn^{II}_6(CO_3)_2(OH)_7(Cl,OH)$	54.98	599.54	no	no
Kutnohorite	$Ca(Mn,Mg,Fe^{II})(CO_3)_2$	16.01	205.94	no	yes
Loseyite	$(Mn,Zn)_7(CO_3)_2(OH)_{10}$	41.62	692.95	no	no
Manganotychite	$Na_6(Mn^{II},Fe^{II},Mg)_2(SO_4)(CO_3)_4$	11.40	578.33	no	no
Nakauriite	$(Mn,Ni,Cu)_8(SO_4)_4(CO_3)(OH)_6•48(H_2O)$	11.75	1870.41	no	no
Nasledovite	$PbMn_3Al_4(CO_3)_4(SO_4)O_5•5(H_2O)$	16.71	986.11	no	no
Rhodochrosite	$MnCO_3$	47.79	114.95	no	yes
Sailaufite	$Ca_2Mn_3O_2(AsO_4)_2(CO_3)•3(H_2O)$	23.65	650.52	no	no
Sidorenkite	$Na_3Mn(PO_4)(CO_3)$	19.70	278.89	no	no
Mn(III)					
Desautelsite	$Mg_6Mn^{III}_2(CO_3)(OH)_{16}•4(H_2O)$	16.65	659.89	no	no
Gaudefroyite	$Ca_4Mn^{III}_{3-x}(BO_3)_3(CO_3)(O,OH)_3$	23.56	582.85	no	no

*Data taken primarily from a compilation given by the Mineralogy Database (http://webmineral.com).

References

Ageno, F. and Valla, E. (1911). Contributo allo studio dell'idrolisi. I. Idrolisi dei carbonate. Atti della Accademia Nazionale dei Lincei, Classe di Scienze Fisiche, Matematiche e Naturali, Rendiconti 20(II), 706-12.

Anderson, C.T. (1934). The heat capacities of magnesium, zinc, lead, manganese and iron carbonates at low temperatures1. Journal of the American Chemical Society, 56(4), 849-851.

Antao, S.M. and Hassan, I. (2008). Gaudefroyite, $Ca_8Mn^{3+}{}_6[(BO_3)_6(CO_3)_2O_6]$: high-temperature crystal structure. Canadian Mineralogist, 46, 183-193.

Barin (1989). Thermochemical Data of Pure Substances. VCH Velagsgesellschaft, Weinheim, Germany,

Bauman, J.E., Jr. (1981). Thermodynamic measurements of carbonate equilibriums involving metal ions. U.S. Bureau of Mines, Information Circular No. 8853. 268-274.

Berner. A. (1967). Thermodynamic stability of sedimentary iron sulfides. American Journal of Science, 265, 773-785.

BSC (Bechtel SAIC Company) (2007). Qualification of Thermodynamic Data for Geochemical Modeling of Mineral–Water Interactions in Dilute Systems. ANL-WIS-GS-000003 REV 01. Las Vegas, Nevada: Bechtel SAIC Company.DOC.20070619.0007. [EQ3/6 Data0.YMP.R5 database]

Dobrydiev, S.V., Nilova, E.V. and Beskov, V.S. (2005). Calculation of $\Delta_f G^0(298)$ and $\Delta_f H^0(298)$ for sparingly soluble metal carbonates and oxalates in the solid state. Zhurnal Neorganicheskoi Khimii, 50(12), 2015-2018. [In Russian].

Chao, G.Y. and Gault, R.A. (1997). Quintinite-2H, quintinite-3T, charmarite-2H, charmarite-3T, and caresite-3T, a new group of carbonate minerals related to the hydrotalcite-manasseite group. Canadian Mineralogist, 35 1541-1549.

Dunn, P.J., Peacor, D.R. and Palmer, T.D. (1979). Desautelsite, a new mineral of the pyroaurite group. American Mineralogist, 64, 127-130.

Dunn, P.J., Peacor, D.R. and Sturman, B.D. (1980). Hauckite, $Fe_3^{3+}(Mg,Mn)_{24}Zn_{18}(SO_4)_4(CO_3)_2(OH)_{81}$, a new mineral from Sterling Hill, New Jersey. American Mineralogist, 65, 192-195.

Egorov, V.M. (1985). Solubility and growth of rhodochrosite in hydrothermal chloride solutions. Kristallografiya, 30(1), 161-165. [In Russian].

Emerson, S. (1976). EarIy diagenesis in anaerobic lake sediments: chemical equilibria in interstitial waters. Geochimica et Cosmochimica Acta, 40, 925-934.

Fattahi, M., Musikas, C., Brousse, T. and Abbe, J.Ch. (1999). Studies on aqueous soluble carbonato complexes of MnII, MnIII and MnIV: oxidation-reduction relationships. Acta Chemica Scandinavica, 53(12), 1063-1068.

Fazeli, A.R., Tareen, J.A.K., Basavalingu, B. and Bhandage, G.T. (1991). Standard thermodynamic data for Rhodochrosite from equilibrium decomposition curve. Proceedings, Indian Academy of Sciences (Earth and Planetary Science), 100(1), 37-39.

Fouillac, A. and Criaud, A. (1984). Carbonate and bicarbonate trace metal complexes: Critical reevaluation of stability constants. Geochemical Journal, 18, 297-303.

Gaines, R.V., Skinner, H.C.W., Foord, E.E., Mason, B., Rosenzweig, A. King, V.T. and Dowty, E. (1997). Dana's New Mineralogy (Eighth edition). John Wiley and Sons, Inc., New York. 1819 p.

Gamsjäger, H. (1974). Wechselwirkung von Metalloxiden, -hydroxiden, -carbonaten und -sulfiden mit Wasser. Radex-Rundschau, 4, 274-285.

Gamsjäger, H. (1985). Solid state chemical model for the solubility behavior of homogeneous solid cobalt manganese carbonate mixtures. Berichte der Bunsen-Gesellschaft, 89(12), 1318-1322.

Gamsjäger, H., Kraft, W. and Schindler, P. (1970). Zur Thermodynamik der Metallcarbonate 4. Potentiometrische Untersuchungen am System Mn^{2+}-CO_2-H_2O, Helvetica Chimica Acta, 53(2), 290-300.

Garrels, R.M., Thompson, M.E. and Siever, R. (1960). Stability of some carbonates at 25°C and one atmosphere total pressure. American Journal of Science, 258, 402-418.

Goldsmith, J.R. and Graff, D.L. (1957). The system CaO-MnO-CO_2: Solid-solution and decomposition relations. Geochimica et Cosmochimica Acta, l1, 310-334.

Goskhimizdat. (1952). Chemical Reference, vol. 3. [In Russian]. (As cited in Zhuk, 1954).

Graf, D.L. (1961). Crystallographic tables for the rhombohedral carbonates. American Mineralogist, 46, 1283-1316.

Grauer R. (1999). Solubility products of M(II) carbonates (edited and translated by U. Berner). Waste Management Laboratory, PSI Bericht Nr. 99-04 January 1999 ISSN 1019-0643.

Haehnel, O. (1924). Über die Löslichkeit der Carbonate des Strontiums, des Bariums und der Schwermetalle in Wasser unter hohen Kohlendioxyddrucken sowie über die Eigenschaften solcher Lösungen. Journal für praktische Chemie (Leipzig), 108, 187-193.

Dunn, P.J., Peacor, D.R. and Sturman, B.D. (1980). Hauckite, $Fe_3^{3+}(Mg,Mn)_{24}Zn_{18}(SO_4)_4(CO_3)_2(OH)_{81}$, a new mineral from Sterling Hill, New Jersey. American Mineralogist, 65, 192-195.

Helgeson, H.C., Delany, J.M., Nesbitt, H.W. and Bird, D.K. (1978). Summary and critique of the thermodynamic properties of rock forming minerals. American Journal of Science, 278-A, 229 p.

Hem, J.D. (1963a). Manganese complexes with bicarbonate and sulfate in natural water. Journal of Chemical and Engineering Data, 8, 99-101.

Hem, J.D. (1963). Chemical equilibria and rates of manganese oxidation. US Geological Survey of Water Supply Paper 1667-A, A1-A64.

Hill, R.J. (1981). The structure of loseyite. Acta Crystallographica, B37, 1323-1328.

Holland, T.J.B. and Powell, R. (1990). An enlarged and updated internally consistent thermodynamic dataset with uncertainties and correlation: the system K_2O-Na_2O-CaO-MgO-MnO-FeO-Fe_2O_3-Al_2O_3-TiO_2-SiO_2-C-H_2-O_2. Journal of Metamorphic Geology, 8, 89-124.

Holland, T.J.B. and Powell, R. (1998). An internally consistent thermodynamic dataset for phases of petrological interest. Journal of Metamorphic Geology, 16, 309-343.

Jensen, D.L., Boddum, J.K., Tjell, J.C. and Christensen, T.H. (2002). The solubility of rhodochrosite ($MnCO_3$) and siderite ($FeCO_3$) in anaerobic aquatic environments. Applied Geochemistry, 17(4), 503-511.

Johnson, K.S. (1982). Solubility of rhodochrosite ($MnCO_3$) in water and seawater. Geochimica et Cosmochimica Acta, 46, 1805-1809.

Johnson, G.K. and Bauman, J.E., Jr. (1978). Equilibrium constants for the aquated iron(II) cation. Inorganic Chemistry, 17(10), 2774–2779.

Karapet'yants, M. Kh. (1953). Khimicheskaya Termodinamika (Chemical Thermodynamics). 2nd Edition. Goshkhimizdat. 611 p. [In Russian].

Karapet'yants, M. Kh. (1955). Approximate method for the calculation of the isobaric potential and heat of formation of different substances. Trudy Instituta - Moskovskii Khimiko-Tekhnologicheskii Institut imeni D. I. Mendeleeva, No. 20, 10–28. [In Russian].

Karapet'yants, M.Kh. and Karapet'yants, M.L. (1970). Thermodynamic constants of Inorganic and Organic Compounds (trans. By J. Schmorak). Humphrey Science Publishers, Ann Arbor, Michigan. 461 p.

Karpov, I.K., Kashik, S.A. and Pampura, V.D. (1968). Thermodynamic Constants for Calculations in Geochemistry and Petrology. Izdva, Nauka, 143 p. [In Russian].

Karpov, I.K., Kiseleva, I. and Letnikov, F.A. (1971). Chemical Thermodynamics in Petrology and Geochemistry. Akademia Nauka, Irkutsk, 385 p.

Kelley, K.K. and Anderson, C.T. (1935). Theoretical metallurgy. IV. Metal carbonates-correlations and applications of thermodynamic properties. U.S. Bureau of Mines Bulletin No. 384, 73 p.

Kelley, K.K. (1960). Contributions to the data on theoretical metallurgy, XIII. High temperature heat-content, heat-capacity and entropy data for the elements and inorganic compounds. U.S. Bureau of Mines Bulletin No. 584, 232 p.

Kelley, K.K. and King. E.G. (1961). Contribution to the Data on Theoretical Metallurgy. XIV. Entropies of the Elements and Inorganic Compounds. U.S. Bureau of Mines Bulletin No. 592, 149 p.

Kireev, V.A. (1964). Acid-base properties of oxides. Zhurnal Fizicheskoi Khimii, 38(8), 1881-1894. [In Russian].

Kostryukov, V.N. and Kalinkina, I.N. (1964). Heat capacity and entropy for manganese, iron, cobalt, and nickel carbonates at low temperatures. Zhurnal Fizicheskoi Khimii, 38, 780-781. [In Russian].

Krishnamurty, K.V. Harris, G.M. and Sastri, V.S. (1970). The chemistry of the metal carbonato complexes. Chemical Reviews, 70(2), 171-197.

Kurova, T.A., Shumyatskaya, N.G., Voronkov, A.A. and Pyatenko, Y.A. (1980). Crystal structure of sidorenkite $Na_3Mn(PO_4)(CO_3)$. Soviet Physics Doklady, 25, 156-157.

La Iglesia, A. and Félix, J.F. (1994). Estimation of thermodynamic properties of mineral carbonates at high and low temperatures from the sum of polyhedral contributions. Geochimica et Cosmochimica Acta, 58(19), 3983-3991.

Langmuir, D. (1979). Techniques of estimating thermodynamic properties for some aqueous complexes of geochemical interest. In Chemical Modeling in Aqueous Systems, (E.A. Jenne, Ed.). ACS Symposium Series 93, American Chemical Society.

Latimer, W.M. (1952). The Oxidation States of the Elements and their Potentials in Aqueous Solutions. Second edition. Prentice Hall, New York, 392 p.

Lesht, D. (1977). M.A. Thesis, University of Missouri-Columbia, cited by Johnson and Bauman (1978).

Lesht, D. and Bauman, I.E., Jr. (1978). Thermodynamics of the manganese (II) bicarbonate system. lnorganic Chemistry, 17, 3332-3334.

Maslen, E.N., Streltsov, V.A., Streltsova, N.R. and Ishizawa, N. (1995). Electron density and optical anisotropy in rhombohedral carbonates. III. Synchrotron X-ray studies of $CaCO_3$, $MgCO_3$ and $MnCO_3$. Acta Crystallographica, B51, 929-939.

Mattigod, S.V. and Sposito, G. (1977). Estimated association constants for some complexes of trace metals with inorganic ligands. Soil Science Society of America Journal, 41(6), 1092-1097.

McBeath, M.K., Rock, P.A., Casey, W.H. and Mandell, G.K. (1998). Gibbs energies of formation of metal-carbonate solid solutions: Part 3. The $CaMn_{1-x}CO_3$ system at 298 K and 1 bar. Geochimica et Cosmochimica Acta, 62, 2799-2808.

McBride, M.B. (1979). Chemisorption and precipitation of Mn^{2+} at $CaCO_3$ surfaces. Soil Science Society of America Journal. 43, 693-698.

Mellor, J.W. (1932). Inorganic and Theoretical Chemistry, 12, 437. Longmans (cited in Latimer, 1952).

Michard, G. and Faucherre, J. (1964). Importance geochimique des complexes sulfate et carbonate du manganese. Comptes Rendus de l'Academie des Sciences de Paris, 259, 1171-1174.

Millero, F.J. and Hawke, D.J. (1992). Ionic interactions of divalent metals in natural waters. Marine Chemistry, 40, 19-48.

Moore, P.B. and Araki, T. (1979). Armangite, $Mn_{26}[As_6(OH)_4O1_4][As_6O_{18}]_2[CO_3]$, a fluorite derivative structure. American Mineralogist, 64, 748-757.

Morgan, J.J. (1967). Chemical equilibria and kinetic properties of manganese in natural waters. In: Principles and Applications of Water Chemistry, (Faust S.D. Hunter J.V., eds.) Proc. Rudolfs Res. Conf., 4th (1967), p. 561-622, discussion p. 622-4. John Wiley and Sons, New York.

Morgan, J.J. (2005). Kinetics of reaction between O_2 and Mn(II) species in aqueous solutions. Geochimica et Cosmochimica Acta, 69(1), 35–48.

Murray, J.W., Grundmanis V. and Smethie, W.M., Jr. (1978). Interstitial water chemistry in sediments of Saanich Inlet. Geochimica et Cosmochimica Acta, 42, 1011-1026.

Näsänen, R. (1942). Die potentiometrische Bestimmung des Loslichkeitproduktes von Manganhydroxyd. Zeitschrift für physikalische Chemie, 191, 54-64.

Neher-Neumann, E. (1994). Studies on metal carbonate equilibria. 26. The hydrogen carbonate complex of manganese(II) in acid solutions and a 3 M $(Na)ClO_4$ ionic medium at 25°C. Determination of the solubility product of $MnCO_3(s)$. Acta Chemica Scandinavica, 48(5), 393-398.

Naumov, G.B., Ryzhenko, B.N. and Khodakovsky, I.L. (1974). Handbook of Thermodynamic Data. National Technical Informtion Service, 722176A, U.S. Dept. Commerce. 328 p.

Nordstrom, D.K., Plummer, L.N., Langmuir, D., Busenberg, E., May, H.M., Jones, B.F. and Parkhurst, D.L. (1990). Revised chemical equilibrium data for major water-mineral reactions and their limitations, Chapter 31 in: Chemical Modelling of Aqueous Systems II, (D.C. Melchoir and R.L Basset, Eds.) ACS Symposium Series 146, 398-413. American Chemical Society, Washington, DC

Palmer, D.A. and van Eldik, R. (1983). The chemistry of metal carbonato and carbon dioxide complexes.

Chemical Reviews, 83, 651-731.

Peacor, D.R, Essene, E.J. and Gaines, A.M. (1987). Petrologic and crystal-chemical implications of cation order-disorder in kutnahorite ($CaMn(CO_3)_2$). American Mineralogist, 72, 319-328.

Peacor, D R, Rouse, R C. (1988). Holdawayite, $Mn6(CO_3)_2(OH)7(Cl,OH)$, a structure containing anions in zeolite-like channels. American Mineralogist, 73, 637-642.

Pearson, F.J., Berner, U. and Hummel, W. (1992). Nagra thermochemical data base, supplemental data 05/92 TR 91-18; (provient de la base 0391 MINEQL- PSY)

Radha, A.V. and Navrotsky, A. (2013). Thermodynamics of carbonates. Reviews in Mineralogy and Geochemistry, 77(1), 73-121.

Reiterer, F. (1980). Lös1ichkeitskonstanten und freie Bildungsenthalpien neutraler Übergangsmetallcarbonate: $MnCO_3$, $FeCO_3$, $CoCO_3$, $NiCO_3$, $CuCO_3$, $ZnCO_3$. PhD thesis, Montanuniversität, Leoben, Austria.

Robie, R.A. (1965). Heat and free energy of formation of herzenbergite, troilite, magnesite, and rhodochrosite calculated from equilibrium data. U.S. Geological Survey Professional Paper 525-D, D65-D72.

Robie, R.A. (1966). Section 20: Thermodynamic properties of minerals. Handbook of Physical Constants, Geological Society of America Memoirs, 97, 437-458.

Robie R.A., Hemingway B.S. and Fischer J.R. (1979). Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 Pa) pressure and at higher temperatures. (Reprinted with corrections). U.S. Bureau of Mines Bulletin No. 1452. U.S. Government Printing Office, Washington, DC. 456 p.

Robie, R.A., Haselton, H.T. and Hemingway, B.S. (1984). Heat capacities and entropies of rhodochrosite ($MnCO_3$) and siderite ($FeCO_3$) between 5 and 600 K. American Mineralogist, 69, 349-357.

Robie, R.A. and Hemingway, B.S. (1995). Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 Pascals) pressure and at higher temperatures. U.S. Geological Survey Bulletin No. 2131, 461 p.

Robie, R.A., Hemingway, B.S., and Fisher, J.R. (1978). Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 Pa) pressure and at higher temperatures. U.S. Bureau of Mines Bulletin No. 1452. U.S. Government Printing Office, Washington, DC. 456 p.

Rossini, F.D., Wagman, D.D., Evans, W.H., Levine, S., and Jaffe, I. (1952). Selected values of chemical tbermodynamical properties. NBS Circular 500. 1268 p., Washington, D.C.

Roth, W.A. (1929). Zur Thermochemie des Eisens, Mangans und Nickels. Zeitschrift für angewandte Chemie, 42, 981-984.

Roth, W.A., Berendt, H. and Wirths, G. (1941). Die Bildungswarmen einiger mineralischer und kunstlicher Carbonate. Zeitschrift für Elektrochemie, 47, 185-190.

Ruff, O. and Ascher, E. (1930). Studien über die fraktionierte Fällung. IV. Einfluß der Bildung von Mischkristallen und Adsorptionsverbindungen. Zeitschrift für anorganische und allgemeine Chemie, 153, 369-386.

Ryabin, V.A., Ostroumov, M.A. and Svit, T.F. (1977). Thermodynamic Properties of Substances:

Handbook (Termodinamicheskie Svoistva Veshchestv: Spravochnik). Khimiya, Leningr. Otd. Leningrad, USSR 389 p. [In Russian].

Sangameshwar, S.R. and Barnes, H.L. (1983). Supergene processes in zinc-lead-silver sulfide ores in carbonates. Economic Geology, 78, 1379-1397.

Shock, E.L. and Koretsky, C.M. (1995). Metal-organic complexes in geochemical processes: Estimation of standard partial molal thermodynamic properties of aqueous complexes between metal cations and monovalent organic acid ligands at high pressures and temperatures. Geochimica et Cosmochimica Acta, 59, 1497-1532.

Sillen, L.G. and Martell, A.E. (1967). Stability Constants of Metal Ion Complexes, 2nd ed. Chemical Society: London, 1967; Spec. Publ. 17, 754 p.

Smith, R.M. and Martell, A.E. (1976). Critical Stability Constants, Volume 4 Inorganic Complexes. Plenum Press: New York.

Stern, K.H. (2000). High Temperature Properties and Thermal Decomposition of Inorganic Salts with Oxyanions. 256 p. CRC Press LLC, 2000 N.W. Corporate Blvd., Boca Raton Florida 33431.

Sternbeck, J., 1997. Kinetics of rhodochrosite crystal growth at 25°C: the role of surface speciation. Geochimica et Cosmochimica Acta, 61, 785-793.

Stumm, W. and Morgan, J.J. (1981). Aquatic Chemistry, 2nd edn. J. Wiley & Sons.

Stumm, W. and Morgan, J.J. (1996). Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters. Wiley.

Suess, E. (1979). Mineral phases formed in anoxic sediments by microbial decomposition of organic matter. Geochimica et Cosmochimica Acta, 43(3), 339-352.

Sverjensky, D.A., Shock, E.L. and Helgeson, H.C. (1997). Prediction of the thermodynamic properties of aqueous metal complexes to 1000 C and 5 kb. Geochimica et Cosmochimica Acta, 61(7), 1359-1412.

Sychev, A.Ya., Pfannmeller, W. and Isak, V.G. (1981). Thermodynamics of the complexing of manganese(II) bicarbonate complexes. Zhurnal Fizicheskoi Khimii, 55(2), 365-368. [In Russian].

Tareen, J.A.K., Fazeli, A.R., Basavalingu, B. and Bhandage, G.T. (1992). Thermodynamic data for dolomite and kutnahorite from the experimental decarbonation curves. Journal of the Geological Society of India, 40(6), 545-656.

Tareen, J.A.K., Fazeli, A.R. Basavalingu, B. and Bhandige, G.T. (1995). Decarbonation curves and associated thermodynamic data for synthetic Cd-dolomites $CdMg(CO_3)_2$, $CdMn(CO_3)_2$ and $CdZn(CO3)_2$. Journal of Thermal Analysis and Calorimetry, 44(4), 937-954.

Turner, D.R., Whitfield, M. and Dickson, A.G. (1981). The equilibrium speciation of dissolved components in freshwater and seawater at 25°C and 1 atm pressure. Geochimica et Cosmochimica Acta, 45, 855-881.

Wagman, D.D. et al. (1965-1969). U.S. NBS Technical Note No. 207-1; 207-2; No. 207-3

Wagman, D.D., Evans, W.H., Parker, V.B., Halow, I., Bailey, S.M. and Schumm, R.H. (1969). Selected Values of Chemical Thermodynamic Properties. Tables for elements 35 through 53 in the standard order of arrangement. NBS Technical Note 270-4, U.S. Department of Commerce, National Bureau of Standards, 141 p.

Wagman, D.D., Evans, W.H., Parker, V.B., Schumm, R.H., Halow, I., Bailey, S.M., Churney, K.L. and Nuttall, R.L. (1982). The NBS Tables of Chemical Thermodynamic Properties: Selected Values for Inorganic and C1 and C2 Organic Substances in SI Units. American Chemical Society and the American Institute of Physics for the National Bureau of Standards (Journal of Physical Chemical Reference Data, 11, supp. 2, 392 p.).

Wartel, M., Skiker, M., Auger, Y. and Boughriet, A. (1990). Interaction of manganese(II) with carbonates in seawater: assessment of the solubility product of manganese carbonate and manganese distribution coefficient between the liquid phase and calcium carbonate particles. Marine Chemistry, 29(2-3), 99-117.

Wilcox. D.E. and Bromley, L.A. (1963). Computer Estimation of heat and free energy for simple inorganic compounds. Industrial and Engineering Chemistry, 55(7), 32-39.

Wolfram, O. and Krupp, R.E. (1996). Hydrothermal solubility of rhodochrosite, Mn(II) speciation, and equilibrium constants. Geochimica et Cosmochimica Acta, 60(21), 3983-3994.

Woods, T.L. and Garrels, R.M. (1987). Thermodynamic Values at Low Temperature for Natural Inorganic Materials. An Uncritical Summary. Oxford University Press. 242 p. plus references.

Wersin, P., Charlet, L., Karthein, R. and Stumm, W. (1989). From adsorption to precipitation: Sorption of Mn^{2+} on $FeCO_3$(s). Geochimica et Cosmochimica Acta, 53(11), 2787-2796.

Wildner, M., Tillmanns, E, Andrut, M., and Lorenz, J. (2003). Sailaufite, $(Ca,Na,)_2Mn_3O_2(AsO_4)_2(CO_3).3H_2O$, a new mineral from Hartkoppe hill, Ober-Sailauf (Spessart mountains, Germany), and its relationship to mitridatite-group minerals and pararobertsite. European Journal of Mineralogy, 15, 555-564.

Yatsimirskii, K.B. (1958). Thermochemistry of transition metal compounds and the crystal field theory. Zhurnal Neorganicheskoi Khimii, 3, 2244-2252. [In Russian].

Yoder, C.H. and Rowand, J.P. (2006). Application of the simple salt lattice energy approximation to the solubility of minerals. American Mineralogist, 91(5-6), 747-752.

Zhuk, N.P. (1954). Thermodynamic constants of sulfates, carbonates, chromates, bromates, iodates, oxalates, and other salts slightly soluble in water. Zhurnal Fizicheskoi Khimii, 28, 1690-1697. [In Russian].

Zirino, A. and Yamamoto, S. (1972). A pH-dependent model for the chemical speciation of copper, zinc, cadmium, and lead in seawater. Limnology and Oceanography, 17, 661-671.

MERCURY

Table 1. Association Constants for Aqueous Carbonate Complexes in the System $Hg_2O/HgO-CO_2-H_2O$

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
Hg(II)					
$Hg^{2+} + CO_3^{2-} = HgCO_3(aq)$	10.65 ± 0.20		3 *M* $NaClO_4$		Hietanen and Högfeldt (1976b)
	11.00	-	3 *M* $NaClO_4$	Bilinski et al. (1980)	Hietanen and Högfeldt (1976b)
	11.01 ± 0.20	-	0.5 *M* $NaClO_4$		Bilinski et al. (1980)
	11.00	-	3 *M* $NaClO_4$	Clever et al. (1985)	Bilinski et al. (1980) after Hietanen and Högfeldt (1976b)
	11.01 ± 0.20	-	0.5 *M* $NaClO_4$	Clever et al. (1985)	Bilinski et al. (1980)
$Hg^{2+} + CO_3^{2--} + H_2O = Hg(OH)CO_3^- + H^+$	4.40 ± 0.10		3 *M* $NaClO_4$		Hietanen and Högfeldt (1976b)
	4.40	-	3 *M* $NaClO_4$	Bilinski et al. (1980)	Hietanen and Högfeldt (1976b)
	4.40 ± 0.10	-	0.5 *M* $NaClO_4$		Bilinski et al. (1980)
	4.40	-	3 *M* $NaClO_4$	Clever et al. (1985)	Bilinski et al. (1980) after Hietanen and Högfeldt (1976b)
	4.40 ± 0.10	-	0.5 *M* $NaClO_4$	Clever et al. (1985)	Bilinski et al. (1980)
$Hg^{2+} + CO_3^{2-} + H^+ = HgHCO_3^+$	15.05 ± 0.10		3 *M* $NaClO_4$		Hietanen and Högfeldt (1976b)
	14.72	-	3 *M* $NaClO_4$	Bilinski et al. (1980)	Hietanen and Högfeldt (1976b)
	15.08 ± 0.10	-	0.5 *M* $NaClO_4$		Bilinski et al. (1980)
	15.08 ± 0.10	-	0.5 *M* $NaClO_4$	Clever et al. (1985)	Bilinski et al. (1980)
	14.72	-	3 *M* $NaClO_4$	Clever et al. (1985)	Bilinski et al. (1980) after Hietanen and Högfeldt (1976b)
$Hg^{2+} + 2CO_3^{2-} = Hg(CO_3)_2^{2-}$	14.00	-	3 *M* $NaClO_4$	Bilinski et al. (1980)	Hietanen and Högfeldt (1976b)
	14.50 ± 0.20	-	0.5 *M* $NaClO_4$		Bilinski et al. (1980)
	14.00	-	I3 *M* $NaClO_4$	Clever et al. (1985)	Bilinski et al. (1980)
	14.50 ± 0.20	-	0.5 *M* $NaClO_4$	Clever et al. (1985)	Bilinski et al. (1980)
$Hg(OH)_2(aq) + CO_2(g) = HgCO_3(aq) + H_2O$	–0.70 ± 0.20	-	Recommended. See Note		Powell et al. (2005)

Table 1. Association Constants for Aqueous Carbonate Complexes in the System $Hg_2O/HgO-CO_2-H_2O$ (Continued)

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
$Hg(OH)_2(aq) + HCO_3^- = Hg(OH)CO_3^- + H_2O$	0.98 ± 0.10	-	Recommended. See Note		Powell et al. (2005)
$Hg(OH)_2(aq) + CO_2(g) + H+ = HgHCO_3^+ + H_2O$	3.63 ± 0.10	-	Recommended. See Note		Powell et al. (2005)
$CH_3Hg^+ + CO_3^{2-} = CH_3HgCO_3^-$	-	-	No evidence for complex		Sanz et al. (2002)
$CH_3Hg^+ + CO_3^{2-} + OH^- = CH_3HgOHCO_3^{2-}$	-	-	No evidence for complex		Sanz et al. (2002)

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Note: The Log K values presented are from a reevaluation of equilibrium studies at 25°C and 3.0 mol dm^{-3} $NaClO_4$ by Hietanen and Högfeldt (1976a,b), which, although "somewhat lacking in precision," are regarded as "more reliable" than those by Bilinski et al. (1980) at 25°C and 0.5 mol dm^{-3}. Because extrapolation to zero ionic strength was not possible, the cited isocoulombic reactions were derived, which should have minimal ionic strength dependence.

Table 2. Solubility Constants of Solid Carbonates in the System Hg_2O/HgO-CO_2-H_2O

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
Minerals					
Hg(I)					
Hg(II)					
Synthetic Phases					
Hg(I)					
Hg_2CO_3					
$Hg_2CO_3 = Hg_2^{2+} + CO_3^{2-}$	-16.06	-		Brodsky (1929),	Immerwahr (1901)
	-16.05		25°C	Clever et al. (1985)	Brodsky (1929) after Immerwahr (1901)
	-16.05			Latimer (1952)	Brodsky (1929)
	-16.04			Kryukova (1939)	Brodsky (1929)
	-15.40		Original citation not located.	Kryukova (1939)	Bennet (1934)
	-16.046	-	Review. No correction for activity coefficients		Kelley and Anderson (1935)
	-16.11	-			Kryukova (1939)
	-16.11		25°C, based on solubility measurement	Clever et al. (1985)	Kryukova (1939)
	-16.96		25°C, Calculated from EMF study and data from Latimer (1952)	Clever et al. (1985)	Saegusa (1950)
	-16.05	-		Zhuk (1954)	Goskhimizdat (1952)
	-16.44		25°C	Clever et al. (1985)	Hepler and Olofsson (1975)
	-13.37 ± 0.05		25°C, 3 *M* $NaClO_4$		Hietanen and Högfeldt (1976a)
	-13.37 ± 0.05		25°C, 3 *M* $NaClO_4$	Clever et al. (1985)	Hietanen and Högfeldt (1976a)
$Hg_2CO_3 + 2H^+ = Hg_2^{2+} + + CO_2(g) + H_2O^-$	-4.19 ± 0.03		25°C, 3 *M* $NaClO_4$		Hietanen and Högfeldt (1976a)

Table 2. Solubility Constants of Solid Carbonates in the System $Hg_2O/HgO-CO_2-H_2O$ (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
Hg(II)					
$HgCO_3$					
$HgCO_3(s) = Hg^{2+} + CO_3^{2-}$	-16,96	-	Calc. from electrochemical cell data		Saegusa (1950)
	-16.05	-	$I = 0$	Palmer and Van Eldik (1983)	Smith and Martell (1976)
$HgCO_3.2HgO$					
$HgCO_3.2HgO(s) + 4H^+ = 3Hg^{2+} + CO_3^{2-} + 2H_2O$	-10.36 ± 0.33	-	3 *M* $NaClO_4$		Hietanen and Högfeldt (1976a)
$HgCO_3.2HgO(s) + 6H^+ = 3Hg^{2+} + CO_2(g) + 3H_2O$	7.26	-	3 *M* $NaClO_4$	Bilinski et al. (1980)	Weber (1972)
	7.20 ± 0.33	-	3 *M* $NaClO_4$		Hietanen and Högfeldt (1976a)
	7.20	-	3 *M* $NaClO_4$	Bilinski et al. (1980)	Hietanen and Högfeldt (1976a)
	7.12	-	3 *M* $NaClO_4$	Bilinski et al. (1980)	Hietanen and Högfeldt (1976b)
	7.12 – 7.26		25°C, 3 *M* $NaClO_4$	Clever et al. (1985)	Hietanen and Högfeldt (1976a,b) and Bilinski et al. (1980)
	5.40 ± 0.25	-	0.5 *M* $NaClO_4$		Bilinski et al. (1980)
	7.02 ± 0.25	-	$I = 0$		Bilinski et al. (1980)
	5.40 ± 0.25		25°C, 0.5 *M* $NaClO_4$	Clever et al. (1985)	Bilinski et al. (1980)
	7.02 ± 0.25		25°C, $I = 0$	Clever et al. (1985)	Bilinski et al. (1980)
$HgCO_3.2HgO(s) + 3H_2O = 3Hg(OH)_2(aq) + CO_2(g)$	–11.27 ± 0.35	-	Provisional. See Note		Powell et al. (2005)

(1) At standard state (25°C, 1 atm, $I = 0$), unless otherwise noted.

Note: the Log K value presented is from a reevaluation of an equilibrium study at 25°C and 3.0 mol dm^{-3} $NaClO_4$ by Hietanen and Hogfeldt (1976b). Because extrapolation to zero ionic strength was not possible, the cited neutral-species reaction was derived, which should have minimal ionic strength dependence.

Table 3a. Association Constants of Aqueous Carbonate Complexes in the System $Hg_2O/HgO-CO_2-H_2O$ extracted from Databases of Distribution-of-Species Codes

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Database	Source
Hg(II)				
$Hg(OH)_2 + 2H+ + CO_3^{-2} = HgCO_3 + 2H_2O$	-	-	Minteq (2009)	
	18.272	0	Minteq (2006)	NIST46.4, MTQ3.11
	-	-	Phreeqc (2009)	
	-	-	Wateq4f (2005)	
	-	-	ThermoChimie v.7.b	
	-	-	NAGRA/PSI (2001)	
	-	-	Data0.YMP.R5	
			Thermoddem (2009)	
$Hg(OH)_2 + 2H^+ + 2CO_3^{-2} = Hg(CO_3)_2^{-2} + 2H_2O$	-	-	Minteq (2009)	
	21.772	0	Minteq (2006)	NIST46.4, MTQ3.11
	-	-	Phreeqc (2009)	
	-	-	Wateq4f (2005)	
	-	-	ThermoChimie v.7.b	
	-	-	NAGRA/PSI (2001)	
	-	-	Data0.YMP.R5	
			Thermoddem (2009)	
$Hg(OH)_2 + 3H^+ + CO_3^{-2} = HgHCO_3^+ + 2H_2O$	-	-	Minteq (2009)	
	22.542	0	Minteq (2006)	NIST46.4, MTQ3.11
	-	-	Phreeqc (2009)	
	-	-	Wateq4f (2005)	
	-	-	ThermoChimie v.7.b	
	-	-	NAGRA/PSI (2001)	
	-	-	Data0.YMP.R5	
			Thermoddem (2009)	

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Table 3b. Solubility Constants of Solid Phases containing the System $Hg_2O/HgO-CO_2-H_2O$ extracted from Databases of Distribution-of-Species Codes

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Database	Source
Hg(II)				
$HgCO_3$				
$HgCO_3(s) + H2O = Hg(OH)2 + CO_3^{2-} + 2H+$	-28.6817	110.58	Minteq (2009)	
	-	-	Minteq (2006)	
	-	-	Phreeqc (2009)	
	-	-	Wateq4f (2005)	
	-	-	ThermoChimie v.7.b	
	-	-	NAGRA/PSI (2001)	
	-	-	Data0.YMP.R5	
			Thermoddem (2009)	
Hg_2CO_3				
$Hg_2CO_3 = Hg_2^{2+} + CO_3^{2-}$	-13.9586	0	Minteq (2009)	
	-16.05	45.14	Minteq (2006)	
	-	-	Phreeqc (2009)	
	-	-	Wateq4f (2005)	
	-	-	ThermoChimie v.7.b	
	-	-	NAGRA/PSI (2001)	
	-	-	Data0.YMP.R5	
			Thermoddem (2009)	
$Hg_3O_2CO_3$				
$Hg_3O_2CO_3 + 4H_2O = 3Hg(OH)_2 + 2H^+ + CO_3^{-2}$			Minteq (2009)	
	-29.682	-0	Minteq (2006)	
	-	-	Phreeqc (2009)	
	-	-	Wateq4f (2005)	
	-	-	ThermoChimie v.7.b	
	-	-	NAGRA/PSI (2001)	
	-	-	Data0.YMP.R5	
			Thermoddem (2009)	

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Table 3c. Distribution-of-Species Codes: Database References

Database	Reference
Data0.com.VR.R6+	Wolery, T.J. (1994). EQ3NR, Letter report: EQ3/6 version 8.0. Differences from version 7. UCRL-ID-129749. Lawrence Livermore National Laboratory, Livermore, California. USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/LLNL.DAT
Data0.YMP.R5	BSC (Bechtel SAIC Company) (2007). Qualification of Thermodynamic Data for Geochemical Modeling of Mineral–Water Interactions in Dilute Systems. ANL-WIS-GS-000003 REV 01. Las Vegas, Nevada: Bechtel SAIC Company.DOC.20070619.0007.
MinteqA2	HydroGeoLogic, Inc. and Allison Geoscience Consultants, Inc. (1999). MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: User Manual Supplement for Version 4.0, Appendix A: thermodynamic database for MINTEQA2 V4.0, p. 44-74.
Minteq (2009)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/MINTEQ.DAT
Minteq (2006)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/minteq.v4.dat
NAGRA/PSI (2001)	Hummel, W., Berner, U., Curti, E., Pearson, F.J. and Thoenen, T. (2002). Nagra/PSI Chemical Thermodynamic Data Base 01/01. Universal Publishers/uPublish.com, Parkland, Florida. 565 p.
Phreeqc (2009)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/PHREEQC.DAT
ThermoChimie v.7.b	Duro, L., Grivém M. and Giffaut, E. (2010). ThermoChimie, the ANDRA thermodynamic database In Buckau G, Kienzler B, Duro L, Grivé M, Montoya V (eds). 2nd Annual Workshop Proceedings of the Collaborative Project “Redox Phenomena Controlling Systems” (7th EC FP CP Recosy) Larnaca (Cyprus) 16–19 March 2010. Karlsruhe: KIT Scientific Publishing, 275–283.
Thermoddem (2009)	Blanc P., Lassin A. and Piantone P. (2007) THERMODDEM a database devoted to waste minerals. BRGM (Orléans, France). For updates: http://thermoddem.brgm.fr
Wateq4f	Ball, J. W., & Nordstrom, D. K. (1991). User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters. U.S. GEOLOGICAL SURVEY, Open-File Report 91-183, Revised and reprinted - April, 2001. p. 81-94
Wateq4f (2005)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/WATEQ4F.DAT

Table 4a. Thermodynamic properties of Mercury Carbonate Minerals and Synthetic Solid Carbonates: Gibbs Free Energies of Formation

Mineral		$\Delta G^0_{f,P_r,T_r}$ kJ/gfw $^{-1}$	Secondary Reference	Primary Reference
Name	Formula			
Minerals				
Hg(I)				
Hg(II)				
Mosesite	$Hg^{II}_2N(Cl,SO_4,MoO_4,CO_3)\bullet(H_2O)$			
Synthetic Phases				
Hg(I)				
$Hg^{I}_2CO_3$	$Hg^{I}_2CO_3$	-465.26		Kelley and Anderson (1935)
		-468.61		Saegusa (1950)
		-442.67		Latimer (1952)
		-442.67	Karpov et al. (1968)	Latimer (1952)
		-442.67	Karapet'yants and Karapet'yants (1970)	Latimer (1952)
		-442.7	Woods and Garrels (1987)	Latimer (1952)
		-468.61	Zhuk (1954)	Rossini et al. (1952), Karapet'yants (1953)
calculated		-465.51		Zhuk (1954)
		-465.67	Karpov et al. (1968)	Zhuk (1954)
		-465.51	Karapet'yants and Karapet'yants (1970)	Zhuk (1954)
		-468.19		Wagman et al. (1969)
		-468.1	Woods and Garrels (1987)	Wagman et al. (1982)
		-607.17	Stern (2000)	CRC (1994)
Hg(II)				
$HgCO_3$	$HgCO_3$	-468.61	Karpov et al. (1968)	Saegusa (1950)
		-468.61	Karapet'yants and Karapet'yants (1970)	Saegusa (1950)

Table 4a. Thermodynamic properties of Mercury Carbonate Minerals and Synthetic Solid Carbonates: Gibbs Free Energies of Formation (Continued)

Mineral		$\Delta G^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
		-605.42	Karapet'yants and Karapet'yants (1970)	Karapet'yants (1957)
		-479.90	Karpov et al. (1968)	Karapet'yants and Karapet'yants (1961)
		-608.18	Stern (2000)	Karapet'yants and karapet'yants (1970)
$HgCO_3.2HgO$	$HgCO_3.2HgO$			

Table 4b. Thermodynamic properties of Mercury Carbonate Minerals and Synthetic Solid Carbonates: Enthalpies of Formation

Mineral		$\Delta H^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
Minerals				
Hg(I)				
Hg(II)				
Mosesite	$Hg^{II}_2N(Cl,SO_4,MoO_4,CO_3)\bullet(H_2O)$			
Synthetic Phases				
Hg(I)				
$Hg^{I}_2CO_3$	$Hg^{I}_2CO_3$	-533.29		Saegusa (1950)
		-553.29	Zhuk (1954)	Rossini et al. (1952), Karapet'yants (1953)
		-514.63 ± 62.76	Estimated value for fictive compound	Wilcox and Bromley (1963)
		-514.63	Karapet'yants and Karapet'yants (1970)	Wilcox and Bromley (1963)
		-553.54		Wagman et al. (1969)
		-553.5	Woods and Garrels (1987)	Wagman et al. (1982)
		-553.50	Stern (2000)	CRC (1994)
$Hg_2(HCO_3)_2$	$Hg_2(HCO_3)_2$	-1292.86 ± 62.76	Estimated value for fictive compound	Wilcox and Bromley (1963)
		-1292.86	Karapet'yants and Karapet'yants (1970)	Wilcox and Bromley (1963)
Hg(II)				
$HgCO_3$	$HgCO_3$	-553.29	Karpov et al. (1968)	Saegusa (1950)
		-553.29	Karapet'yants and Karapet'yants (1970)	Saegusa (1950)
		-493.71± 62.76	Estimated value for fictive compound	Wilcox and Bromley (1963)
		-493.71	Karapet'yants and Karapet'yants (1970)	Wilcox and Bromley (1963)
		-553.29	Stern (2000)	Karapet'yants and karapet'yants (1970)

Table 4b. Thermodynamic properties of Mercury Carbonate Minerals and Synthetic Solid Carbonates: Enthalpies of Formation (Continued)

Mineral		$\Delta H^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
$Hg(HCO_3)_2$	$Hg(HCO_3)_2$	-1271.94 ± 62.76	Estimated value for fictive compound	Wilcox and Bromley (1963)
		-1271.94	Karapet'yants and Karapet'yants (1970)	Wilcox and Bromley (1963)
$HgCO_3.2HgO$	$HgCO_3.2HgO$			

Table 4c. Thermodynamic properties of Mercury Carbonate Minerals and Synthetic Solid Carbonates: Entropies

Mineral		$S^0_{P_r,T_r}$	Secondary Reference	Primary Reference
Name	Formula	J K^{-1} gfw^{-1}		
Mninerals				
Hg(I)				
Hg(II)				
Mosesite	$Hg^{II}_2N(Cl,SO_4,MoO_4,CO_3)•(H_2O)$			
Synthetic Phases				
Hg(I)				
$Hg^{I}_2CO_3$ Synthetic	$Hg^{I}_2CO_3$	180.10		Saegusa (1950)
		184.10	Zhuk (1954)	Rossini et al. (1952), Karapet'yants (1953)
calculated		173.64		Zhuk (1954)
		173.64	Karpov et al. (1968)	Zhuk (1954)
		173.64	Karapet'yants and Karapet'yants (1970)	Zhuk (1954)
		179.91		Wagman et al. (1969)
		180.	Woods and Garrels (1987)	Wagman et al. (1982)
		180.00	Stern (2000)	CRC (1994)
Hg(II)				
$HgCO_3$	$HgCO_3$	184.10	Karpov et al. (1968)	Saegusa (1950)
		184.10	Karapet'yants and Karapet'yants (1970)	Saegusa (1950)
		184.10	Stern (2000)	Karapet'yants and karapet'yants (1970)
$HgCO_3.2HgO$	$HgCO_3.2HgO$			

Table 5. Crystallographic Properties of Mercury Carbonate Minerals and Synthetic Solid Carbonates

	Name	Formula	Reference
	Minerals		
	Hg(I)		
1	Clearcreekite	$Hg^{I}_{3}(CO_3)(OH)\bullet 2(H_2O)$	Roberts et al. (2001)
2	Clearcreekite	$Hg^{I}_{2.9}(CO_3)(OH)_{0.9}\bullet 2.1(H_2O)$	Mineralogy Database (http://webmineral.com/))
3	Peterbaylissite	$Hg^{I}_{3}(CO_3)(OH)\bullet 2(H_2O)$	Roberts et al. (1995), Roberts and Williams (1995)
4	Peterbaylissite	$Hg^{I}_{3}(CO_3)(OH)\bullet 2(H_2O)$	Gaines et al. (1997)
5	Szymańskiite	$Hg^{I}_{16}(Ni_{4.1}Mg_{1.9})(H_3O)_8(CO_3)_{12}(OH)_{12}\bullet 3(H_2O)$	Roberts et al. (1990)
6	Szymańskiite	$Hg^{I}_{16}(Ni_{4.1}Mg_{1.9})(H_3O)_8(CO_3)_{12}(OH)_{12}\bullet 3(H_2O)$	Szymanski and Roberts (1990)
7	Szymańskiite	$Hg^{I}_{16}(Ni_{0.75}Mg_{0.25})_6(H_3O)_8(CO_3)_{12}(OH)_{12}\bullet 3(H_2O)$	Gaines et al. (1997)
8	Vasilyevite	$(Hg^{I}_{20.8}O_{6.9}I_{2.7}Br_{1.5}Cl_{0.8}(CO_3)_{0.9}S_{0.1}$	Gaines et al. (1997)
9	Vasilyevite	$(Hg^{I}_{2})_{10}O_6I_3Br_2Cl(CO_3)$	Roberts et al. (2003), Cooper and Hawthorne (2003)

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
	Minerals									
	Hg(I)									
1	Clearcreekite	6.760(4)	9.580(4)	10.931(4)		105.53(5)		4	P21/c	102.69
2	Clearcreekite	6.76	9.58	10.931		105.53		4	P21/c	102.69
3	Peterbaylissite	11.130(2)	11.139(3)	10.725(3)				8	Pcab	100.09
4	Peterbaylissite	11.130	11.139	10.725				8	Pcab	100.09
5	Szymańskiite	17.415(5)		6.011(4)				1	$P6_3$	950.77
6	Szymańskiite	17.3964(7)		6.0078(4)				1	$P6_3$	948.23
7	Szymańskiite	17.415		6.011				1	$P6_3$	950.77
8	Vasilyevite	9.344	10.653	18.265	93.262	90.548	115.422	2	P-1	493.30
9	Vasilyevite	9.344(2)	10.653(2)	18.265(4)	93.262(5)	90.548(4)	115.422(4)	2	P-1	493.30

	Name	Formula	Reference
	Hg(II)		
10	Mosesite	$Hg^{II}_{16}N_8Cl_3(SO_4)_{1.5}(MoO_4)_{0.5}(CO_3)_{0.5})•8(H_2O)$	Switzer et al. (1953)
11	Mosesite	$Hg^{II}_2NCl_{0.5}(SO_4)_{0.3}(MoO_4)_{0.1}(CO_3)_{0.1})•(H_2O)$	Gaines et al. (1997)
	Synthetic phases		
	Hg(I)		
12			
	Hg(II)		
13			

	Name	Cell Constants							Space Group	$V^{o\#}$ cm^3 gfw^{-1}
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
	Hg(II)									
10	Mosesite	9.524						1	(cubic)	520.25
11	Mosesite	9.524						8	(cubic)	65.031
	Synthetic phases									
	Hg(I)									
12										
	Hg(II)									
13										

[#]Calculated from cell constants, this work

Table 6. Carbonate Minerals containing greater than 10 wt.% Mercury*

Name	Formula	Mercury, wt.%	gfw	Thermodynamic Data	
				Est.	Meas.
Hg(I)					
Clearcreekite	$Hg^{I}_{3}(CO_3)(OH)•2(H_2O)$	83.72	694.86	no	no
Peterbaylissite	$Hg^{I}_{3}(CO_3)(OH)•2(H_2O)$	84.19	714.82	no	no
Szymańskiite	$Hg^{I}_{16}(Ni,Mg)_6(H_3O)_8(CO_3)_{12}•3(H_2O)$	72.34	4436.34	no	no
Vasilyevite	$(Hg^{I}_{2})_{10}O_6I_3Cl(CO_3)$	86.36	4836.00	no	no
Hg(II)					
Mosesite	$Hg_2N(Cl,SO_4,MoO_4,CO_3)•(H_2O)$	79.96	501.74	no	no

*Data taken primarily from a compilation given by the Mineralogy Database (http://webmineral.com).

References

Bennet, P. Phys. Chem., 38, 577, 1934. [Reference not traced]

Bilinski, H., Markovic, M. and Gessner, M. (1980). Solubility and equilibrium constants of mercury(II) in carbonate solutions (25°C, I = 0.5 mol dm^{-3}). Inorganic Chemistry, 19(11), 3440-3443.

Brodsky, A.E. (1929). Zur Elektrochemie des Mercuroions. Zeitschrift für Elektrochemie, 35(11), 833-637.

Clever, H.L. Johnson, S.A. and Derrick, M.E. (1985). The solubility of mercury and some sparingly soluble mercury salts in water and aqueous electrolyte solutions. Journal of Physical and Chemical Reference Data, vol. 14(3), p. 631-680.

Cooper, M.A. and Hawthorne, F.C. (2003). The crystal structure of vasilyevite, $(Hg_2)_{10}^{2+}O_6I_3(Br,Cl)_3(CO_3)$. Canadian Mineralogist, 41, 1173-1181.

CRC (1994). Handbook of Chemistry and Physics, 74th edition. CRC Press, Boca Raton, FL

Goskhimizdat. (1952). Chemical Reference, vol. 3. [In Russian]. (As cited in Zhuk, 1954).

Hepler, L.G. and Olofsson, G. (1975). Mercury. Thermodynamic properties, chemical equilibria, and standard potentials. Chemical Reviews, 75(5), 585-602.

Hietanen, S. and Högfeldt, E. (1976a). A potentiometric study of the solid phases in the systems mercury(I)-hydrogen carbonate and mercury(II)-hydrogen carbonate. Chemica Scripta, 9(1), 24-29.

Hietanen, S. and Högfeldt, E. (1976b). On the complex formation between mercury(II) and carbonate. Chemica Scripta, 10(1), 37-38.

Immerwahr, C. (1901). Electrochemical studies of the solubility of precipitates containing heavy metals. Zeitschrift fur Elektrochemie und angewandte physikalische Chemie, 7, 477-483.

Karapet'yants, M. Kh. (1953). Khimicheskaya Termodinamika (Chemical Thermodynamics). 2nd Edition. Goshkhimizdat. 611 p. [In Russian].

Karapet'yants, M. Kh. (1957). Investigation of specific methods for the comparative calculation of physico-chmical properties of different substances. Author's dissertation for a degree in chemical sciences, MKhTI im D.I. Mendeleeva. [In Russian].

Karapet'yants, M.Kh. and Karapet'yants, M.L. (1970). Thermodynamic constants of Inorganic and Organic Compounds (trans. By J. Schmorak). Humphrey Science Publishers, Ann Arbor, Michigan. 461 p.

Karpov, I.K., Kashik, S.A. and Pampura, V.D. (1968). Thermodynamic Constants for Calculations in Geochemistry and Petrology. Izdva, Nauka, 143 p. [In Russian].

Kelley, K.K. and Anderson, C.T. (1935). Theoretical metallurgy. IV. Metal carbonates-correlations and applications of thermodynamic properties. U.S. Bureau of Mines Bulletin No. 384, 73 p.

Kryukova, T.A. (1939). Polarographic determination of the solubilities of slightly soluble salts. Zhurnal Fizicheskoi Khimii, 13, 693-700. [In Russian].

Latimer, W.M. (1952). The Oxidation States of the Elements and their Potentials in Aqueous Solutions. Second edition. Prentice Hall, New York, 392 p.

Powell, K.J., Brown, P.L., Byrne, R.H., Gajda, T., Hefter, G., Sjoberg, S. and Wanner, H. (2005). Chemical speciation of environmentally significant heavy metals with inorganic ligands. Part 1: The Hg^{2+} – Cl^-, OH^-, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-} aqueous systems. Pure and Applied Chemistry, 77(4), 739-800.

Roberts, A.C., Ercit, T.S., Erd, R.C. and Oscarson, R.L. (1990). Szymańskiite, $Hg_{16}^{1+}(Ni,Mg)_6(CO_3)_{12}(OH)_{12}(H_3O)_8^{1+}•3H_2O$, a new mineral species from the Clear Creek claim, San Benito County, California. Canadian Mineralogist, 28, 703-707.

Roberts, A.C. and Williams, R.S. (1995). Peterbaylissite, $Hg^{1+}{}_3(CO_3)(OH)•2H_2O$, a new mineral species from the Clear Creek Claim, San Benito County, California. Canadian Mineralogist, 33, 47-53.

Roberts, A.C., Ercit, T.S., Groat, L.A., Criddle, A.J., Erd, R.C. and Williams, R.S. (1995). Peterbaylissite, $Hg_3^{1+}(CO_3)(OH).2H_2O$, a new mineral species from the Clear Creek Claim, San Benito County, California. Canadian Mineralogist, 33(1), 47-53.

Roberts, A.C., Groat, L.A., Raudsepp, M., Ercit, T.S., Erd, R.C., Moffatt, E.A. and Stirling, J.A.R. (2001). Clearcreekite, a new polymorph of $Hg^{1+}{}_3(CO_3)(OH)•2H_2O$, from the Clear Creek claim, San Benito County, California. Canadian Mineralogist, 39, 779-784.

Roberts, A.C., Cooper, M.A., Hawthorne, F.C., Stirling, J.A.R., Paar, W.H., Stanley, C.J., Dunning, G.E. and Burns, P.C. (2003). Vasilyevite, $(Hg_2)^{2+}{}_{10}O_6I_3Br_2Cl(CO_3)$, a new mineral species from the Clear Creek claim, San Benito County, California. Canadian Mineralogist, 41, 1167-1172.

Rossini F.D., Wagman D.D., Evans W.H., Levine S. and Jaffe I. (1952). Selected values of chemical thermodynamical properties. NBS Circular 500. 1268 p., Washington, D.C.

Saegusa, F. (1950). Thermodynamic studies on carbonates. Part I. Thermodynamic studies of cadmium, zinc, lead, mercurous, and thallous carbonates. Science Reports, Tohoku University, First Series, 34(1), 55-65.

Sanz, J., Raposo, J.C., de Diego, A. and Madariaga, J.M. (2002). Complexation of CH_3Hg^+ with chloride, sulfate and carbonate in NaClO4: construction of thermodynamic models. Applied Organometallic Chemistry, 16, 339-346.

Sinha, S.P. (2000). Theoretical investigation on structures and bonding of environmentally important mercury aquo ions and its complexes. Inorganic Reaction Mechanisms (Amsterdam), 2(1-2), 33-48. [Reference not examined, as library was unable to locate a copy.]

Smith, R.M. and Martell, A.E. (1976). Critical Stability Constants, Volume 4, Inorganic Complexes. Plenum Press: New York.

Stern, K.H. (2000). High Temperature Properties and Thermal Decomposition of Inorganic Salts with Oxyanions. 256 p. CRC Press LLC, 2000 N.W. Corporate Blvd., Boca Raton Florida 33431.

Switzer, G., Foshag, W.F., Murata, K.J. and Fahey, J.J. (1953). Re-examination of mosesite. American Mineralogist, 38(11-12), 1225-1234.

Szymanski, J.T. and Roberts, A.C. (1990). The crystal structure of szymańskiite, a partly ordered $(Hg-Hg)^{2+}$, $(Ni,Mg)^{2+}$ hydronium-carbonate-hydroxide-hydrate. Canadian Mineralogist, 28, 709-718.

Wagman, D.D., Evans, W.H., Parker, V.B., Halow, I., Bailey, S.M. and Schumm, R.H. (1968). Selected Values of Chemical Thermodynamic Properties. NBS Technical Note 270-3.

Wagman, D.D., Evans, W.H., Parker, V.B., Halow, I., Bailey, S.M. and Schumm, R.H. (1969). Selected Values of Chemical Thermodynamic Properties. Tables for elements 35 through 53 in the standard order of arrangement. NBS Technical Note 270-4, U.S. Department of Commerce, National Bureau of Standards, 141 p.

Weber, R. (1972). Lizentiatsarbeit (Leitung von H. Gamsjäger) Universität Bern. (Cited by Bilinski et al., 1980).

Wilcox. D.E. and Bromley, L.A. (1963). Computer Estimation of heat and free energy for simple inorganic compounds. Industrial and Engineering Chemistry, 55(7), 32-39.

Woods, T.L. and Garrels, R.M. (1987). Thermodynamic Values at Low Temperature for Natural Inorganic Materials. An Uncritical Summary. Oxford University Press. 242 p. plus references.

Zhuk, N.P. (1954). Thermodynamic constants of sulfates, carbonates, chromates, bromates, iodates, oxalates, and other salts slightly soluble in water. Zhurnal Fizicheskoi Khimii, 28, 1690-1697. [In Russian].

NICKEL

Table 1. Association Constants for Aqueous Carbonate Complexes in the System $NiO-CO_2-H_2O$

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
$Ni^{2+} + CO_3^{2-} = NiCO_3(aq)$	6.87		Estimate		Mattigod and Sposito (1977)
	4.2 ± 0.3	-			Baeyens et al. (2003)
	4.0 ± 0.3	-			Hummel et al. (2002)
	4.00 ± 0.30	-		Duro et al. (2006)	Hummel et al. (2002)
	4.7 ± 0.8	-	Estimated through correlation with corresponding Co aq. species		Hummel and Curti (2003)
	4.6 ± 0.8	-	Estimated through correlation with corresponding Zn aq. species		Hummel and Curti (2003)
$Ni^{2+} + 2CO_3^{2-} = Ni(CO_3)_2^{2-}$	10.11		Estimate		Mattigod and Sposito (1977)
	< 6.				Hummel et al. (2002)
	< 6.			Duro et al. (2006)	Hummel et al. (2002)
$Ni^{2+} + CO_3^{2-} + H^+ = NiHCO_3^+$	≈ 11.3*				Hummel et al. (2002)
	11.33*			Duro et al. (2006)	Hummel et al. (2002)
	< 12.3*				Baeyens et al. (2003)
	≤ 12.3*		Estimated using correlation plots		Hummel and Curti (2003)
$Ni^{2+} + HCO_3^- = NiHCO_3^+$	2.14		Estimate		Mattigod and Sposito (1977)
$NiCO_3(aq) + CO_3^{2-} = Ni(CO_3)_2^{2-}$	< 2.				Baeyens et al. (2003)
	< 2. - <3.5		Estimated using correlation plots		Hummel and Curti (2003)

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

* Corrected using bicarbonate dissociation equation from PHREEQC

Table 2. Solubility Constants of Solid Carbonates in the System $NiO-CO_2-H_2O$

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
Minerals					
Ni(II)					
Gaspeite					
$NiCO_3(s) = Ni^{2+} + CO_3^{2-}$					
	-6.87		estimated	Latimer (1952)	Ageno and Valla (1911)
	-6.87	-		Zhuk (1954)	Goskhimizdat (1952)
	-6.87	-	$I = 0$	Palmer and Van Eldik (1983)	Smith and Martell (1976)
	-11.2 ± 0.3	-		Grauer (1999)	Reiterer (1980)
	-11.2 ± 0.3	-		Hummel and Curti (2003)	Grauer (1999)
	-11.20 ± 0.30			Duro et al. (2006)	Hummel et al. (2002)
	-11.03 ± 0.18	-		Hummel and Curti (2003)	Wallner et al. (2002), Reiterer (1980)
		4.687 ± 6.491	Based on Sverjensky et al. (1997) approach		Duro et al. (2006)
$NiCO_3(s) + 2H+ = Ni^{2+} + CO_2 + H_2O$	11.28		25°C, $I = 0$. Note: value appears to be incorrectly transcribed.	Gamsjäger (1974)	Kelley and Anderson (1935)
	6.99 ± 0.12	-		Gamsjäger et al. (1998)	Reiterer (1980), Gamsjäger et al. (1982)
	7.22 ± 0.10		50°C, 1 *M* $NaClO_4$,	Gamsjäger (1985)	Reiterer (1980)
	7.12 ± 0.18	-		Wallner et al. (2002)	Gamsjäger et al. (1982)
$NiCO_3(s) + CO_2(g) + H_2O = Ni^{2} + 2HCO_3^-$	-4.38			Naumov et al. (1974)	Ageno and Valla (1911), Sillen and Martell (1964)
Hellyerite					
$NiCO_3•6(H_2O)(s) = Ni^{2+} + CO_3^{2-} + 6H_2O$	-7.51 ± 0.10	-		Hummel and Curti (2003)	Wallner et al. (2002), Gamsjäger et al. (2001)

Table 2. Solubility Constants of Solid Carbonates in the System $NiO-CO_2-H_2O$ (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
$NiCO_3•6(H_2O)(s) + 2H+ = Ni^{2+} + CO_2 + 7H_2O$	10.54 ± 0.10	-	T assumed to be 25°C. Re-interpretation of solubility measurements assumed to be of hellyerite instead of $NiCO_3$.	Wallner et al. (2002)	Ageno and Valla (1911), Mueller and Luber (1930)
	10.64 ± 0.10	-		Wallner et al. (2002)	Wallner et al. (2002), Gamsjäger et al. (2001)
Takovite					
$Ni_2Al^{III}(CO_3)_{0.5}(OH)_6•(H_2O) + 6H^+ = 2Mg^{2+} + Al^{3+} +0.5CO_3^{2-} + 7H_2O$	19.37 19.71 ± 0.34 20.37 20.34 ± 0.52	- - - -	*I* = 0, corrected using the Davies equation. *I* = 6.5 m*M* and 12.8 m*M*. Equilibration up to 147 days		Johnson and Glasser (2003)
$Ni_{0.69}Al_{0.31}(OH)_2(CO_3)_{0.16}•0.37(H_2O) + 2H^+ = 0.69Ni^{2+} + 0.31Al^{3+} +0.16CO_3^{2-} + 2.37H_2O$	2.24	-	Calculated from thermochemical data.		Allada et al. (2006)
$Ni_{0.67}Al_{0.33}(OH)_2(CO_3)_{0.165}•0.505(H_2O) + 2H^+ = 0.67Ni^{2+} + 0.33Al^{3+} +0.33CO_3^{2-} + 2.505H_2O$	4.20	-	Calculated from estimated ΔG_f^o for compound		Peltier et al. (2006)
Ni(III)					
Synthetic Phases					
Ni(II)					
Ni(III)					

(1) At standard state (25°C, 1 atm, *I* = 0), unless otherwise noted.

Table 3a. Association Constants of Aqueous Carbonate Complexes in the System NiO-CO_2-H_2O extracted from Databases of Distribution-of-Species Codes

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Database	Source
Ni(II)				
$Ni^{2+} + CO_3^{2-} = NiCO_3(aq)$	6.87	0	Minteq (2009)	
	4.5718	0	Minteq (2006)	NIST46.4; MTQ3.11
	-	-	Phreeqc (2009)	
	6.87	-	Wateq4f (2005)	
	4.2	-	ThermoChimie v.9	
	4.000	-	NAGRA/PSI (2001)	
	-	-	Data0.com.V8.R6+	
	-	-	Data0.YMP.R5	
	-	-	Thermoddem (2009)	
$Ni^{2+} + 2CO_3^{2-} = Ni(CO_3)_2^{2-}$	10.11	0	Minteq (2009)	
	-	-	Minteq (2006)	
	-	-	Phreeqc (2009)	
	10.11	-	Wateq4f (2005)	
	6.2	-	ThermoChimie v.9	
	6.000	-	NAGRA/PSI (2001)	
	-	-	Data0.com.V8.R6+	
	-	-	Data0.YMP.R5	
	-	-	Thermoddem (2009)	
$Ni^{2+} + CO_3^{2-} + H^+ = NiHCO_3^+$	12.47	0	Minteq (2009)	
	12.4199	0	Minteq (2006)	NIST46.4; MTQ3.11
	-	-	Phreeqc (2009)	
	11.73	-	ThermoChimie v.9	
$Ni^{2+} + HCO_3^{2-} = NiHCO_3^+$	2.14	-	Wateq4f (2005)	
	1.000	-	NAGRA/PSI (2001)	
	-	-	Data0.com.V8.R6+	
	-	-	Data0.YMP.R5	
	-	-	Thermoddem (2009)	
Ni(III)				
No entries				

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Table 3b. Solubility Constants of Solid Carbonates in the System NiO-CO_2-H_2O extracted from Databases of Distribution-of-Species Codes

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Database	Source
Gaspeite				
$NiCO_3(s) = Ni^{2+} + CO_3^{2-}$	-6.84	-9.94	Minteq (2009)	
	-6.87	-41.589	Minteq (2006)	
	-	-	Phreeqc (2009)	
	-6.840	-9.940	Wateq4f (2005)	
	-	-	ThermoChimie v.9	
	-11.200	-	NAGRA/PSI (2001)	
$NiCO_3(s) + H^+ = Ni^{2+} + CO_3^{2-}$	3.5118	-	Data0.com.V8.R6+	
	2.5700	-	Data0.YMP.R5	95Bar/Pla; 99Bin/Mil
	-	-	Thermoddem (2009)	
Hellyerite				
$NiCO_3$•$5.5(H_2O)(s) = Ni^{2+} + CO_3^{2-} + 5.5H_2O$	-	-	Minteq (2009)	
	-	-	Minteq (2006)	
	-	-	Phreeqc (2009)	
	-	-	Wateq4f (2005)	
	-7.52	-	ThermoChimie v.9	
	-	-	NAGRA/PSI (2001)	
	-	-	Data0.com.V8.R6+	
	-	-	Data0.YMP.R5	
	-	-	Thermoddem (2009)	

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Table 3c. Distribution-of-Species Codes: Database References

Database	Reference
Data0.com.V8.R6+	Wolery, T.J. (1994). EQ3NR, Letter report: EQ3/6 version 8.0. Differences from version 7. UCRL-ID-129749. Lawrence Livermore National Laboratory, Livermore, California. USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/LLNL.DAT
Data0.YMP.R5	BSC (Bechtel SAIC Company) (2007). Qualification of Thermodynamic Data for Geochemical Modeling of Mineral–Water Interactions in Dilute Systems. ANL-WIS-GS-000003 REV 01. Las Vegas, Nevada: Bechtel SAIC Company.DOC.20070619.0007.
MinteqA2	HydroGeoLogic, Inc. and Allison Geoscience Consultants, Inc. (1999). MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: User Manual Supplement for Version 4.0, Appendix A: thermodynamic database for MINTEQA2 V4.0, p. 44-74.
Minteq (2009)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/MINTEQ.DAT
Minteq (2006)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/minteq.v4.dat
NAGRA/PSI (2001)	Hummel, W., Berner, U., Curti, E., Pearson, F.J. and Thoenen, T. (2002). Nagra/PSI Chemical Thermodynamic Data Base 01/01. Universal Publishers/uPublish.com, Parkland, Florida. 565 p.
Phreeqc (2009)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/PHREEQC.DAT
ThermoChimie v.7.b	Duro, L., Grivém M. and Giffaut, E. (2010). ThermoChimie, the ANDRA thermodynamic database In Buckau G, Kienzler B, Duro L, Grivé M, Montoya V (eds). 2nd Annual Workshop Proceedings of the Collaborative Project “Redox Phenomena Controlling Systems” (7th EC FP CP Recosy) Larnaca (Cyprus) 16–19 March 2010. Karlsruhe: KIT Scientific Publishing, 275–283.
Thermoddem (2009)	Blanc P., Lassin A. and Piantone P. (2007) THERMODDEM a database devoted to waste minerals. BRGM (Orléans, France). For updates: http://thermoddem.brgm.fr
Wateq4f	Ball, J. W., & Nordstrom, D. K. (1991). User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters. U.S. GEOLOGICAL SURVEY, Open-File Report 91-183, Revised and reprinted - April, 2001. p. 81-94
Wateq4f (2005)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/WATEQ4F.DAT

Table 4a. Thermodynamic Properties of Nickel Carbonate Minerals and Synthetic Solid Carbonates: Gibbs Free Energies of Formation

Mineral Name	Formula	$\Delta G^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Minerals				
Ni(II)				
Gaspeite	$NiCO_3$	-615.05	Latimer (1952)	Ageno and Valla (1911)
		-615.05	Karpov et al. (1968)	Latimer (1952)
		-615.05	Karapet'yants and Karapet'yants (1970)	Latimer (1952)
		-615.0	Woods and Garrels (1987)	Latimer (1952)
		-613.79	Zhuk (1954)	Rossini et al. (1952), Karapet'yants (1953)
calculated		-613.75		Zhuk (1954)
		-613.75	Karpov et al. (1968)	Zhuk (1954)
		-613.75	Karapet'yants and Karapet'yants (1970)	Zhuk (1954)
		10.46[(1)]	Karpov et al. (1968)	Kireev (1964)
		-612.12	Naumov et al. (1974)	Ageno and Valla (1911), Sillen and Martell (1964)
		-612.54		Wagman et al. (1969)
		-612.1	Woods and Garrels (1987)	Naumov et al. (1974)
		-612.5	Woods and Garrels (1987)	Wagman et al. (1982)
		-628.359 ± 1.24		Tareen et al. (1991)
		-636.5 ± 1.4	Gamsjäger et al. (2001), Wallner et al. (2002)	Gamsjäger et al. (1998)
Hellyerite	$NiCO_3$•6(H_2O)	-2039.2 ± 1.1		Gamsjäger et al. (2001), Wallner et al. (2002)
Takovite				
CO_3(2:1), *synthesized*	$Ni_{0.64}Al_{0.36}(OH)_2[(CO_3)_{0.18}]$•$0.46H_2O$	-862.0		Peltier et al. (2006)
CO_3(2:1,h), *synthesized*	$Ni_{0.66}Al_{0.34}(OH)_2[(CO_3)_{0.17}]$•$0.42(H_2O)$	-851.4	-	Peltier et al. (2006)
CO_3(5:1), *synthesized*	$Ni_{0.67}Al_{0.33}(OH)_2[(CO_3)_{0.17}]$•$0.41(H_2O)$	-828.7	-	Peltier et al. (2006)
CO_3(2:1,h,Si), *synthesized*	$Ni_{0.65}Al_{0.35}(OH)_2[(CO_3)_{0.10}(H_3SiO_4)_{0.15}]$• $0.08(H_2O)$	-925.4	-	Peltier et al. (2006)

Table 4a. Thermodynamic Properties of Nickel Carbonate Minerals and Synthetic Solid Carbonates: Gibbs Free Energies of Formation (Continued)

Mineral Name	Formula	$\Delta G^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
estimated	$Ni_{0.67}Al_{0.33}(OH)_2[(CO_3)_{0.125}]\bullet 0.505(H_2O)$	-856.5	-	Peltier et al. (2006)
Zaratite	$Ni_3(CO_3)[?]$	-720.24	Stern (2000)	Barin (1989)
Synthetic Phases				
Ni(II)				

(1) Formation from the oxides

Table 4b. Thermodynamic properties of Nickel Carbonate Minerals and Synthetic Solid Carbonates: Enthalpies of Formation

Mineral Name	Formula	$\Delta H^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Minerals				
Ni(II)				
Gaspeite	$NiCO_3$	-685.34	Karpov et al. (1968)	Kelley and Anderson (1935)
		-685.34	Karapet'yants and Karapet'yants (1970)	Kelley and Anderson (1935)
		-664.00		Latimer (1952)
		-664.00	Karpov et al. (1968)	Latimer (1952)
		-664.00	Karapet'yants and Karapet'yants (1970)	Latimer (1952)
		-664.0	Woods and Garrels (1987)	Latimer (1952)
		-689.10	Zhuk (1954)	Rossini et al. (1952), Karapet'yants (1953)
		-689.10	Karpov et al. (1968)	Karapet'yants (1955)
		-689.10	Karapet'yants and Karapet'yants (1970)	Karapent'yants (1955)
		-711 ± 8		Yatsimirskii (1958)
		-711.28	Reznitskii (1961)	Yatsimirskii (1958)
		-711.28	Karpov et al. (1968)	Yatsimirskii (1958)
		-38.91[(1)]	Karpov et al. (1968)	Kireev (1964)
		-711.28	Karapet'yants and Karapet'yants (1970)	Yatsimirskii (1958)
calculated		-711.28		Reznitskii (1961)
		-711.28	Karapet'yants and Karapet'yants (1970)	Reznitskii (1961)
		-689.10	Naumov et al. (1974)	Ageno and Valla (1911), Sillen and Martell (1964)
		-689.1	Woods and Garrels (1987)	Naumov et al. (1974)
		-703.380 ± 1.24		Tareen et al. (1991)
		-713.4 ± 1.6		Gamsjäger et al. (2001), Wallner et al. (2002)
Hellyerite	$NiCO_3$•6(H_2O)	-2456.7 ± 3.1		Gamsjäger et al. (2001), Wallner et al. (2002)
Takovite. *synthesized*	$Ni_{0.69}Al_{0.31}(OH)_2(CO_3)_{0.16}$•0.37($H_2O$)	-918.42 ± 1.21		Allada et al. (2006)
synthesized	$Ni_{0.66}Al_{0.34}(OH)_2(CO_3)_{0.17}$•0.42($H_2O$)	-904.031 ± 0.93		Allada et al. (2006)

Table 4b. Thermodynamic properties of Nickel Carbonate Minerals and Synthetic Solid Carbonates: Enthalpies of Formation (Continued)

Mineral Name	Formula	$\Delta H^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
synthesized	$Ni_{0.77}Al_{0.23}(OH)_2(CO_3)_{0.12}$•0.33($H_2O$)	-838.18 ± 1.26		Allada et al. (2006)
synthesized	$Ni_{0.67}Al_{0.33}(OH)_2(CO_3)_{0.17}$•0.41($H_2O$)	-908.42 ± 2.06		Allada et al. (2006)
synthesized	$Ni_{0.64}Al_{0.36}(OH)_2(CO_3)_{0.18}$•0.46($H_2O$)	-942.41 ± 1.53		Allada et al. (2006)
CO_3(2:1), *synthesized*	$Ni_{0.64}Al_{0.36}(OH)_2[(CO_3)_{0.18}]$•0.46($H_2O$)	-987.30 ± 1.53	Peltier et al. (2006)	Allada et al. (2006)
CO_3(2:1,h), *synthesized*	$Ni_{0.66}Al_{0.34}(OH)_2[(CO_3)_{0.17}]$•0.42($H_2O$)	-950.57 ± 0.93	Peltier et al. (2006)	Allada et al. (2006)
CO_3(5:1), *synthesized*	$Ni_{0.67}Al_{0.33}(OH)_2[(CO_3)_{0.17}]$•0.41($H_2O$)	-930.47 ± 2.06	Peltier et al. (2006)	Allada et al. (2006)
CO_3(2:1,h,Si), *synthesized*	$Ni_{0.65}Al_{0.35}(OH)_2[(CO_3)_{0.10}(H_3SiO_4)_{0.15}]$•0.08($H_2O$)	-1132.27± 1.37		Peltier et al. (2006)
Zaratite	$Ni_3(CO_3)$[?]	-694.19	Stern (2000)	Barin (1989)
Synthetic Phases				
Ni(II)				
$Ni(HCO_3)_2$	$Ni(HCO_3)_2$	-1447.66 ± 62.76	Estimated value for fictive compound	Wilcox and Bromley (1963)
$Ni(HCO_3)_2$	$Ni(HCO_3)_2$	-1447.66	Karapet'yants and Karapet'yants (1970)	Wilcox and Bromley (1963)

(1) Formation from the oxides

Table 4c. Thermodynamic Properties of Nickel Carbonate Minerals and Synthetic Solid Carbonates: Entropies

Mineral		$S^0_{P_r,T_r}$	Secondary Reference	Primary Reference
Name	Formula	J K^{-1} gfw^{-1}		
Minerals				
Ni(II)				
Gaspeite *estimated*	$NiCO_3$	91.63		Latimer (1952)
		91.63	Karpov et al. (1968)	Latimer (1952)
		91.6	Woods and Garrels (1987)	Latimer (1952)
		90.37	Zhuk (1954)	Rossini et al. (1952), Karapet'yants (1953)
calculated		90.79		Zhuk (1954)
		90.79	Karpov et al. (1968)	Zhuk (1954)
		90.79	Karapet'yants and Karapet'yants (1970)	Zhuk (1954)
		90.37	Karpov et al. (1968)	Karapet'yants (1955)
		91.63	Karapet'yants and Karapet'yants (1970)	Latimer (1952)
		90.37	Karapet'yants and Karapet'yants (1970)	Karapet'yants (1953)
		85.4		Kostryukov and Kalinkina (1964)
		85.52 ± 1.67	Naumov et al. (1974)	Kostryukov and Kalinkina (1964)
		85.4 ± 2.0	Robie and Hemingway (1995)	Kostryukov and Kalinkina (1964)
		85.5	Woods and Garrels (1987)	Naumov et al. (1974)
Hellyerite	$NiCO_3.6(H_2O)$	343 ± 10.		Gamsjäger et al. (2001), Wallner et al. (2002)
Zaratite	$Ni_3(CO_3)$[?]	86.19	Stern (2000)	Barin (1989)
Synthetic Phases				
Ni(II)				

Table 5. Crystallographic Properties of Nickel Carbonate Minerals and Synthetic Solid Carbonates

	Name	Formula	Reference
	Minerals		
	Ni(II)		
1	Carrboydite	$Ni_{6.50}Cu_{0.40}Al_{4.80}(SO_4)_{2.30}(CO_3)_{0.48}(OH)_{21.69}•3.67(H_2O)$	Nickel and Clarke (1976)
2	Carrboydite	$Ni_{13}Cu_1Al_9(SO_4)_4(CO_3)_2(OH)_{43}•7(H_2O)$, assumed	Gaines et al. (1997)
3	Carrboydite	$Ni_{10}Cu_4Al_9(SO_4)_4(CO_3)_2(OH)_{43}•7(H_2O)$	Mineralogy Database (http://webmineral.com/)
4	Comblainite	$Ni^{II}_6Co^{III}_2(CO_3)(OH)_{16}•4(H_2O)$	Gaines et al. (1997)
5	Comblainite	$Ni^{II}_6Co^{III}_2(CO_3)(OH)_{16}•4(H_2O)$	Piret and Deliens(1980)
6	Gaspeite	$NiCO_3$	Graf (1961)
7	Gaspeite	$NiCO_3$	Pertlik (1986)
8	Gaspeite	$Ni_{0.6}Mg_{0.3}Fe^{II}_{0.1}(CO_3)$	Gaines et al. (1997)
9	Glaukosphaerite	$(Cu_{1.5}Ni_{0.5})(CO_3)(OH)_2$	Gaines et al. (1997)
10	Glaukosphaerite	$(Cu_{1.5}Ni_{0.5})(CO_3)(OH)_2$	Mineralogy Database (http://webmineral.com/)

	Name	Cell Constants							Space Group	$V^{o\#}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		$cm^3\ gfw^{-1}$
	Minerals									
	Ni(II)									
1	Carrboydite	9.14		10.34				1	hex	450.05
2	Carrboydite	9.14		10.34				1/2	hex	901.00
3	Carrboydite	18.28		20.68				4	hex	901.00
4	Comblainite	6.08		45.58				3	R-3m,	292.92
5	Comblainite	3.038		22.79				3/8	R-3m, R3m, R32, R-3, or R3	292.53
6	Gaspeite	4.5975		14.723				6	R3c	27.050
7	Gaspeite	4.6117(5)		14.735(2)				6	R3c	27.240
8	Gaspeite	4.621		14.93				6	R3c	27.712
9	Glaukosphaerite	9.35	11.97	3.13		96		4	$P2_1/a$	52.451
10	Glaukosphaerite	9.34	11.93	3.07		90.0		4	$P2_1/a$	51.501

	Name	Formula	Reference
11	Glaukosphaerite	$(Cu_{1.5}Ni_{0.5})(CO_3)(OH)_2$	Perchiazzi and Merlino (2006)
12	Hellyerite	$NiCO_3•6(H_2O)$	Gaines et al. (1997), after Threadgold (1963)?
13	Kambaldaite	$NaNi_4(CO_3)_3(OH)_3•3(H_2O)$	Engelhardt et al. (1985), Nickel and Robinson (1985)
14	Nullaginite	$Ni_2(CO_3)(OH)_2$	Gaines et al. (1997), Nickel and Berry (1981)
15	Omsite	$(Ni_{1.1}Cu_{0.7}Mg_{0.2})Fe^{III}(OH)_6[Sb(OH)_6$	Mills et al. (2012)
16	Otwayite	$Ni_2(CO_3)(OH)_2•(H_2O)$	Gaines et al. (1997), Nickel et al. (1977)
17	Paraotwayite	$Ni(OH)_{1.5}(SO_4)_{0.125}(CO_3)_{0.125}$	Gaines et al. (1997)
18	Reevesite	$Ni_6Fe^{III}_2(CO_3)(OH)_{16}•4(H_2O)$	Gaines et al. (1997), de Waal and Viljoen (1971)
19	Szymanskiite	$Hg^{I}_{16}(Ni_{1.5}Mg_{0.5})(H_3O)_8(CO_3)_{12}•3(H_2O)$	Gaines et al. (1997)
20	Takovite	$Ni_6Al_2(OH)_{16}(CO_3,OH)•4(H_2O)$	Gaines et al. (1997)

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
11	Glaukosphaerite	12.0613(4)	9.3653(4)	3.1361(1)		90.085(5)		4	$P2_1/a$	53.333
12	Hellyerite	10.770	7.30	19.68		94.0		8	C2/c	116.19
13	Kambaldaite	10.340(3)		6.097(2)				1	P6-3	169.98
14	Nullaginite	9.236(3)	12.001(6)	3.091(2)		90.48(7)		4	$P2_1/m$ or $P2_1$	51.580
15	Omsite	5.3506(8)		19.5802(15)				2	P-3	146.18
16	Otwayite	10.18	27.4	3.22				8	Orthorh	67.611
17	Paraotwayite	7.89	2.96	13.63		91.1		6	Pm	319.44
18	Reevesite	6.614(3)		45.54(2)				3	R-3m	346.32
19	Szymanskiite	17.3964(7)		6.0078(4)				1	$P6_3$	948.23
20	Takovite	6.04		45.16				3	R-3m	286.41

	Name	Formula	Reference
21	Takovite	$Ni_6Al_2(OH)_{16}(CO_3,OH)•4(H_2O)$	Bish and Brindley (1977)
22	Takovite	$Ni_6Al_2(OH)_{16}(CO_3,OH)•4(H_2O)$	Mills et al. (2012)
23	Widgiemoolthalite	$(Ni_{4.6}Mg_{0.4})(CO_3)_4(OH)_2•5(H_2O)$	Gaines et al. (1997), Nickel et al. (1993)
24	Zaratite*	$Ni_3(CO_3)(OH)_4•4(H_2O)$	Mineralogy Database (http://webmineral.com/)
	Synthetic Phases		
	Ni(II)		
25			

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
21	Takovite	3.0250(1)		22.595(3)				3/8	hex	287.55
22	Takovite	3.0290(2)		22.5995(15)				3/8	R-3m	288.37
23	Widgiemoolthalite	10.06(17)	8.75(5)	8.32(4)		114.3(8)		2	$P2_1/c$	200.99
24	Zaratite*	6.16						1	Isomet	140.76
	Synthetic Phases									
	Ni(II)									
25										

*See Garcia-Guinea et al. (2014) regarding the validity of this mineral

#Calculated from cell constants, this work

Table 6. Carbonate Minerals containing greater than 10 wt.% Nickel*

Name	Formula	Nickel, wt.%	gfw	Thermodynamic Data	
				Est.	Meas.
Carrboydite	$(Ni,Cu)_{14}Al_9(SO_4,CO_3)_6(OH)_{43}•7(H_2O)$	24.00	2445.61	No	No
Comblainite	$Ni^{II}_6Co^{III}_2(CO_3)(OH)_{16}•4(H_2O)$	40.28	874.19	No	No
Gaspeite	$(Ni,Mg,Fe^{II})CO_3$	32.58	108.10	No	yes
Glaukosphaerite	$(Cu,Ni)_2(CO_3)(OH)_2$	13.42	218.69	No	No
Hellyerite	$NiCO_3•6(H_2O)$	25.88	226.79	No	yes
Kambaldaite	$NaNi_4(CO_3)_3(OH)_3•3(H_2O)$	43.25	542.85	No	No
Nullaginite	$Ni_2(CO_3)(OH)_2$	55.52	211.40	No	No
Otwayite	$Ni_2(CO_3)(OH)_2•(H_2O)$	51.16	229.42	No	No
Paraotwayite	$\mathbf{Ni}(OH)_{2-x}(SO_4,CO_3)_{0-5x}$ x =.5	56.59	103.71	No	No
Reevesite	$Ni_6Fe^{III}_2(CO_3)(OH)_{16}•4(H_2O)$	40.57	868.02	No	No
Takovite	$Ni_6Al_2(OH)_{16}(CO_3,OH)•4(H_2O)$	44.04	799.54	yes	yes
Widgiemoolthalite	$(Ni,Mg)_5(CO_3)_4(OH)_2•4\text{-}5(H_2O)$	34.41	596.99	No	No
Zaratite	$Ni_3(CO_3)(OH)_4•4(H_2O)$	46.81	376.17	No	Yes?

*Data taken primarily from a compilation given by the Mineralogy Database (http://webmineral.com).

References

Ageno, F. and Valla, E. (1911). Contributo allo studio dell'idrolisi. I. Idrolisi dei carbonate. Atti della Accademia Nazionale dei Lincei, Classe di Scienze Fisiche, Matematiche e Naturali, Rendiconti, 20(II), 706-12.

Allada, R.K., Peltier, E., Navrotsky, A., Casey, W.H., Johnson, A., Thompson-Berbeco, H. and Sparks, D.L. (2006). Calorimetric determination of the enthalpies of formation of hydrotalcite-like solids and their use in the geochemical modeling of metals in natural waters. Clays and Clay Minerals, 54(4), 409-417.

Baeyens, B., Bradbury, M.H. and Hummel, W. (2003). Determination of aqueous nickel–carbonate and nickel–oxalate complexation constants. Journal of Solution Chemistry, 32(4), 319-339.

Barin, I. (1989). Thermochemical Data of Pure Substances. Wiley-VCH Velagsgesellschaft, Weinheim, Germany. 1836 p.

Bish, D.L. and G.W. Brindley (1977). A reinvestigation of takovite, a nickel aluminum hydroxy-carbonate of the pyroaurite group. American Mineralogist, 62, 458-464.

de Waal, S.A. and Viljoen, E.A. (1971). Nickel minerals from Barberton, South Africa: IV. Reevesite, a member of the hydrotalcite group. American Mineralogist, 56, 1077-1081.

Duro, L., Grivé, M., Cera, E., Domènech, C. and Bruno, J. (2006). Update of a thermodynamic database for radionuclides to assist solubility limits calculation for performance assessment. Swedish Nuclear Fuel and Waste Management Co., Stockholm, Sweden. 128 p.

Engelhardt, L.M., Hall, S.R. and White, A.H. (1985). Crystal Structure of kambaldaite, $Na_2Ni_8(CO_3)_6(OH)_6(H_2O)_6$. American Mineralogist, 70, 423-427.

Gaines, R.V., Skinner, H.C.W., Foord, E.E., Mason, B., Rosenzweig, A. King, V.T. and Dowty, E. (1997). Dana's New Mineralogy (Eighth edition). John Wiley and Sons, Inc., New York. 1819 p.

Gamsjäger, H. (1974). Wechselwirkung von Metalloxiden, -hydroxiden, -carbonaten und -sulfiden mit Wasser. Radex-Rundschau, 4, 274-285.

Gamsjäger, H. (1985). Solid state chemical model for the solubility behavior of homogeneous solid cobalt manganese carbonate mixtures. Berichte der Bunsen-Gesellschaft, 89(12), 1318-1322.

Gamsjäger, H., Reiterer, F. and Heindl, R. (1982). Solubility constants and free enthalpies of metal sulfides and carbonates. Berichte der Bunsen-Gesellschaft, physikalische Chemie, 86(11), 1046-1049.

Gamsjäger, H., Königsberger, E. and Preis, W. (1998). Solubilities of metal carbonates. Pure and Applied Chemistry, 70(10), 1913-1920.

Gamsjäger, H., Preis, W., and Wallner, H. (2001). Solid-solute phase equilibria in aqueous solutions XIV. Thermodynamic analysis of the solubility of hellyerite in water. Monatshefte für Chemie, 132(3), 411-415.

Garcia-Guinea, J., La Iglesia, A., Crespo-Feo, E., Del Tánago, J.G. and Correcher, V. (2014). The status of zaratite: investigation of the type specimen from Cape Ortegal, Galicia, Spain. European Journal of Mineralogy, 25(6), 995-1004.

Goskhimizdat. (1952). Chemical Reference, vol. 3. [In Russian]. (As cited in Zhuk, 1954).

Graf, D.L. (1961). Crystallographic tables for the rhombohedral carbonates. American Mineralogist, 46, 1283-1316.

Grauer, R. (1999). Solubility products of M(II)-Carbonates [edited and translated by U. Berner]. Paul Scherrer Institute, Waste Management Laboratory, PSI Bericht Nr. 99-04, ISSN 1019-0643, 24 p.

Hummel, W., Berner, U., Curti, E., Pearson, F.J. and Thoenen, T. (2002). Nagra/PSI Chemical Thermodynamic Data Base 01/01. Universal Publishers/uPublish.com, Parkland, Florida. 565 p.

Hummel, W. and Curti, E. (2003). Nickel Aqueous Speciation and Solubility at Ambient Conditions: A Thermodynamic Elegy. Monatshefte für Chemie, 134, 941-973.

Johnson, C.A., and Glasser, F.P. (2003). Hydrotalcite-like minerals ($M_2Al(OH)_6(CO_3)_{0.5}.XH_2O$, where M = Mg, Zn, Co, Ni) in the environment: synthesis, characterization and thermodynamic stability. Clays and Clay Minerals, 51(1), 1-8.

Karapet'yants, M. Kh. (1953). Khimicheskaya Termodinamika (Chemical Thermodynamics). 2nd Edition. Goshkhimizdat. 611 p. [In Russian].

Karapet'yants, M. Kh. (1955). Approximate method for the calculation of the isobaric potential and heat of formation of different substances. Trudy Instituta - Moskovskii Khimiko-Tekhnologicheskii Institut imeni D. I. Mendeleeva, No. 20, 10-28

Karapet'yants, M.Kh. and Karapet'yants, M.L. (1970). Thermodynamic constants of Inorganic and Organic Compounds (trans. By J. Schmorak). Humphrey Science Publishers, Ann Arbor, Michigan. 461 p.

Karpov, I.K., Kashik, S.A. and Pampura, V.D. (1968). Thermodynamic Constants for Calculations in Geochemistry and Petrology. Izdva, Nauka, 143 p. [In Russian].

Kelley, K.K. and Anderson, C.T. (1935). Theoretical metallurgy. IV. Metal carbonates-correlations and applications of thermodynamic properties. U.S. Bureau of Mines Bulletin No. 384, 73 p.

Kireev, V.A. (1964). Acid-base properties of oxides. Zhurnal Fizicheskoi Khimii, 38(8), 1881-1894. [In Russian].

Kostryukov, V.N. and Kalinkina, I.N. (1964). Heat capacity and entropy for manganese, iron, cobalt, and nickel carbonates at low temperatures. Zhurnal Fizicheskoi Khimii, 38, 780-781. [In Russian].

Latimer, W.M. (1952). The Oxidation States of the Elements and their Potentials in Aqueous Solutions. Second edition. Prentice Hall, New York, 392 p.

Mattigod, S.V. and Sposito, G. (1977). Estimated association constants for some complexes of trace metals with inorganic ligands. Soil Science Society of America Journal, 41(6), 1092-1097.

Mills, S.J., Kampf, A.R., Housley, R.M., Favreau, G., Pasero, M., Biagioni, C., Merlino, S., Berbain, C. and Orlandi, P. (2012). Omsite, $(Ni,Cu)_2Fe^{3+}(OH)_6[Sb(OH)_6]$, a new member of the cualstibite group from Oms, France. Mineralogical Magazine, 76(5), 1347-1354.

Mills, S.J., Whitfield, P.S., Kampf, A.R., Wilson, S.A., Dipple, G.M., Raudsepp, M. and Favreau, G. (2012). Contribution to the crystallography of hydrotalcites: the crystal structures of woodallite and takovite. Journal of Geosciences, 57(4), 273-279.

Müller, E., and A. Luber (1930). Über die Dissoziation der Kohlensäure und über ihre Einwirkung auf metallisches Nickel unter Druck. Zeitschrift für anorganische und allgemeine Chemie, 187, 209-230.

Naumov, G.B., Ryzhenko, B.N. and Khodakovsky, I.L. (1974). Handbook of Thermodynamic Data. Natl. Tech. Inf. Service, 722176A, U.S. Dept. Commerce. 328 p.

Nickel, E.H. and Clarke, R.M. (1976). Carrboydite, a hydrated sulfate of nickel and aluminum: a new mineral from Western Australia. American Mineralogist, 61, 366-372.

Nickel, E.H., Robinson, B.W. and Davis, C.E.S. (1977). Otwayite, a new nickel mineral from Western Australia. American Mineralogist, 62, 999-1002.

Nickel, E.H. and Berry, L.G. (1981). The new mineral nullaginite and additional data on the related minerals rosasite and glaukosphaerite. Canadian Mineralogist, 19, 315-324.

Nickel, E.H. and Robinson, B.W. (1985). Kambaldaite; a new hydrated Ni-Na carbonate mineral from Kambalda, Western Australia. American Mineralogist, 70(3-4), 419-422.

Nickel, E.H., Robinson, B.W. and Mumme, W.G. (1993). Widgiemoolthalite: the new nickel analogue of hydromagnesite from Western Australia. American Mineralogist, 78, 819-821.

Palmer, D.A. and van Eldik, R. (1983). The chemistry of metal carbonato and carbon dioxide complexes. Chemical Reviews, 83, 651-731.

Peltier, E. Allada, R., Navrotsky, A. and Sparks, D.L. (2006). Nickel solubility and precipitation in soils: A thermodynamic study. Clays and Clay Minerals, 54(2), 153-164.

Perchiazzi, N. and Merlino, S. (2006). The malachite-rosasite group: crystal structures of glaukosphaerite and pokrovskite. European Journal of Mineralogy, 18(6), 787-792.

Pertlik, F. (1986). Structures of hydrothermally synthesized cobalt (II) carbonate and nickel (II) carbonate. Acta Crystallographica Section C: Crystal Structure Communications, 42(1), 4-5.

Piret, P. and Deliens, M. (1980). La comblainite, $((Ni_x^{2+},Co_{1-x}^{3+})(OH)_2)(CO_3)_{(1-x)/2}$. yH_2O, nouveau mineral du groupe de la pyroaurite. Bulletin de Mineralogie, 103(1), 113-117.

Reiterer, F. (1980). Löslichkeitskonstanten und Freie Bildungsenthalpien neutraler Übergangsmetallcarbonate: $MnCO_3$, $FeCO_3$, $CoCO_3$, $NiCO_3$, $CuCO_3$, $ZnCO_3$. PhD Thesis, Montanuniversität Leoben, Austria.

Robie, R.A. and Hemingway B.S. (1995). Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 Pa) pressure and at higher temperatures. U.S. Geological Survey Bulletin No. 2131.

Rossini, F.D., Wagman, D.D., Evans, W.H., Levine, S. and Jaffe, I. (1952). Selected values of chemical tbermodynamical properties. NBS Circular 500. 1268 p., Washington, D.C.

Reznitskii, L.A. (1961). Approximate method for calculating the heats of formation of inorganic compounds Zhurnal Fizicheskoi Khimii, 35, p. 1853-. [In Russian].

Sillen., L.G. and Martell, A.E. (1964). Stability Constants of Metal-ion Complexes. Special Publication No. 17, The Chemical Society, London. 754 p.

Smith, R.M. and Martell, A.E. (1976). Critical Stability Constants, Volume 4, Inorganic Complexes. Plenum Press: New York.

Stern, K.H. (2000). High Temperature Properties and Thermal Decomposition of Inorganic Salts with Oxyanions. 265 p. CRC Press LLC, 2000 N.W. Corporate Blvd., Boca Raton Florida 33431.

Sverjensky, D.A., Shock, E.L. and Helgeson, H.C. (1997). Prediction of the thermodynamic properties of aqueous metal complexes to 1,000°C and 5kb. Geochimica et Cosmochimica Acta, 61(7), 1359-1412.

Tareen, J.A.K., Fazeli, A.R., Basavalingu, B. and Bhandage, G.T. (1991). Hydrothermal decomposition curves and thermodynamic data for spherocobaltite ($CoCO_3$) and gaspeite ($NiCO_3$). European Journal of Mineralogy, 3, 501-505.

Threadgold, I.M. (1963). The crystal structure of hellyerite and nacrite. Thesis (Ph.D.), University of Wisconsin – Madison. Dissertation Abstracts, 24(1), 252-253.

Wagman, D.D., Evans, W.H., Parker, V.B., Halow, I., Bailey, S.M. and Schumm, R.H. (1969). Selected Values of Chemical Thermodynamic Properties. Tables for elements 35 through 53 in the standard order of arrangement. NBS Technical Note 270-4, U.S. Department of Commerce, National Bureau of Standards, 141 p.

Wagman, D.D., Evans, W.H., Parker, V.B., Schumm, R.H., Halow, I., Bailey, S.M., Churney, K.L. and Nuttall, R.L. (1982). The NBS Tables of Chemical Thermodynamic Properties: Selected Values for Inorganic and C1 and C2 Organic Substances in SI Units. American Chemical Society and the American Institute of Physics for the National Bureau of Standards (Journal of Phys. Chemical Reference Data, 11, supp. 2, 392 p.).

Wallner H, Preis W. and Gamsjäger, H. (2002). Solid–solute phase equilibria in aqueous solutions XV [1]. Thermodynamic analysis of the solubility of nickel carbonates. Thermochimica Acta, 382, 289-296.

Wilcox. D.E. and Bromley, L.A. (1963). Computer Estimation of heat and free energy for simple inorganic compounds. Industrial and Engineering Chemistry, 55(7), 32-39.

Woods, T.L. and Garrels, R.M. (1987). Thermodynamic Values at Low Temperature for Natural Inorganic Materials. An Uncritical Summary. Oxford University Press. 242 p. plus references.

Yatsimirskii, K.B. (1958). Thermochemistry of transition metal compounds and the crystal field theory. Zhurnal Neorganicheskoi Khimii, 3, 2244-2252. [In Russian].

Zhuk, N.P. (1954). Thermodynamic constants of sulfates, carbonates, chromates, bromates, iodates, oxalates, and other salts slightly soluble in water. Zhurnal Fizicheskoi Khimii, 28, 1690-1697. [In Russian].

THALLIUM

Table 1. Association Constants for Aqueous Carbonate Complexes in the System $Tl_2O/TlO/Tl_2O_3$-CO_2-H_2O

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
Tl(II)					
$Tl^{2+} + CO_3^{2-} = TlCO_3(aq)$	2.16				Xiong (2007)
$Tl^{2+} + CO_3^{2-} + H^+ = TlHCO_3^+$	11.23				Xiong (2007)

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Table 2. Solubility Constants of Solid Carbonates in the System $Tl_2O/TlO/Tl_2O_3$-CO_2-H_2O

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
Minerals					
Tl(I)					
Tl(II)					
Tl(III)					
Synthetic phases					
Tl(I)					
Tl(II)					
Tl(III)					
Tl_2CO_3					
$Tl_2CO_3 = 2Tl^+ + CO_3^{2-}$	-2.658	-	Calculated from solubility. No correction for activity coefficients.		Kelley and Anderson (1935) after Lamy (not cited)
	-3.89	-	From electrochemical cell data		Saegusa (1950)

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Table 3a. Association Constants of Aqueous Carbonate Complexes the System $Tl_2O/TlO/Tl_2O_3$-CO_2-H_2O extracted from Databases of Distribution-of-Species Codes

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Reference	Comments
Tl(I)				
	No data	No data		
Tl(II)				
	No data	No data		
Tl(III)				
	No data	No data		

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Table 3b. Solubility Constants of Solid Carbonates in the System Tl_2O/Tl_2O_3-CO_2-H_2O extracted from Databases of Distribution-of-Species Codes

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Database	Source
Tl(I)				
Tl_2CO_3				
$Tl_2CO_3 = 2Tl^+ + CO_3^{2-}$	-3.8482	33.56	Minteq (2009)	
	-3.8367	35.49	Minteq (2006)	
	-	-	Phreeqc (2009)	
			Wateq4f (2005)	
			ThermoChimie v.7.b	
	-	-	NAGRA/PSI (2001)	
			Data0.YMP.R5	
			Thermoddem (2009)	
Tl(II)				
	No data	No data		
Tl(III)				
	No data	No data		

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Table 3c. Distribution-of-Species Codes: Database References

Database	Reference
Data0.com.V8.R6+	Wolery, T.J. (1994). EQ3NR, Letter report: EQ3/6 version 8.0. Differences from version 7. UCRL-ID-129749. Lawrence Livermore National Laboratory, Livermore, California. USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/LLNL.DAT
Data0.YMP.R5	BSC (Bechtel SAIC Company) (2007). Qualification of Thermodynamic Data for Geochemical Modeling of Mineral–Water Interactions in Dilute Systems. ANL-WIS-GS-000003 REV 01. Las Vegas, Nevada: Bechtel SAIC Company.DOC.20070619.0007.
MinteqA2	HydroGeoLogic, Inc. and Allison Geoscience Consultants, Inc. (1999). MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: User Manual Supplement for Version 4.0, Appendix A: thermodynamic database for MINTEQA2 V4.0, p. 44-74.
Minteq (2009)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/MINTEQ.DAT
Minteq (2006)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/minteq.v4.dat
NAGRA/PSI (2001)	Hummel, W., Berner, U., Curti, E., Pearson, F.J. and Thoenen, T. (2002). Nagra/PSI Chemical Thermodynamic Data Base 01/01. Universal Publishers/uPublish.com, Parkland, Florida. 565 p.
Phreeqc (2009)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/PHREEQC.DAT
ThermoChimie v.7.b	Duro, L., Grivém M. and Giffaut, E. (2010). ThermoChimie, the ANDRA thermodynamic database In Buckau G, Kienzler B, Duro L, Grivé M, Montoya V (eds). 2nd Annual Workshop Proceedings of the Collaborative Project “Redox Phenomena Controlling Systems” (7th EC FP CP Recosy) Larnaca (Cyprus) 16–19 March 2010. Karlsruhe: KIT Scientific Publishing, 275–283.
Thermoddem (2009)	Blanc P., Lassin A. and Piantone P. (2007) THERMODDEM a database devoted to waste minerals. BRGM (Orléans, France). For updates: http://thermoddem.brgm.fr
Wateq4f	Ball, J. W., & Nordstrom, D. K. (1991). User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters. U.S. GEOLOGICAL SURVEY, Open-File Report 91-183, Revised and reprinted - April, 2001. p. 81-94
Wateq4f (2005)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/WATEQ4F.DAT

Table 4a. Thermodynamic Properties of Thallium Carbonate Minerals and Synthetic Solid Carbonates: Gibbs Free Energies of Formation

Mineral		$\Delta G^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
Minerals				
Tl(I)				
Tl(II)				
Tl(III)				
Synthetic phases				
Tl(I)				
$TlCu(OH)CO_3$	$TlCu(OH)CO_3$			
$Tl_2Cu(CO_3)_2$	$Tl_2Cu(CO_3)_2$			
$TlCr^{III}(CO_3)_2$	$TlCr^{III}(CO_3)_2$			
$Tl_3Cr^{III}(CO_3)_3$	$Tl_3Cr^{III}(CO_3)_3$			
$Tl_3V(CO_3)_3$	$Tl_3V(CO_3)_3$			
Tl(II)				
Tl(III)				
Tl_2CO_3	Tl_2CO_3			
		-615.05		Saegusa (1950)
		-615.05	Karpov et al. (1968)	Saegusa (1950)
		-615.05	Karapet'yants and Karapet'yants (1970)	Saegusa (1950)
		-624.25	Karpov et al. (1968)	Karapet'yantz (1957)
		-624.25	Karapet'yants and Karapet'yants (1970)	Karapet'yantz (1957)

Table 4b. Thermodynamic properties of Thallium Carbonate Minerals and Synthetic Solid Carbonates: Enthalpies of Formation

Mineral		$\Delta H^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
Minerals				
Tl(I)				
Tl(II)				
Tl(III)				
Synthetic phases				
Tl(I)				
Tl_2CO_3	Tl_2CO_3	-699.44		De Forcrand (1927)
		-699.85		Saegusa (1950)
		-699.85	Karpov et al. (1968)	Saegusa (1950)
		-699.849	Karapet'yants and Karapet'yants (1970)	Saegusa (1950)
		-703.33 ± 7.11		Gattow (1958)
		-703.33	Karapet'yants and Karapet'yants (1970)	Gattow (1958)
		-703.33	Karpov et al. (1968)	Karapet'yantz and Karapet'yantz (1961)
		-700.0	Stern (2000)	Tompkins (1976)
$TlHCO_3$	$TlHCO_3$	-736.38 ± 62.76	Estimated value for fictive compound	Wilcox and Bromley (1963)
		-736.38	Karapet'yants and Karapet'yants (1970)	Wilcox and Bromley (1963)
$TlCu(OH)CO_3$	$TlCu(OH)CO_3$			
$Tl_2Cu(CO_3)_2$	$Tl_2Cu(CO_3)_2$			
$TlCr(CO_3)_2$	$TlCr(CO_3)_2$			
$Tl_3Cr(CO_3)_3$	$Tl_3Cr(CO_3)_3$			
$Tl_3V(CO_3)_3$	$Tl_3V(CO_3)_3$			

Table 4c. Thermodynamic properties of Thallium Carbonate Minerals and Synthetic Solid Carbonates: Entropies

Mineral		$S^0_{P_r,T_r}$	Secondary Reference	Primary Reference
Name	Formula	J K^{-1} gfw^{-1}		
Minerals				
Tl(I)				
Tl(II)				
Tl(III)				
Synthetic phases				
Tl(I)				
Tl_2CO_3	Tl_2CO_3	158.57 ± 10.46		Saegusa (1950)
		158.57	Karpov et al. (1968)	Saegusa (1950)
		158.57	Karapet'yants and Karapet'yants (1970)	Saegusa (1950)
		143.51		Gattow (1958)
		143.51	Karapet'yants and Karapet'yants (1970)	Gattow (1958)
		143.51	Karpov et al. (1968)	Karapet'yantz and Karapet'yantz (1961)
		155.2	Stern (2000)	Tompkins (1976)
$TlCu(OH)CO_3$	$TlCu(OH)CO_3$			
$Tl_2Cu(CO_3)_2$	$Tl_2Cu(CO_3)_2$			
$TlCr(CO_3)_2$	$TlCr(CO_3)_2$			
$Tl_3Cr(CO_3)_3$	$Tl_3Cr(CO_3)_3$			
$Tl_3V(CO_3)_3$	$Tl_3V(CO_3)_3$			

Table 5. Crystallographic Properties of Thallium Carbonate Minerals and Synthetic Solid Carbonates

	Name	Formula	Reference
	Minerals		
	Tl(I)		
1			
	Tl(II)		
2			
	Tl(III)		
3			

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
	Minerals									
	Tl(I)									
1										
	Tl(II)									
2										
	Tl(III)									
3										

	Name	Formula	Reference
	Synthetic phases		
	Tl(I)		
4	$TlCu(OH)CO_3$	$TlCu(OH)CO_3$	Adam and Zheng (1994)
5	$Tl_2Cu(CO_3)_2$	$Tl_2Cu(CO_3)_2$	Ehrhardt et al. (1981)
6	$TlCr^{III}(CO_3)_2$	$TlCr^{III}(CO_3)_2$	Ehrhardt et al. (1981)
7	$Tl_3Cr^{III}(CO_3)_3$	$Tl_3Cr^{III}(CO_3)_3$	Ehrhardt et al. (1981)
8	$Tl_3V^{III}(CO_3)_3$	$Tl_3V^{III}(CO_3)_3$	Ehrhardt et al. (1981)
	Tl(I)		
9			
	Tl(III)		
10			

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
	Synthetic phases									
	Tl(I)									
4	$TlCu(OH)CO_3$	10.849(1)		6.118(1)				6	$P6_3/m$	62.592
5	$Tl_2Cu(CO_3)_2$	7.583(1)	9.799(1)	9.119(1)		111.51(1)		4	$P2_1/c$	94.911
6	$TlCr(CO_3)_2$	19.917(7)	8.605(3)	19.138(5)		104.79(3)		24	$P2_1/c$	79.576
7	$Tl_3Cr(CO_3)_3$									
8	$Tl_3V(CO_3)_3$									
	Tl(I)									
9										
	Tl(III)									
10										

[#]Calculated from cell constants, this work

Table 6. Carbonate Minerals containing greater than 10 wt.% Thallium

Name	Formula	gfw	Thermodynamic Data	
			Est.	Meas.
No entries				

References

Adam, A. and Zheng, Y.Q. (1994). $TlCu(OH)CO_3$ - Ein neues basisches Thallium-Kupfer-Carbonat. Zeitschrift für anorganische und allgemeine Chemie, 620, 1707-1713.

de Forcrand, R. (1927). Investigations on thallium carbonates. Comptes Rendus de l'Academie des Sciences de Paris, 184, 987-990.

Ehrhardt, H., Lemor, R. and Seidel, H. (1981). Hochdrucksynthesen von Carbonaten. V [l]. Carbonatdarstellungen durch Schmelzreaktionen unter hohen CO_2-Drücken. Zeitschrift für anorganische und allgemeine Chemie, 477, 183-195.

Gattow, G. (1958). Zur Thermochemie von Tl_2CO_3 und Tl_2CS_3. Naturwissenschaften, 45, 623.

Karapet'yants, M.Kh. (1955). Approximate method for the calculation of the isobaric potential and heat of formation of different substances. Trudy Instituta - Moskovskii Khimiko-Tekhnologicheskii Institut imeni D. I. Mendeleeva, No. 20, p. 10-28. [In Russian].

Karapet'yants, M. Kh. (1957). Investigation of specific methods for the comparative calculation of physico-chmical properties of different substances. Author's dissertation for a degree in chemical sciences, MKhTI im D.I. Mendeleeva. [In Russian].

Karapet'yants, M.Kh. and Karapet'yants, M.L. (1961). Tablitsy nekotorykh termodinamicheskikh svoistv razlichnykh veshestv (Tables of Certain Thermodynaic parameters of Different Substances). Trudy MKhTI im D.I. Mendeleeva, vol. 34. [In Russian].

Karapet'yants, M.Kh. and Karapet'yants, M.L. (1970). Thermodynamic constants of Inorganic and Organic Compounds (trans. By J. Schmorak). Humphrey Science Publishers, Ann Arbor, Michigan. 461 p.

Karpov, I.K., Kashik, S.A. and Pampura, V.D. (1968). Thermodynamic Constants for Calculations in Geochemistry and Petrology. Izdva, Nauka, 143 p. [In Russian].

Kelley, K.K. and Anderson, C.T. (1935). Theoretical metallurgy. IV. Metal carbonates-correlations and applications of thermodynamic properties. U.S. Bureau of Mines Bulletin No. 384, 73 p.

Saegusa, F. (1950a). Thermodynamic studies on carbonates. Part I. Thermodynamic studies of cadmium, zinc, lead, mercurous, and thallous carbonates. Science Reports. Tohoku University, First Series, 34(1), 55-65.

Stern, K.H. (2000). High Temperature Properties and Thermal Decomposition of Inorganic Salts with Oxyanions. 256 p. CRC Press LLC, 2000 N.W. Corporate Blvd., Boca Raton Florida 33431.

Tompkins, D.A. (1976). Decomposition reactions. In Reactivity of Solids, Treatise on Solid State Chemistry, vol. 4 (Hannay, N.B., Ed.), Plenum Press, New York.

Wllcox. D.E. and Bromley, L.A. (1963). Computer Estimation of heat and free energy for simple inorganic compounds. Industrial and Engineering Chemistry, 55(7), 32-39.

Xiong, Y. (2007). Hydrothermal thallium mineralization up to 300°C: A thermodynamic approach. Ore Geology Reviews, 32, 291-313.

URANIUM

Table 1a. Association Constants Aqueous Carbonate Complexes in the System $UO_2/U_2O_5/UO_3$-CO_2-H_2O

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
U(IV)					
$U^{4+} + 5CO_3^{2-} = U(CO_3)_5^{6-}$	-	-	Evidence for the existence of, preparative	Krishnamurty et al. (1970)	Rosenheim and Kelmy (1932)
	-	-	Evidence for the existence of, solubility	Krishnamurty et al. (1970)	McClaine et al. (1956)
	-	-	Evidence for the existence of, spectrophotometry	Krishnamurty et al. (1970)	Golovnya et al. (1960)
	-	-	Evidence for the existence of, preparative, excess HCO_3^- and CO_3^{2-}	Krishnamurty et al. (1970)	Stabrovskii (1960)
		-20 ± 4	25ºC, 3 *M* $(Na,H)ClO_4$		Grenthe et al. (1984b)
	31.29				Rai et al. (1998)
	32.3 ± 1.4		Recalculation	Guillaumont et al. (2003)	Rai et al. (1998)
`	34.1 ± 1	-20 ± 4		Duro et al. (2006)	Hummel et al. (2002), Grenthe et al. (1992)
	34.0 ± 0.9			Duro et al. (2006)	Guillaumont et al. (2003)
$U^{4+} + 2CO_3^{2-} + 2OH^- = U(OH)_2(CO_3)_2^{2-}$	41.33				Rai et al. (1998)
	42.2		Recalculation	Guillaumont et al. (2003)	Rai et al. (1998)
$U^{4+} + 4CO_3^{2-} + 2OH^- = U(OH)_2(CO_3)_4^{6-}$	-	-	Evidence for the existence of, preparative, excess CO_3^{2-}	Krishnamurty et al. (1970)	Rosenheim and Kelmy (1932)
$U^{4+} + 4CO_3^{2-} = U(CO_3)_4^{4-}$	-	-	Evidence for the existence of, preparative, excess CO_3^{2-}	Krishnamurty et al. (1970)	Golovnya et al. (1960)
	35.22 ± 1.03			Duro et al. (2006)	Hummel et al. (2002), Grenthe et al. (1992)
	35.12 ± 0.93			Duro et al. (2006)	Guillaumont et al. (2003)
$U(CO_3)_4^{4-} + CO_3^{2} = U(CO_3)_5^{6-}$	-1.12 ± 0.25	-	25ºC, *I* = 0		Bruno et al. (1989)

Table 1a. Association Constants Aqueous Carbonate Complexes in the System $UO_2/U_2O_5/UO_3$-CO_2-H_2O (Continued)

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
$U(CO_3)_5^{6-} + 0.5O_2(g) + H_2O = UO_2(CO_3)_3^{4-} + 2HCO_3^-$		-170 ± 8	25ºC, 3 *M* $(Na,H)ClO_4$		Grenthe et al. (1984b)
U(V)					
$UO_2^+ + 3CO_3^{2-} = UO_2(CO_3)_3^{5-}$	13.3 ± 0.4		25°C, 3.0 *M* ClO_4^-		Ferri et al. (1983)
	6.95 ± 0.36			Capdevila and Vitorge (1999)	Capdevila and Vitorge (1990) and Capdevila (1992)
$2U^VO_2(CO_3)_3^{5-} + 4HCO_3^- = U^{VI}O_2(CO_3)_3^{4-} + U^{IV}(CO_3)_5^{6-} + 2\ CO_3^{2-} + 2H_2O$	4.98 ± 0.07		25°C, 3.0 *M* ClO_4^-		Ferri et al. (1983)
$(U^{VI}O_2)(CO_3)_2^{4-} + e^- = (U^VO_2)(CO_3)_2^{5-}$	-	-	Polarography in 3 *M* $NaClO_4$		Ferri et al. (1983)
$(U^{VI}O_2)(CO_3)_2^{4-} + e^- = (U^VO_2)(CO_3)_2^{5-}$	-	-	Polarography and spectrophotometry 0.01 *M* $Na_4[UO_2(CO_3)_2]$ and 1 *M* Na_2CO_3		Mizuguchi et al. (1993)
U(VI)					
$UO_2^{2+} + CO_3^{2-} = UO_2CO_3(aq)$	9.87		25°C, *I* = 0		Sergeeva et al. (1972a)
	10.18		50°C, *I* = 0		Sergeeva et al. (1972a)
	9.87		*I* = 0	Kramer-Schnabel et al. (1992)	Sergeeva et al. (1972a)
	2.78		*I* = 0.22-0.36	Palmer and Van Eldik (1983)	Almagro et al. (1973)
	2.23		*I* = 0.40-0.53	Palmer and Van Eldik (1983)	Almagro et al. (1973)
	10.09		25ºC, *I* = 3 x 10^{-4}. pH-metric and soly. methods		Pirozhkov and Nikolaeva (1976)
	10.09		25ºC, *I* = 3 x 10^{-4}	Kramer-Schnabel et al. (1992)	Pirozhkov and Nikolaeva (1976)
	9.87			Palmer and Van Eldik (1983)	Babinets et al. (1977)
	9.0		0.1 *M* $NaNO_3$	Kramer-Schnabel et al. (1992)	Scanlan (1977)
	10.1		25°C, *I* = 0?		Langmuir (1978)

Table 1a. Association Constants Aqueous Carbonate Complexes in the System $UO_2/U_2O_5/UO_3$-CO_2-H_2O (Continued)

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	9.14 ± 0.23				Ciavatta et al. (1979)
	9.02		I = 3	Palmer and Van Eldik (1983)	Ciavatta et al. (1979)
	9.02		3 M $NaClO_4$	Kramer-Schnabel et al. (1992)	Ciavatta et al. (1979)
	10.1 ± 0.4		25°C, I = 0		Lemire and Tremaine (1980)
	10.2 ± 0.5		60°C, I = 0, modified Crlss-Cobble entropy extrapolation		Lemire and Tremaine (1980)
	10.6 ± 0.7		100°C, I = 0, modified Crlss-Cobble entropy extrapolation		Lemire and Tremaine (1980)
	12 ± 1		150°C, I = 0, modified Crlss-Cobble entropy extrapolation		Lemire and Tremaine (1980)
	13 ± 1		200°C, I = 0, modified Crlss-Cobble entropy extrapolation		Lemire and Tremaine (1980)
	9.5 ± 0.2		I = 0		Grenthe et al. (1984a)
	8.3	-	0.5 M $NaClO_4$	Kramer-Schnabel et al. (1992)	Grenthe et al. (1984a)
	8.3	-	3 M $NaClO_4$	Kramer-Schnabel et al. (1992)	Grenthe et al. (1984a)
	9.94	-	25ºC	Götz et al. (2011)	Grenthe et al. (1992)
	9.63		25ºC, I = 0	Kimura et al. (1992)	Grenthe et al. (1992)?
	8.70 ± 0.04		25°C, $P(CO_2)$ = 1.0, 0.1 $NaClO_4$		Kramer-Schnabel et al. (1992)
	9.23 ± 0.04		25ºC, 0.1 M $NaClO_4$		Meinrath and Kimura (1993a)
	9.65 ± 0.08				Meinrath et al. (1996a)
	9.97 ± 0.05		22 ± 2ºC. Recalculation	Guillaumont et al. (2003)	Pashalidis et al. (1997)
	10.27 ± 0.05		25ºC, I = 0	Nitzsche et al. (2000)	Meinrath et al. (1999)
	9.67 ± 0.05			Duro et al. (2006)	Hummel et al. (2002), Grenthe et al. (1992)
	9.94 ± 0.03			Duro et al. (2006)	Guillaumont et al. (2003)
	9.94		25ºC, I = 0	Berto et al. (2012)	Guillaumont et al. (2003)

Table 1a. Association Constants Aqueous Carbonate Complexes in the System $UO_2/U_2O_5/UO_3$-CO_2-H_2O (Continued)

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	9.89	-	10ºC, calculated value		Götz et al. (2011)
	9.98	-	40ºC, calculated value		Götz et al. (2011)
	10.05	-	60ºC, calculated value		Götz et al. (2011)
$UO_2^{2+} + CO_2(g) + H_2O(l) = UO_2CO_3(aq) + 2H^+$	9.02 ± 0.03	-	EMF, 3 *M* $NaClO_4$		Ciavatta et al. (1979)
	10.042				Lemire and Tremaine (1980)
	9.67 ± 0.05		As revised in Appendix D	Silva et al. (1995)	Grenthe et al. (1992)
	10.122				Redkin and Wood (2007)
$UO_2^{2+} + tCO_3^{2-} = (UO_2CO_3)_t$ t = 1-3	9.5 ± 0.2		*I* = 0		Grenthe et al. (1984a)
$UO_2^{2+} + 2CO_3^{2-} + 2H_2O = [UO_2(CO_3)_2(H_2O)_2]^{2-}$	14.60		*I* = 0		McClaine et al. (1956)
$UO_2^{2+} + 2CO_3^{2-} = UO_2(CO_3)_2^{2-}$	14.6		*I* = 0	Palmer and Van Eldik (1983)	McClaine et al. (1956)
	14.6		*I* = 0	Kramer-Schnabel et al. (1992)	McClaine et al. (1956)
	15.57		*I* = 0.2	Palmer and Van Eldik (1983)	Babko et al. (1960)
	15.57		0.2 *M* NH_4NO_3	Kramer-Schnabel et al. (1992)	Babko et al. (1960)
	14.57	-	Sol., *I* = 0.2 *M*.	Krishnamurty et al. (1970)	Babko and Kodenskaya (1960),
	16.16		25°C, *I* = 0.1	Langmuir (1978)	Tsymball (1969)
	17.6		Corrected, 25°C, *I* = 0	Langmuir (1978)	Tsymball (1969)
	16.16		*I* = 0.1	Palmer and Van Eldik (1983)	Tsymball (1969)
	16.16		0.1 *M* $NaClO_4$	Kramer-Schnabel et al. (1992)	Tsymball (1969)
	16.7		25°C, *I* = 0	Kramer-Schnabel et al. (1992)	Sergeeva et al. (1972a)

Table 1a. Association Constants Aqueous Carbonate Complexes in the System $UO_2/U_2O_5/UO_3$-CO_2-H_2O (Continued)

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	16.95		50°C, I = 0		Sergeeva et al. (1972a)
	16.7		I = 0	Kramer-Schnabel et al. (1992)	Sergeeva et al. (1972a)
	4.03		I = 0.03-0.18	Palmer and Van Eldik (1983)	Almagro et al. (1973)
	14.7; 16.7			Palmer and Van Eldik (1983)	Babinets et al. (1977)
	16.22	-	20ºC, Solv. Extn, 0.1 M $NaNO_3$		Scanlan (1977)
	16.22		20ºC, I = 0.1	Langmuir (1978)	Scanlan (1977)
	17.1		Corrected, I = 0	Langmuir (1978)	Scanlan (1977)
	16.2		20ºC, I = 0.1	Palmer and Van Eldik (1983)	Scanlan (1977)
	16.22		0.1 M $NaNO_3$	Kramer-Schnabel et al. (1992)	Scanlan (1977)
	17.1 ± 0.4		25°C, I = 0		Lemire and Tremaine (1980)
	17.4 ± 0.4		60°C, I = 0, modified Crlss-Cobble entropy extrapolation		Lemire and Tremaine (1980)
	18 ± 1		100°C, I = 0, modified Crlss-Cobble entropy extrapolation		Lemire and Tremaine (1980)
	18 ± 1		150°C, I = 0, modified Crlss-Cobble entropy extrapolation		Lemire and Tremaine (1980)
	19 ± 2		200°C, I = 0, modified Crlss-Cobble entropy extrapolation		Lemire and Tremaine (1980)
	16.15		0.1 M $NaClO_4$	Kramer-Schnabel et al. (1992)	Maya (1982)
	16.6 ± 0.2		I = 0		Grenthe et al. (1984a)
	15.36		0.5 M $NaClO_4$	Kramer-Schnabel et al. (1992)	Grenthe et al. (1984a)
	16.2		3 M $NaClO_4$	Kramer-Schnabel et al. (1992)	Grenthe et al. (1984a)
	16.94 ± 0.12				Grenthe et al. (1992)
	17.0		25ºC, I = 0	Kimura et al. (1992)	Grenthe et al. (1992)?

Table 1a. Association Constants Aqueous Carbonate Complexes in the System $UO_2/U_2O_5/UO_3$-CO_2-H_2O (Continued)

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	16.61		25ºC	Götz et al. (2011)	Grenthe et al. (1992)
	16.33 ± 0.07		25°C, P(CO_2) = 1.0, *I* = 0.1 $NaClO_4$		Kramer-Schnabel et al. (1992)
	15.38 ± 0.17		25ºC, 0.1 *M* $NaClO_4$		Meinrath and Kimura (1993a)
	16.3 ± 0.8				Meinrath et al. (1996a)
	16.5 ± 0.2		22 ± 2ºC, Recalculation	Guillaumont et al. (2003)	Pashalidis et al. (1997)
	16.7 ± 0.4		25ºC, *I* = 0	Nitzsche et al. (2000)	Meinrath et al. (1999)
	16.9 ± 0.12			Duro et al. (2006)	Hummel et al. (2002), Grenthe et al. (1992)
	16.61 ± 0.09			Duro et al. (2006)	Guillaumont et al. (2003)
	16.61		25ºC, *I* = 0	Berto et al. (2012)	Guillaumont et al. (2003)
	16.681				Redkin and Wood (2007)
	16.44	-	10ºC, calculated value		Götz et al. (2011)
	16.77	-	40ºC, calculated value		Götz et al. (2011)
	17.04	-	60ºC, calculated value		Götz et al. (2011)
$UO_2^{2+} + 2CO_3^{2-} = 1/3(UO_2)_3(CO_3)_6^{6-}$		-20.5 ± 0.9	25ºC, 3 *M* (Na,H)ClO_4		Grenthe et al. (1984b)
$UO_2(CO_3)_2^{2-} = 1/3(UO_2)_3(CO_3)_6^{6-}$		-35.1	25ºC, 3 *M* (Na,H)ClO_4		Grenthe et al. (1984b)
$UO_2^{2+} + 3CO_3^{2-} = UO_2(CO_3)_3^{4-}$	18.3	-	Thermodynamic data	Cinnéide et al. (1975)	Bullwinkel (1954)
	18.30		*I* = 0		McClaine et al. (1956)
	18.3			Palmer and Van Eldik (1983)	Bullwinkel (1954), McClaine et al. (1956)
	18.3		*I* = 0	Kramer-Schnabel et al. (1992)	McClaine et al. (1956)
	22.77	-	1.0 *M* NH_4Cl	Cinnéide et al. (1975)	Klygin and Smirnova (1959)
	22.77	-	1 *M* NH_4Cl	Kramer-Schnabel et al. (1992)	Klygin and Smirnova (1959)

Table 1a. Association Constants Aqueous Carbonate Complexes in the System $UO_2/U_2O_5/UO_3$-CO_2-H_2O (Continued)

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	22.8		I = 1	Palmer and Van Eldik (1983)	Klygin et al. (1959)
	20.7	-			Babko and Kondenskaya (1960)
	20.7	-	0.2 M NH_4NO_3	Cinnéide et al. (1975)	Babko and Kondenskaya (1960)
	20.7	-	0.2 M NH_4NO_3	Kramer-Schnabel et al. (1992)	Babko and Kondenskaya (1960)
	20.7	-	Sol., I = 0.2 M.	Krishnamurty et al. (1970)	Babko and Kodenskaya (1960)
	20.7		I = 0.2	Palmer and Van Eldik (1983)	Babko and Kondenskaya (1960)
	23.0	-	0.5 M $NaNO_3$	Cinnéide et al. (1975)	Paramonova and Nikolaeva (1962)
	23.0		I = 0.5	Palmer and Van Eldik (1983)	Paramonova and Nikolaeva (1962)
	21.57		25°C, I = 0.1	Langmuir (1978)	Tsymball (1969)
	21.57		I = 0.1	Palmer and Van Eldik (1983)	Tsymball (1970)
	21.57		0.1 M $NaClO_4$	Kramer-Schnabel et al. (1992)	Tsymball (1970)
	21.4		25°C, I = 0	Langmuir (1978)	Sergeyeva et al. (1972)
	7.71		I = 0.1-0.29	Palmer and Van Eldik (1983)	Almagro et al. (1973)
	21.54 ± 0.03		20ºC, Solv. Extn., I = 0.1 M $NaNO_3$		Cinnéide et al. (1975)
	21.54		25°C, I = 0.1	Langmuir (1978)	Cinnéide et al. (1975)
	21.54		I = 0.1	Palmer and Van Eldik (1983)	Cinnéide et al. (1975)
	21.54		20ºC, 0.1 M $NaNO_3$	Kramer-Schnabel et al. (1992)	Cinnéide et al. (1975)
	21.7		20°C, I = 0.1	Langmuir (1978)	Scanlan (1977)
	21.4		Corrected, 25°C, I = 0	Langmuir (1978)	Cinnéide et al. (1975), Tsymball (1969), Scanlan (1977),

Table 1a. Association Constants Aqueous Carbonate Complexes in the System $UO_2/U_2O_5/UO_3$-CO_2-H_2O (Continued)

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	21.4			Palmer and Van Eldik (1983)	Babinets et al. (1977)
		-40.3	25°C, *I* = 0	Lemire and Tremaine (1980)	Devina et al. (1977), Langmuir (1978)
	21.70		0.1 *M* $NaNO_3$	Kramer-Schnabel et al. (1992)	Scanlan (1977)
	21.4 ± 0.4		25°C, *I* = 0		Lemire and Tremaine (1980)
	21.0 ± 0.3		60°C, *I* = 0, modified Crlss-Cobble entropy extrapolation		Lemire and Tremaine (1980)
	21.3 ± 0.3		100°C, *I* = 0, modified Crlss-Cobble entropy extrapolation		Lemire and Tremaine (1980)
	22.4 ± 0.3		150°C, *I* = 0, modified Crlss-Cobble entropy extrapolation		Lemire and Tremaine (1980)
	24.0 ± 0.4		200°C, *I* = 0, modified Crlss-Cobble entropy extrapolation		Lemire and Tremaine (1980)
	22.81		0.1 *M* $NaClO_4$	Kramer-Schnabel et al. (1992)	Maya (1982)
	22.6 ± 0.1		25°C, 3.0 *M* $NaClO_4$		Ferri et al. (1983)
	21.3 ± 0.2		*I* = 0		Grenthe et al. (1984a)
	21.46		0.5 *M* $NaClO_4$	Kramer-Schnabel et al. (1992)	Grenthe et al. (1984a)
	22.61		1 *M* $NaClO_4$	Kramer-Schnabel et al. (1992)	Grenthe et al. (1984a)
		-35.9 ± 0.8	25ºC, 3 *M* $(Na,H)ClO_4$		Grenthe et al. (1984b)
	21.60 ± 0.05				Grenthe et al. (1992)
	21.63		25ºC, *I* = 0	Kimura et al. (1992)	Grenthe et al. (1992)?
	21.84		25ºC	Götz et al. (2011)	Grenthe et al. (1992)
	23.92 ± 0.03		25°C, $P(CO_2)$ = 1.0, 0.1 $NaClO_4$		Kramer-Schnabel et al. (1992)
	21.86 ± 0.05		25ºC, 0.1 *M* $NaClO_4$		Meinrath and Kimura (1993a)

Table 1a. Association Constants Aqueous Carbonate Complexes in the System $UO_2/U_2O_5/UO_3$-CO_2-H_2O (Continued)

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	21.74 ± 0.44				Meinrath et al. (1996a)
	21.6 ± 0.3		22 ± 2ºC. Recalculation	Guillaumont et al. (2003)	Pashalidis et al. (1997)
	21.57 ± 0.70		Using laser inducedphotoacoustic spectroscopy (LIPAS)		Geipel et al. (1998a)
	22.9 ± 0.3		25ºC, *I* = 0	Nitzsche et al. (2000)	Meinrath et al. (1999)
	21.6 ± 0.05			Duro et al. (2006)	Hummel et al. (2002), Grenthe et al. (1992)
	21.84 ± 0.04			Duro et al. (2006)	Guillaumont et al. (2003)
	21.84		25ºC, *I* = 0	Berto et al. (2012)	Guillaumont et al. (2003)
	21.326				Redkin and Wood (2007)
	21.95	-	10ºC, calculated value		Götz et al. (2011)
	21.29	-	40ºC, calculated value		Götz et al. (2011)
	30.75	-	60ºC, calculated value		Götz et al. (2011)
$UO_2(CO_3)(aq) + HCO_3^- = UO_2(CO_3)_2^{2-} + H^+$	1.4		*I* = 0. Stoichiometry of reaction in Palmer and Van Eldik (1983) not balanced. Source reference refers to dissolution of solid phase, See Table 2.	Palmer and Van Eldik (1983)	McClaine et al. (1956)
$[UO_2(CO_3)_2(H_2O)_2]^{2-} + 2HCO_3^- = [UO_2(CO_3)3]_4^- + CO_2(g) + 3H_2O$	1.81		*I* = 0		McClaine et al. (1956)
$UO_2(CO_3)_2^{2-} + HCO_3^- = UO_2(CO_3)_3^{4-} + H^+$	1.8		*I* = 0. Stoichiometry of reaction in Palmer and Van Eldik (1983) not balanced	Palmer and Van Eldik (1983)	McClaine et al. (1956)
$UO_2^{2+} + CO_3^{2-} + H_2O = UO_2(OH)(CO_3)_2^- + H^+$	4.1		*I* = 0.1. Stoichiometry of reaction in Palmer and Van Eldik (1983) not balanced	Palmer and Van Eldik (1983)	Tsymball (1970)
$3UO_2^{2+} + CO_3^{2-} + 3OH^- = (UO_2)_3CO_3(OH)_3^+$	16.34		*I* = 3	Palmer and Van Eldik (1983)	Ciavatta et al. (1979)

Table 1a. Association Constants Aqueous Carbonate Complexes in the System $UO_2/U_2O_5/UO_3$-CO_2-H_2O (Continued)

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
$(UO_2)_3(OH)_5^+ + 9CO_3^{2-} + 5H^+ = 3UO_2(CO_3)_3^{4-} + 5H_2O$	80.4		Stoichiometry of reaction in Palmer and Van Eldik (1983) not balanced	Palmer and Van Eldik (1983)	Cleveland (1970)
$(UO_2)_3(CO_3)_6^{6-} + 3CO_2 + 3H_2O = 3UO_2(CO_3)_3^{4-} + 6H^+$	-41.5 ± 0.1		*I* = 3. Stoichiometry of reaction in Palmer and Van Eldik (1983) not balanced	Palmer and Van Eldik (1983)	Ferri et al. (1981)
$(UO_2)_3(CO_3)_6^{6-} + 6HCO_3^- = 3UO_2(CO_3)_3^{4-} + 3CO_2 + + 3H_2O$	6.4 ± 0.1		*I* = 3. Stoichiometry of reaction in Palmer and Van Eldik (1983) not balanced	Palmer and Van Eldik (1983)	Ciavatta et al. (1981)
$3UO_2(CO_3)_3^4 = (UO_2)_3(CO_3)_6^{6-} + 3CO_3^{2-}$	-11.3 ± 0.1		25ºC, 3 *M* $NaClO_4$		Grenthe et al. (1996)
$2UO_2(CO_3)_3^4 + UO_2(CO_3)_3^4 = (UO_2)_3(CO_3)_6^{6-} + 3CO_3^{2-}$	-11.3 ± 0.1		25ºC, 3 *M* $NaClO_4$		Grenthe et al. (1996)
$UO_2(CO_3)_2^{2-} + CO_3^{2-} = UO_2(CO_3)_3^{4-}$	3.77			Palmer and Van Eldik (1983)	Bullwinkel (1954)
	3.5		*I* = 2	Palmer and Van Eldik (1983)	Blake et al. (1956)
	5.48	-	20ºC, Spec., 0.1 *M* $NaNO_3$,		Scanlan (1977)
	5.48		*I* = 0.1	Palmer and Van Eldik (1983)	Scanlan (1977)
	6.20 ± 0.11		recalculated	Bidoglio et al. (1991)	Grenthe et al. (1984a), Grenthe et al. (1992)
	4.49				Sergeyeva et al. (1989)
	6.35 ± 0.05		25ºC, 0.5 *M* $NaClO_4$,		Bidoglio et al. (1991)
	-	-	Ligand exchange kinetics at variable T using ^{13}C NMR in 1 *M* $NaClO_4$		Brücher et al. (1991)
$UO_2(CO_3)_3^{4-} + 3H^+ = (UO_2)_3(CO_3)_6^{6-} + 3HCO_3^-$	12.4 ± 0.7				Allen et al. (1995)

Table 1a. Association Constants Aqueous Carbonate Complexes in the System $UO_2/U_2O_5/UO_3$-CO_2-H_2O (Continued)

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
$3UO_2(CO_3)_3^{4-} + 6H^+ = (UO_2)_3(CO_3)_6^{6-} + 3CO_2(g) + 3H_2O$	-41.5		3 *M* $NaClO_4$	Kramer-Schnabel et al. (1992)	Hietanen and Sillen (1959)
$3UO_2^{2+} + 6CO_3^{2-} = (UO_2)_3(CO_3)_6^{6-}$	53.4 ± 0.8		I = 0		Grenthe et al. (1984a)
	53.91				Grenthe et al. (1992)
	53.88			Redkin and Wood (2007)	Grenthe et al. (1992) and Shock et al. (1997)
	55.6 ± 0.5				Allen et al. (1995)
	54 ± 1			Duro et al. (2006)	Hummel et al. (2002), Grenthe et al. (1992)
$UO_2(OH)_3^- + 3HCO_3^- = UO_2(CO_3)_3^{4-} + 3H_2O$	7.2 ± 0.5				Geipel et al. (1998b)
$UO_2^{2+} + CO_2(g) + 2H_2O(l) = UO_2CO_2(OH)_2(aq) + 2H^+$	-8.71 ± 0.05		25ºC, 0.50 *M* $NaClO_4$		Grenthe and Lagerman (1991)
$UO_2^{2+} + 3CO_2(g) + 6H_2O(l) = UO_2(CO_2)_3(OH)_6^{4-} + 6H^+$	-29.45 ± 0.08		25ºC, 0.50 *M* $NaClO_4$		Grenthe and Lagerman (1991)
$11UO_2^{2+} + 6CO_2(g) + 24H_2O(l) = (UO_2)_{11}(CO_2)_6(OH)_{24}^{2-} + 24H^+$	-72.48 ± 0.31		25ºC, 0.50 *M* $NaClO_4$		Grenthe and Lagerman (1991)
$2UO_2^{2+} + CO_3^{2-} + 3H_2O(l) = (UO_2)_2CO_3(OH)_3^- + 3H^+$	-0.86 ± 0.5			Duro et al. (2006)	Hummel et al. (2002), Grenthe et al. (1992)
$2UO_2^{2+} + CO_2(g) + 4H_2O(l) = (UO_2)_2CO_3(OH)_3^- + 5H^+$	-18.63		0.1 *M* $NaClO_4$	Kramer-Schnabel et al. (1992)	Maya (1982)
	-19.0		25ºC, I = 0	Kimura et al. (1992)	Grenthe et al. (1992)?
	-18.9 ± 1.0		Not corrected to standard state conditions ($I < 10^{-3}$ M). Erroneous reaction stoichiometry in source.		Geipel et al. (1998c)

Table 1a. Association Constants Aqueous Carbonate Complexes in the System $UO_2/U_2O_5/UO_3$-CO_2-H_2O (Continued)

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
$2UO_2^{2+} + CO_2(g) + 5H_2O(l) = (UO_2)_2CO_2(OH)_5^- + 5H^+$	-19.40 ± 0.11		25ºC, 0.50 *M* $NaClO_4$		Grenthe and Lagerman (1991)
$UO_2^{2+} + 2CO_2(g) + 4H_2O(l) = UO_2(CO_2)_2(OH)_4^{2-} + 4H^+$	-19.57 ± 0.30		25ºC, 0.50 *M* $NaClO_4$		Grenthe and Lagerman (1991)
	-	-	The structure and ligand exchange dynamics of four potential isomers, A. B. C and D of $(UO_2)_2(CO_3)(OH)_3$ were investigated by EXAFS and NMR. 80% of C, and 5 and 15% of A and B, respectively were found		Szabo and Grenthe (2000)
$3UO_2^{2+} + CO_3^{2-} + 3H_2O(l) = (UO_2)_3CO_3(OH)_3^+ + 3H^+$	0.68 ± 0.5	-		Duro et al. (2006)	Hummel et al. (2002), Grenthe et al. (1992)
$3UO_2^{2+} + CO_2(g) + 4H_2O(l) = (UO_2)_3CO_3(OH)_3^+ + 5H^+$	-16.34 ± 0.06	-	EMF, 3 *M* $NaClO_4$		Ciavatta et al. (1979)
	-16.34	-	3 *M* $NaClO_4$	Kramer-Schnabel et al. (1992)	Ciavatta et al. (1979)
$3UO_2^{2+} + 6CO_2(g) + 12H_2O(l) = (UO_2)_3(CO_2)_6(OH)_{12}^{6-} + 12H^+$	-49.68 ± 0.17		25ºC, 0.50 *M* $NaClO_4$		Grenthe and Lagerman (1991)
$UO_2^{2+} + CO_3^{2-} + 2OH^- = (UO_2)CO_3(OH)_2^{2-}$	<22.6		Not corrected to standard state conditions (I = 0.5 - 5 M)		Yamamura et al. (1998)
$UO_2^{2+} + 2CO_3^{2-} + 2OH^- = (UO_2)(CO_3)_2(OH)_2^{4-}$	-	-	Pol., Na_2CO_3 soln	Krishnamurty et al. (1970)	Stabrovskii (1960)
	<23.5		Not corrected to standard state conditions (I = 0.5 - 5 M)		Yamamura et al. (1998)
$11UO_2^{2+} + 6CO_2(g) + 18H_2O(l) = (UO_2)_{11}(CO_3)_6(OH)_{12}^{2-} + 24H^+$	-72.06 ± 0.11	-	EMF, 3 *M* $NaClO_4$		Ciavatta et al. (1979)

Table 1a. Association Constants Aqueous Carbonate Complexes in the System $UO_2/U_2O_5/UO_3$-CO_2-H_2O (Continued)

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	-72.0	-	3 *M* $NaClO_4$	Kramer-Schnabel et al. (1992)	Ciavatta et al. (1979)
$3UO_2(CO_3)_3^{4-} + 3CO_2(g) + 3H_2O = (UO_2)_3(CO_3)_6^{6-} + 6HCO_3^-$	-6.43 ± 0.08	-	EMF, 3 *M* $NaClO_4$		Ciavatta et al. (1981)
-	-6.43	-	3 *M* $NaClO_4$	Kramer-Schnabel et al. (1992)	Ciavatta et al. (1981)
$3UO_2(CO_3)_3^{4-} + 6H^+ = (UO_2)_3(CO_3)_6^{6-} + 3CO_2(g) + 3H_2O$	41.5 ± 0.1	-	25°C, EMF, 3 *M* $NaClO_4$		Ferri et al. (1981)
$UO_2(CO_3)_3^{4-} + H_2O_2 = (UO_2)(CO_3)_2(HO_2)^{3-} + HCO_3^-$	-2.00 ± 0.13		*I* = 0.4, Spectrophotometry and cryoscopy		Komarov (1959)
	-2.20 ± 0.13		*I* = 0.0, Spectrophotometry and cryoscopy		Komarov (1959)
$(UO_2)(CO_3)_2(HO_2)^{3-} = (UO_2)(CO_3)_2(O_2)^{4-} + H^{+-}$	-10.60	-	Spectrophotometry		Komarov et al. (1959)
	-	-	Artificial seawater		Djogić and Branica (1991)
$(U^{VI}O_2)(CO_3)_2(HO_2)^{3-} + e^- = (U^VO_2)(CO_3)_2(O_2)^{4-}$	-	-	Normal pulse polarography (NPP) and spectrophotometry in artificial seawater at pH = 8		Djogić and Branica (1991)
$(U^VO_2)(CO_3)_2(HO_2)^{4-} + 2e^- + H^+ = (U^VO_2)(CO_3)_2^{3-} + 2OH^-$	-	-	Normal pulse polarography (NPP) and spectrophotometry in artificial seawater at pH = 8		Djogić and Branica (1991)

Table 1b. Association Constants for Ternary Aqueous Complexes in the System UO_3-CO_2-H_2O with MO (M = Mg, Ca, Sr or Ba), or with F^-

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Reference
$Mg^{2+} + UO_2^{2+} + 3CO_3^{2-} = MgUO_2(CO_3)_3^{2-}$	26.11 ± 0.04				Dong and Brooks (2006)
$Ca^{2+} + UO_2^{2+} + 3CO_3^{2-} = CaUO_2(CO_3)_3^{2-}$	25.6 ± 0.25				Bernhard et al. (2001)
	25.4			Kelly et al. (2007)	Bernhard et al. (2001)
	27.18 ± 0.06				Dong and Brooks (2006)
	27.18			Kelly et al. (2007)	Dong and Brooks (2006)
$Sr^{2+} + UO_2^{2+} + 3CO_3^{2-} = SrUO_2(CO_3)_3^{2-}$	26.86 ± 0.04				Dong and Brooks (2006)
$Ba^{2+} + UO_2^{2+} + 3CO_3^{2-} = BaUO_2(CO_3)_3^{2-}$	26.68 ± 0.04				Dong and Brooks (2006)
$2Ca^{2+} + UO_2^{2+} + 3CO_3^{2-} = Ca_2UO_2(CO_3)_3(aq)$	29.41 ± 0.7				Bernhard et al. (1996)
	26.3		I = 0.1		Geipel et al. (1997)
	25.7 ± 0.7				Bernhard et al. (1998)
	26.5 ± 0.3				Geipel et al. (1999)
	29.8 ± 0.7				Kalmykov and Choppin (2000)
	30.79 ± 0.24				Bernhard et al. (2001)
	30.55			Kelly et al. (2007)	Bernhard et al. (2001)
	30.70 ± 0.05				Dong and Brooks (2006)
	30.70			Kelly et al. (2007)	Dong and Brooks (2006)
$2Ba^{2+} + UO_2^{2+} + 3CO_3^{2-} = Ba_2UO_2(CO_3)_3(aq)$	29.75 ± 0.07				Dong and Brooks (2006)
$UO_2^{2+} + CO_3^{2-} + F^- = UO_2(CO_3)F^-$	13.75 ± 0.09		Corrected to standard state by Guillaumont et al. (2003)		Aas et al. (1998)
$UO_2^{2+} + CO_3^{2-} + 2F^- = UO_2(CO_3)F_2^{2-}$	15.57 ± 0.14		Corrected to standard state by Guillaumont et al. (2003)		Aas et al. (1998)

Table 1b. Association Constants for Ternary Aqueous Complexes in the System UO_3-CO_2-H_2O with M (M = Mg, Ca, Sr or Ba) or with F^- (Continued)

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Reference
$UO_2^{2+} + CO_3^{2-} + 3F^- = UO_2(CO_3)F_3^{-3}$	16.38 ± 0.11		Corrected to standard state by Guillaumont et al. (2003)		Aas et al. (1998)

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Table 2. Solubility Constants of Solid Carbonates in the Sub-system UO_3-CO_2-H_2O

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
Minerals					
Andersonite					
$Na_2Ca(UO_2)(CO_3)_3$•$6(H_2O)$ = $2Na^+$ +Ca^{2+} + UO_2^{2+} +$3CO_3^{2-}$ + $6H_2O$	-37.5 ± 4.2		Calculated from reported standard state Gibbs free energy of formation	Gorman-Lewis et al. (2008)	Alwan and Williams (1980)
Bayleyite					
$Mg_2(UO_2)(CO_3)_3$•$18(H_2O)$ = $2Mg^{2+}$ + UO_2^{2+} +$3CO_3^{2-}$ + $18H_2O$	-36.9 ± 2.1				Alwan and Williams (1980)
	-36.6 ± 1.4		Calculated from reported standard state Gibbs free energy of formation	Gorman-Lewis et al. (2008)	Alwan and Williams (1980)
Cejkaite					
$Na_4UO_2(CO_3)_3(s)$ = $4Na^+$ + UO_2^{2+} + $3CO_3^{2-}$	-27.1760		(errata and corrigenda)		Grenthe et al. (1992)
	-27.18				Guillaumont et al. (2003)
$Na_4UO_2(CO_3)_3(s)$ = $4Na^+$ + $UO_2(CO_3)_3^{4-}$	-2.8	-	26ºC, Sol.		Blake et al. (1956)
Grimselite					
$NaK_3UO_2(CO_3)_3$•$(H_2O)(cr)$ = Na^+ +$3K^+$ + UO_2^{2+} +$3CO_3^{2-}$ + H_2O	29.91		5.6ºC, *I* = 0		O'Brien and Williams (1983)
	29.84		9.9ºC, *I* = 0		O'Brien and Williams (1983)
	29.83		10.6ºC, *I* = 0		O'Brien and Williams (1983)
	29.76		14.8ºC, *I* = 0		O'Brien and Williams (1983)
	29.76		14.8ºC, *I* = 0		O'Brien and Williams (1983)
	29.67		20.1ºC, *I* = 0		O'Brien and Williams (1983)
	29.59		25.0ºC, *I* = 0		O'Brien and Williams (1983)

Table 2. Solubility Constants of Solid Carbonates in the Sub-system UO_3-CO_2-H_2O (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	-37.1 ± 0.3		Calculated from reported standard state Gibbs free energy of formation	Gorman-Lewis et al. (2008)	O'Brien and Williams (1983)
Liebigite					
$Ca_2(UO_2)(CO_3)_3$•$11(H_2O)$ = $2Ca^{2+}$ + UO_2^{2+} +$3CO_3^{2-}$ + $11H_2O$	-36.9 ± 2.1		Calculated from reported standard state Gibbs free energy of formation	Gorman-Lewis et al. (2008)	Alwan and Williams (1980)
					Hemingway (1982)
			Solubility of liebigite at pH 8.0 was determined to be 9.9 ± 0.5 g/L		Amayri et al. (1998), Amayri et al. (1999)
	-34.36				Liu et al. (2002)
Rabbittite					
$Ca_3Mg_3(UO_2)_2(CO_3)_6(OH)_4$•$18(H_2O)$ = $3Ca^{2+}$ + $3Mg^{2+}$ + $2UO_2^{2+}$ +$6CO_3^{2-}$ + $18H_2O$					Hemingway (1982)
Rutherfordine*					
UO_2CO_3(cr) = UO_2^{2+} + CO_3^{2-}	-14.26		25ºC, I = 0		Sergeeva et al. (1972a)
	-14.55		50ºC, I = 0		Sergeeva et al. (1972a)
	-14.26			Kramer-Schnabel et al. (1992)	Sergeeva et al. (1972a)
	-14.25		25 ± 0.5ºC, $P(CO_2)$ = 1.0, I = <0.02 $NaClO_4$	Hála and Navratil (2001)	Sergeyeva et al. (1972b)
	-14.15 ± 0.08		25ºC		Nikolaeva (1976)
	-16.14 ± 0.04		125ºC		Nikolaeva (1976)
	-14.15			Kramer-Schnabel et al. (1992)	Pirozhkov and Nikolaeva (1976)
	-14.05 ± 0.08		25 ± 0.1ºC, $P(CO_2)$ = 1.1–1.2, I = 0	Hála and Navratil (2001)	Pirozhkov and Nikolaeva (1976)
	-14.2 ± 0.2		25°C, I = 0		Lemire and Tremaine (1980)

Table 2. Solubility Constants of Solid Carbonates in the Sub-system UO_3-CO_2-H_2O (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	-14.7 ± 0.6		60°C, I = 0, modified Crlss-Cobble entropy extrapolation		Lemire and Tremaine (1980)
	-15 ± 1		100°C, I = 0, modified Crlss-Cobble entropy extrapolation		Lemire and Tremaine (1980)
	-17 ± 2		150°C, I = 0, modified Crlss-Cobble entropy extrapolation		Lemire and Tremaine (1980)
	-18 ± 2		200°C, I = 0, modified Crlss-Cobble entropy extrapolation		Lemire and Tremaine (1980)
	-14.4 ± 0.1		25 ± 2ºC, I = 0		Grenthe et al. (1984a)
	-14.4 ± 0.1		25 ± 2ºC, P(CO_2) = 0.09–0.98, I = 0	Hála and Navratil (2001)	Grenthe et al. (1984a)
	-13.21		0.5 M $NaClO_4$	Kramer-Schnabel et al. (1992)	Grenthe et al. (1984a)
	-13.21 ± 0.06		0.5 $NaClO_4$	Hála and Navratil (2001)	Grenthe et al. (1984a)
	-13.94		3 M $NaClO_4$	Kramer-Schnabel et al. (1992)	Grenthe et al. (1984a)
	-13.94 ± 0.06		3 $NaClO_4$	Hála and Navratil (2001)	Grenthe et al. (1984a)
	-14.456 ± 0.04				Grenthe et al. (1992)
	-14.439		25ºC, I = 0	Kimura et al. (1992)	Grenthe et al. (1992)?
	-14.49 ± 0.04		As revised in Appendix D	Silva et al. (1995)	Grenthe et al. (1992)
	-14.445			Redkin and Wood (2007)	Grenthe et al. (1992) and Shock et al. (1997)
	-13.29 ± 0.01		25ºC, P(CO_2) = 1.0, I = 0.1 $NaClO_4$		Kramer-Schnabel et al. (1992)
	-13.29 ± 0.11		25ºC, P(CO_2) = 1.0, I = 0.1 $NaClO_4$	Hála and Navratil (2001)	Kramer-Schnabel et al. (1992)
	-13.29 ± 0.01		I = 0.1	Gorman-Lewis et al. (2008)	Kramer-Schnabel et al. (1992)
	-13.89 ± 0.11		24 ± 2ºC, 0.1 M $NaClO_4$		Meinrath and Kimura (1993b)
	-14.75 ± 0.12		I = 0	Meinrath et al. (1996b)	Meinrath and Kimura (1993b)

Table 2. Solubility Constants of Solid Carbonates in the Sub-system UO_3-CO_2-H_2O (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	-13.89 ± 0.11		24 ± 2ºC, P(CO_2) = 1.0, *I* = 0.1 $NaClO_4$	Hála and Navratil (2001)	Meinrath and Kimura (1993b)
	-13.89 ± 0.11		*I* = 0.1, under 100% CO_2	Gorman-Lewis et al. (2008)	Meinrath and Kimura (1993b)
	-14.18 ± 0.03		25ºC, 0.1 *M* $NaClO_4$		Meinrath and Kimura (1993a)
	-14.96 ± 0.15		*I* = 0	Meinrath et al. (1996b)	Meinrath and Kimura (1993a)
	-14.18 ± 0.03		25 ± 0.1ºC, P(CO_2) = 1.0, *I* = 0.1 $NaClO_4$	Hála and Navratil (2001)	Meinrath and Kimura (1993a)
	-13.89 ± 0.11		24 ± 2ºC, 0.1 *M* $NaClO_4$		Meinrath et al. (1993)
	-14.39 ± 0.14				Pashalidis et al. (1993)
	-13.35 ± 0.14		22 ± 1ºC, P(CO_2) = 1.0, *I* = 0.1 $NaClO_4$	Hála and Navratil (2001)	Pashalidis et al. (1993)
	-14.21 ± 0.14		*I* = 0	Hála and Navratil (2001)	Pashalidis et al. (1993)
	-14.34 ± 0.22				Meinrath et al. (1996a)
	-14.05 ± 0.09		25 ± 2ºC, P(CO_2) = 0.08, *I* = 0.1 $NaClO_4$	Hála and Navratil (2001)	Meinrath et al. (1996b)
	-14.91 ± 0.1		*I* = 0	Hála and Navratil (2001)	Meinrath et al. (1996b)
	-14.91 ± 0.10		*I* = 0, under 100% CO_2		Meinrath et al. (1996b)
	-14.91 ± 0.10		*I* = 0, under 100% CO_2	Gorman-Lewis et al. (2008)	Meinrath et al. (1996b)
	-14.94 ± 0.14				Kato et al. (1996)
	-15.04 ± 0.04		*I* = 0	Meinrath et al. (1996b)	Kato et al. (1996)
	-14.1 ± 0.14		225 ± 1ºC, P(CO_2) = 1.0, *I* = 0.1 $NaClO_4$	Hála and Navratil (2001)	Kato et al. (1996)
	-14.39 ± 0.14		22 ± 2ºC. Recalculation	Guillaumont et al. (2003)	Pashalidis et al. (1997)
	-14.46				Liu et al. (2002)
	-14.49 ± 0.04			Duro et al. (2006)	Hummel et al. (2002), Grenthe et al. (1992)
	-14.76 ± 0.04			Duro et al. (2006)	Guillaumont et al. (2003)
$UO_2(CO_3)(s) + 2H^+ = UO_2^{2+} + H_2O + CO_2(g)$	3.90		25ºC, at pH 3.2-4.4		Sergeeva et al. (1972a)

Table 2. Solubility Constants of Solid Carbonates in the Sub-system UO_3-CO_2-H_2O (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	3.65		50ºC		
$UO_2(CO_3)(s) = UO_2(CO_3)(aq)$	-4.39		25ºC, at pH 4.4-5.3		Sergeeva et al. (1972a)
	-4.34		50ºC. Also -4.35, -4.34, -4.21 at 100, 150 and 200ºC, respectively.		
$UO_2(CO_3)(s) + H_2O + CO_2(g) = UO_2(CO_3)_2 2^- + 2H^+$	-15.66		25ºC, at pH 5.3-6.3		Sergeeva et al. (1972a)
	-16.00		50ºC		
$[UO_2(CO_3)(s) + 2HCO_3^- + H_2O = [UO_2(CO_3)_2(H_2O)_2]^{2-} + CO_2(g)$	1.42		$I = 0$		McClaine et al. (1956)
Schröckeringerite					
$NaCa_3UO_2(CO_3)_3SO_4F•10(H_2O)(cr) = Na^+ + 3Ca^{2+} + UO_2^{2+} + 3CO_3^{2-} + SO4^{2-} + F^- + 10H_2O$					Hemingway (1982)
	-38.81 ± 0.19		25ºC, $I = 0$, average of 4 readings		O'Brien and Williams (1983)
	-85.5 ± 1.5		Calculated from reported standard state Gibbs free energy of formation	Gorman-Lewis et al. (2008)	O'Brien and Williams (1983)
Swartzite					
$CaMg(UO_2)(CO_3)_3•12(H_2O) = Ca^{2+} + Mg^{2+} + UO_2^{2+} + 3CO_3^{2-} + 12H_2O$	-36.9 ± 2.1				Alwan and Williams (1980)
	-37.9 ± 1.4		Calculated from reported standard state Gibbs free energy of formation	Gorman-Lewis et al. (2008)	Alwan and Williams (1980)
					Hemingway (1982)
Voglite					
$Ca_2Cu(UO_2)(CO_3)_4•6(H_2O) = 2Ca^{2+} + Cu^{2+} + UO_2^{2+} + 4CO_3^{2-} + 6H_2O$					Hemingway (1982)

Table 2. Solubility Constants of Solid Carbonates in the Sub-system UO_3-CO_2-H_2O (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
Zellerite					
$Ca(UO_2)(CO_3)_2 \bullet 5(H_2O) = Ca^{2+} + UO_2^{2+} + 2CO_3^{2-} + 5H_2O$	-23.94				Liu et al. (2002)
Synthetic Phases					
$UO_3 \bullet 2(H_2O)$					
$UO_3 \bullet 2(H_2O) + CO_2(g) + [UO_2(CO_3)](s) + 2H_2O$	4.0		$I = 0$		McClaine et al. (1956)
$UO_2CO_3 \bullet (H_2O)(cr)$					
$UO_2CO_3 \bullet (H_2O)(cr) = UO_2^{2+} + CO_3^{2-}$					Hemingway (1982)
$UO_2(HCO_3)_2 \bullet (H_2O)(cr)$					
$UO_2(HCO_3)_2 \bullet (H_2O)(cr) = UO_2^{2+} + 2CO_3^{2-} + 2H^+ + H_2O$					Cordfunke and O'Hare (1978)
					Fuger (1983)
					Morss (1986)
Surface Adsorption on Calcite					Carroll and Bruno (1991)
$UO_2^{2+} + CaCO_3(cr) = >UO_2CO_3\_Ca^{2+}$	5.12 ± 0.53	-			

(1) At standard state (25°C, 1 atm, $I = 0$), unless otherwise noted.

* Recent spectroscopic data (Frost and Cejka., 2009) have revealed the presence of H_2O and (OH) groups in natural samples of rutherfordine (UO_2CO_3), thus forming limited solid solutions $UO_2(CO_3)_{1-x}(OH)_{2x}.yH_2O$, where x, y ≥ 0.

Table 3a. Association Constants of Aqueous Complexes in the System $UO_2/U_2O_5/UO_3$-CO_2-H_2O extracted from Databases of Distribution-of-Species Codes

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Database	Source
U(IV)				
$U^{4+} + 4CO_3^{2-} = U(CO_3)_4^{4-}$	-	-	Minteq (2009)	
	-	-	Minteq (2006)	
	32.9	-	Wateq4f (2005)	
	35.12	-	ThermoChimie v.7.b	Grenthe et al. (1992)
	35.220	-	NAGRA/PSI (2001)	Hummel et al. (2002)
	35.0541	-	Data0.YMP.R5	Grenthe et al. (1992)
$U^{4+} + 5CO_3^{2-} = U(CO_3)_5^{6-}$	-	-	Minteq (2009)	
	-	-	Minteq (2006)	
	34.0	83.68	Wateq4f (2005)	
	34.	-20.	ThermoChimie v.7.b	Guillaumont et al. (2003)
	34.100	20.000	NAGRA/PSI (2001)	Hummel et al. (2002)
	33.8913	-	Data0.YMP.R5	Grenthe et al. (1992)
U(V)				
$UO_2^{+} + 3CO_3^{2-} + = UO_2(CO_3)_3^{-5}$	-	-	Minteq (2009)	
	-	-	Minteq (2006)	
	7.43	13.93	Wateq4f (2005)	
	6.95	-	ThermoChimie v.7.b	Guillaumont et al. (2003)
	7.410	-	NAGRA/PSI (2001)	Hummel et al. (2002)
	7.3619	-	Data0.YMP.R5	Grenthe et al. (1992)
U(VI)				
$UO_2^{2+} + CO_3^{2-} = UO_2CO_3(aq)$	10.071	3.51	Minteq (2009)	
	9.6	4.	Minteq (2006)	Smith et al. (1997); NIST46.3
	9.63	5.02	Wateq4f (2005)	
	9.94	5.	ThermoChimie v.7.b	Guillaumont et al. (2003)
	9.670	5.000	NAGRA/PSI (2001)	Hummel et al. (2002)
	9.6450	-	Data0.YMP.R5	Silva et al. (1995)
$UO_2^{2+} + 2CO_3^{2-} = UO_2(CO_3)_2^{2-}$	17.008	14.56	Minteq (2009)	
	16.9	16.	Minteq (2006)	Smith et al. (1997) NIST46.3
	17.0	18.49	Wateq4f (2005)	
	16.61	18.5	ThermoChimie v.7.b	Grenthe et al. (1992)
	16.940	18.500	NAGRA/PSI (2001)	Hummel et al. (2002)
	16.8999	-	Data0.YMP.R5	Grenthe et al. (1992)
$UO_2^{2+} + 3CO_3^{2-} = UO_2(CO_3)_3^{4-}$	21.384	-36.74	Minteq (2009)	
	21.6	-40.	Minteq (2006)	Smith et al. (1997) NIST46.3

Table 3a. Association Constants of Aqueous Complexes in the System $UO_2/U_2O_5/UO_3$-CO_2-H_2O extracted from Databases of Distribution-of-Species Codes (Continued)

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Database	Source
	21.63	-38.20	Wateq4f (2005)	
	21.84	-39.2	ThermoChimie v.7.b	Guillaumont et al. (2003)
	21.600	-39.200	NAGRA/PSI (2001)	Hummel et al. (2002)
	21.5453	-	Data0.YMP.R5	Grenthe et al. (1992)
$CO_3^{2-} + 2UO_2^{2+} + 3H_2O = (UO_2)_2CO_3(OH)_3^- + 3H^+$	-	-	Minteq (2009)	
	-	-	Minteq (2006)	
	-	-	Wateq4f (2005)	
	-0.86	-	ThermoChimie v.7.b	Grenthe et al. (1992)
	-	-	NAGRA/PSI (2001)	
	-0.9160	-	Data0.YMP.R5	Grenthe et al. (1992)
$3UO_2^{2+} + CO_3^{2-} + 3H_2O = (UO_2)_3(CO_3)(OH)_3^+ + 3H^+$	-	-	Minteq (2009)	
	-	-	Minteq (2006)	
	-	-	Wateq4f (2005)	
	0.66	81.159	ThermoChimie v.7.b	Grenthe et al. (1992)
	-	-	NAGRA/PSI (2001)	
$CO_3^{2-} + 3UO_2^{2+} + 3H_2O = (UO_2)_3O(OH)_2(HCO_3)^+ + 3H^+$	0.5831	-	Data0.YMP.R5	Grenthe et al. (1992)
$3UO_2^{2+} + 6CO_3^{2-} = (UO_2)_3(CO_3)_6^{6-}$	-	-	Minteq (2009)	
	-	-	Minteq (2006)	
	54.	-	Wateq4f (2005)	
	54.	-62.7	ThermoChimie v.7.b	Grenthe et al. (1992)
	-	-	NAGRA/PSI (2001)	
	53.8798	-	Data0.YMP.R5	Grenthe et al. (1992)
$11UO_2^{2+} + 6CO_3^{2-} + 12H_2O = (UO_2)_{11}(CO_3)_6(OH)_{12}^{2-} + 12H^+$	-	-	Minteq (2009)	
	-	-	Minteq (2006)	
	-	-	Wateq4f (2005)	
	36.43	-	ThermoChimie v.7.b	Grenthe et al. (1992)
	-	-	NAGRA/PSI (2001)	
	36.1179	-	Data0.YMP.R5	Grenthe et al. (1992)
$6CO_3^{2-} + 2UO_2^{2+} + PuO_2^{2+} = (UO_2)_2(PuO_2)(CO_3)_6^{6-}$	-	-	Minteq (2009)	
	-	-	Minteq (2006)	
	-	-	Wateq4f (2005)	
	-	-	ThermoChimie v.7.b	
	-	-	NAGRA/PSI (2001)	
	52.5907	-	Data0.YMP.R5	Lemire (2001)

Table 3a. Association Constants of Aqueous Complexes in the System $UO_2/U_2O_5/UO_3$-CO_2-H_2O extracted from Databases of Distribution-of-Species Codes (Continued)

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Database	Source
$6CO_3^{2-} + 2UO_2^{2+} + NpO_2^{2+} = (UO_2)_2(NpO_2)(CO_3)_6^{6-}$	-	-	Minteq (2009)	
	-	-	Minteq (2006)	
	-	-	Wateq4f (2005)	
	-	-	ThermoChimie v.7.b	
	-	-	NAGRA/PSI (2001)	
	53.4763	-	Data0.YMP.R5	Lemire (2001)

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Note: Neither the PHREEQ-C (2009) nor the THERMODDEM (2009) databases contain data on aqueous uranium species.

Note: Data0.YMP.R5 writes all equations in terms of HCO_3^- basis species. These are corrected to be written in terms of the CO_3^{2-} basis species using the respective translation equation and association constant given in Table 6.

Table 3b. Solubility Constants of Solid Carbonates in the Sub-system UO_3-CO_2-H_2O extracted from Databases of Distribution-of-Species Codes

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Database	Source
$Na_4UO_2(CO_3)_3(s)$				
$Na_4UO_2(CO_3)_3(s) = 4Na^+ + UO_2^{2+} + 3CO_3^{2-}$	-	-	Minteq (2009)	
	-	-	Minteq (2006)	
	-16.290	-	Wateq4f (2005)	
	-27.18	-	ThermoChimie v.7.b	Guillaumont et al. (2003)
	-	-	NAGRA/PSI (2001)	
	-27.1760	-	Data0.YMP.R5	Grenthe et al. (1992) (errata and corrigenda)
$Mg_2UO_2(CO_3)_3 \cdot 18(H_2O)(s)$				
$Mg_2UO_2(CO_3)_3 \cdot 18(H_2O) = +2Mg^{2+} + UO_2^{2+} + 3CO_3^{2-} + 18H_2O$	-	-	Minteq (2009)	
	-	-	Minteq (2006)	
	-	-	Wateq4f (2005)	
	-29.01	40.57	ThermoChimie v.7.b	[not cited]
	-	-	NAGRA/PSI (2001)	
		-	Data0.YMP.R5	
Rutherfordine				
$UO_2CO_3(cr) = UO_2^{2+} + CO_3^{2-}$	-14.439	-6.02	Minteq (2009)	
	-14.5	-3.03	Minteq (2006)	
	-14.450	-6.025	Wateq4f (2005)	
	-14.76	-2.929	ThermoChimie v.7.b	Guillaumont et al. (2003)
	-14.490	-	NAGRA/PSI (2001)	Hummel et al. (2002)
	-14.4646	-	Data0.YMP.R5	Silva et al. (1995)

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Note: Neither the PHREEQ-C (2009) nor the THERMODDEM (2009) databases contain data on uranium minerals.

Note: Data0.YMP.R5 writes all equations in terms of HCO_3^- basis species. These equations are corrected to be written in terms of the CO_3^{2-} basis species using the respective translation equation and association constant given in ThermoTable_HCO_3.

Table 3c. Distribution-of-Species Codes: Database References

Database	Reference
Data0.com.V8.R6+	Wolery, T.J. (1994). EQ3NR, Letter report: EQ3/6 version 8.0. Differences from version 7. UCRL-ID-129749. Lawrence Livermore National Laboratory, Livermore, California. USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/LLNL.DAT
Data0.YMP.R5	BSC (Bechtel SAIC Company) (2007). Qualification of Thermodynamic Data for Geochemical Modeling of Mineral–Water Interactions in Dilute Systems. ANL-WIS-GS-000003 REV 01. Las Vegas, Nevada: Bechtel SAIC Company.DOC.20070619.0007.
MinteqA2	HydroGeoLogic, Inc. and Allison Geoscience Consultants, Inc. (1999). MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: User Manual Supplement for Version 4.0, Appendix A: thermodynamic database for MINTEQA2 V4.0, p. 44-74.
Minteq (2009)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/MINTEQ.DAT
Minteq (2006)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/minteq.v4.dat
NAGRA/PSI (2001)	Hummel, W., Berner, U., Curti, E., Pearson, F.J. and Thoenen, T. (2002). Nagra/PSI Chemical Thermodynamic Data Base 01/01. Universal Publishers/uPublish.com, Parkland, Florida. 565 p.
Phreeqc (2009)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/PHREEQC.DAT
ThermoChimie v.7.b	Duro, L., Grivém M. and Giffaut, E. (2010). ThermoChimie, the ANDRA thermodynamic database In Buckau G, Kienzler B, Duro L, Grivé M, Montoya V (eds). 2nd Annual Workshop Proceedings of the Collaborative Project “Redox Phenomena Controlling Systems” (7th EC FP CP Recosy) Larnaca (Cyprus) 16–19 March 2010. Karlsruhe: KIT Scientific Publishing, 275–283.
Thermoddem (2009)	Blanc P., Lassin A. and Piantone P. (2007) THERMODDEM a database devoted to waste minerals. BRGM (Orléans, France). For updates: http://thermoddem.brgm.fr
Wateq4f	Ball, J. W., & Nordstrom, D. K. (1991). User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters. U.S. GEOLOGICAL SURVEY, Open-File Report 91-183, Revised and reprinted - April, 2001. p. 81-94
Wateq4f (2005)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/WATEQ4F.DAT

Table 4a. Thermodynamic properties of Uranium Carbonate Minerals and Synthetic Solid Carbonates: Gibbs Free Energies of Formation

Mineral		$\Delta G^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
Minerals				
Andersonite	$Na_2CaUO_2(CO_3)_3$•$6(H_2O)$	-5651.0 ± 24.0		Alwan and Williams (1980)
		-5651.000 ± 24.000	Hemingway (1982)	Alwan and Williams (1980)
		-5651.0 ± 24	Kubatko et al. (2005)	Alwan and Williams (1980)
corrected		-5251.0 ± 24.0	O'Brien and Williams (1983)	Alwan and Williams (1980)
Andersonite	$Na_2CaUO_2(CO_3)_3$	-3902.0 ± 10.0		Van Genderen and Van der Weijden (1984)
Bayleyite	$Mg_2UO_2(CO_3)_3$•$18(H_2O)$	-7924.0 ± 10.0		Alwan and Williams (1980)
		-7924.000 ± 10.000	Hemingway (1982)	Alwan and Williams (1980)
Bayleyite	$Mg_2UO_2(CO_3)_3$	-3665.0 ± 10.0		Van Genderen and Van der Weijden (1984)
Fontanite	$Ca[(UO_2)_3(CO_3)_4]$•$3(H_2O)$	-6523.1	Finch (1997)	Deliens and Piret (1992)
		-6524.7		Chen et al. (1999)
Grimselite	$NaK_3UO_2(CO_3)_3$•(H_2O)	-4051.3 ± 1.8		O'Brien and Williams (1983)
		-4051.3 ± 1.8	Kubatko et al. (2005)	O'Brien and Williams (1983)
Grimselite	$NaK_3UO_2(CO_3)_3$	-3869.0 ± 10.0		Van Genderen and Van der Weijden (1984)
Joliotite	UO_2CO_3•$(H_2O)_{1-2}$	-2043.3	Finch (1997)	Nickel and Nichols (1992)
Liebigite	$Ca_2UO_2(CO_3)_3$•$10(H_2O)$	-6226.0 ± 12.0		Alwan and Williams (1980)
		-6226.000 ± 12.000	Hemingway (1982)	Alwan and Williams (1980)
		-6226.0 ± 12.0	O'Brien and Williams (1983)	Alwan and Williams (1980)
		-6226.0 ± 12.0	Finch (1997)	Alwan and Williams (1980)
Liebigite	$Ca_2UO_2(CO_3)_3$	-3844.0 ± 10.0		Van Genderen and Van der Weijden (1984)

Table 4a. Thermodynamic properties of Uranium Carbonate Minerals and Synthetic Solid Carbonates: Gibbs Free Energies of Formation (Continued)

Mineral		$\Delta G^0_{f,P_r,T_r}$ kJ/gfw $^{-1}$	Secondary Reference	Primary Reference
Name	Formula			
Liebigite	$Ca_2UO_2(CO_3)_3 \cdot 11(H_2O)$	-6468.6		Finch (1997)
		-6446.4		Chen et al. (1999)
Rabbittite *estimated*	$Ca_3Mg_3(UO_2)_2(CO_3)_6(OH)_4 \cdot 18(H_2O)$	-13525.000 ± 30.000		Hemingway (1982)
Rabbittite	$Ca_3Mg_3(UO_2)(CO_3)_6$ (?)	-8730.0 ± 20.0		Van Genderen and Van der Weijden (1984)
Rutherfordine*	UO_2CO_3	-1577.4	Woods and Garrels (1987)	Bullwinkel (1954)
		-1577.		McClaine et al. (1956)
estimated		-1577.8		Garrels (1957)
		-1577.79	Karpov et al. (1968)	Garrels (1960)
		-1569.		Sergeyeva et al. (1972a)
		-1562.3	Woods and Garrels (1987)	Sergeyeva et al. (1972b)
		-1563.1	Finch (1997)	Sergeyeva et al. (1972b)
		-1570.26		Naumov et al. (1974)
		-1570.2	Woods and Garrels (1987)	Naumov et al. (1974)
		-1561.9 ± 3.3		Cordfunke and O'Hare (1978)
		-1561.9 ± 3.3	Kubatko et al. (2005)	Cordfunke and O'Hare (1978)
		-1563.1		Langmuir (1978)
		-1563.1 ± 3.4	Kubatko et al. (2005)	Langmuir (1978)
		-1561 ± 2		Lemire and Tremaine (1980)
estimated		-1577.000 ± 2.100		Hemingway (1982)
		-1577.0 ± 2.1	Kubatko et al. (2005)	Hemingway (1982)
		-1562.6	Woods and Garrels (1987)	Wagman et al. (1982)
		-1563.0		Chen et al. (1999)
		-1564.7 ± 1.8		Guillaumont et al. (2003)
		-1564.7 ± 1.8	Kubatko et al. (2005)	Guillaumont et al. (2003)

Table 4a. Thermodynamic properties of Uranium Carbonate Minerals and Synthetic Solid Carbonates: Gibbs Free Energies of Formation (Continued)

Mineral		$\Delta G^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
Schröckingerite *estimated*	$NaCa_3(UO_2)(CO_3)_3(SO_4)F•10(H_2O)$	-8094.000 ± 30.000		Hemingway (1982)
		8077.3± 8.7		O'Brien and Williams (1983)
Sharpite	$UO_2CO_3•(H_2O)$	-1800.400 ± 4.000		Hemingway (1982)
Sharpite	$Ca[(UO_2)_6(CO_3)_5(OH)_4]•6(H_2O)$	-11601.1	Finch (1997)	Nickel and Nichols (1992)
		-11607.6		Chen et al. (1999)
Swartzite	$CaMgUO_2(CO_3)_3•12(H_2O)$	-6607.0 ± 10.0		Alwan and Williams (1980)
		-6607.000 ± 10.000	Hemingway (1982)	Alwan and Williams (1980)
Swartzite	$CaMgUO_2(CO_3)_3$	-3754.0 ± 10.0		Van Genderen and Van der Weijden, (1984)
Urancalcarite	$Ca_2[(UO_2)_3(CO_3)(OH)_6]•3(H_2O)$	-6037.0	Finch (1997)	Nickel and Nichols (1992)
		6036.7		Chen et al. (1999)
Voglite	$Ca_3Cu(UO_2)(CO_3)_4•6(H_2O)$	-5791.4 ± 35.0		Hemingway (1982)
Voglite	$Ca_3Cu(UO_2)(CO_3)_4$	-4469.0 ± 15.0		Van Genderen and Van der Weijden (1984)
Widenmannite	$Pb_2(UO_2)(CO_3)_3$	-2818.0 ± 10.0		Van Genderen and Van der Weijden (1984)
Zellerite	$Ca_2(UO_2)_2(CO_3)_2$	-2703.0 ± 7.0		Van Genderen and Van der Weijden (1984)
Zellerite	$Ca_2(UO_2)_2(CO_3)_2•3(H_2O)$	-3892.1	Finch (1997)	Nickel and Nichols (1992)

Table 4a. Thermodynamic properties of Uranium Carbonate Minerals and Synthetic Solid Carbonates: Gibbs Free Energies of Formation (Continued)

Mineral		$\Delta G^0_{f,P_r,T_r}$ kJ/gfw $^{-1}$	Secondary Reference	Primary Reference
Name	Formula			
Synthetic Phases				
$UO_2(HCO_3)_2 \bullet (H_2O)$	$UO_2(HCO_3)_2 \bullet (H_2O)$			
$Na_4UO_2(CO_3)_3$	$Na_4UO_2(CO_3)_3$	-3720.0 ± 9.7		O'Brien and Williams (1983)

Table 4b. Thermodynamic properties of Uranium Carbonate Minerals and Synthetic Solid Carbonates: Enthalpies of Formation

Mineral		$\Delta H^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
Minerals				
Andersonite	$Na_2CaUO_2(CO_3)_3$•6(H_2O)	-5916 ± 36		Alwan and Williams (1980)
		-5916 ± 36	O'Brien and Williams (1983)	Alwan and Williams (1980)
		-5916 ± 36	Kubatko et al. (2005)	Alwan and Williams (1980)
	$Na_2CaUO_2(CO_3)_3$•5(H_2O)	-5593.6 ± 9.1		Kubatko (2005)
		-5593.6 ± 9.1		Kubatko et al. (2005)
		-5593.6 ± 9.1	Shvareva et al. (2012)	Kubatko et al. (2005)
Andersonite	$Na_2CaUO_2(CO_3)_3$	-4199.0		Van Genderen and Van der Weijden (1984)
Bayleite	$Mg_2UO_2(CO_3)_3$•18(H_2O)			
Bayleite	$Mg_2UO_2(CO_3)_3$	-3950.0		Van Genderen and Van der Weijden (1984)
Fontanite	$Ca[(UO_2)_3(CO_3)_4]$•3(H_2O)			
Grimselite	$NaK_3UO_2(CO_3)_3$•(H_2O)	-4359.9 ± 1.8		O'Brien and Williams (1983)
		-4359.9 ± 1.8	Kubatko et al. (2005)	O'Brien and Williams (1983)
		-4431.6 ± 15.3		Kubatko (2005)
		-4431.6 ± 15.3		Kubatko et al. (2005)
		-4431.6 ± 15.3	Shvareva et al. (2012)	Kubatko et al. (2005)
Grimselite	$NaK_3UO_2(CO_3)_3$	-4182.0		Van Genderen and Van der Weijden (1984)
Joliotite	UO_2CO_3•(H_2O)$_{1-2}$			
Liebigite	$Ca_2UO_2(CO_3)_3$•10(H_2O)	-7037 ± 24		O'Brien and Williams (1983)
Liebigite	$Ca_2UO_2(CO_3)_3$	-4130.0		Van Genderen and Van der Weijden (1984)

Table 4b. Thermodynamic properties of Uranium Carbonate Minerals and Synthetic Solid Carbonates: Enthalpies of Formation (Continued)

Mineral		$\Delta H^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
Rabbittite	$Ca_3Mg_3(UO_2)_2(CO_3)_6(OH)_4$•18($H_2O$)			
Rabbittite	$Ca_3Mg_3(UO_2)(CO_3)_6$ (?)	-9265.0		Van Genderen and Van der Weijden (1984)
Rutherfordine*	UO_2CO_3	-1698.7		Sergeyeva et al. (1972a)
		-1695.4	Woods and Garrels (1987)	Sergeyeva et al. (1972b)
		-1696.19		Naumov et al. (1974)
		-1696.2	Woods and Garrels (1987)	Naumov et al. (1974)
		-1686.1 ± 4.2		Cordfunke and O'Hare (1978)
		-1686.1 ± 4.2	Kubatko et al. (2005)	Cordfunke and O'Hare (1978)
		-1689.9		Langmuir (1978)
		-1689.9 ± 4	Kubatko et al. (2005)	Langmuir (1978)
		-1704.1 ± 2.0		Hemingway (1982)
		-1704.1 ± 2.0	Kubatko et al. (2005)	Hemingway (1982)
		-1691.2	Woods and Garrels (1987)	Wagman et al. (1982)
Calc. using sources		-1691.3 ± 1.8	Kubatko et al. (2005)	Guillaumont et al. (2003), Gurevich et al. (1987)
		-1716.4 ± 4.2		Kubatko (2005)
		-1716.4 ± 4.2		Kubatko et al. (2005)
		-1716.4 ± 4.2	Shvareva et al. (2012)	Kubatko et al. (2005)
Schröckingerite	$NaCa_3(UO_2)(CO_3)_3(SO_4)$·F•10($H_2O$)			
Sharpite *estimated*	UO_2CO_3•(H_2O)	-1982.300 ± 12.000		Hemingway (1982)
Sharpite	$Ca[(UO_2)_6(CO_3)_5(OH)_4]$•6($H_2O$)			

Table 4b. Thermodynamic properties of Uranium Carbonate Minerals and Synthetic Solid Carbonates: Enthalpies of Formation (Continued)

Mineral		$\Delta H^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
Swartzite	$CaMgUO_2(CO_3)_3 \bullet 12(H_2O)$			
Swartzite	$CaMgUO_2(CO_3)_3$	-4039.0		Van Genderen and Van der Weijden, (1984)
Urancalcarite	$Ca_2[(UO_2)_3(CO_3)(OH)_6] \bullet 3(H_2O)$			
Voglite	$Ca_3Cu(UO_2)(CO_3)_4 \bullet 6(H_2O)$			
Voglite	$Ca_3Cu(UO_2)(CO_3)_4$	-4830.0		Van Genderen and Van der Weijden (1984)
Widenmannite	$Pb_2(UO_2)(CO_3)_3$	-3102.0		Van Genderen and Van der Weijden (1984)
Zellerite	$Ca_2(UO_2)_2(CO_3)_2 \bullet 3(H_2O)$			
Zellerite	$Ca_2(UO_2)_2(CO_3)_2$	-2908.0		Van Genderen and Van der Weijden (1984)
Synthetic Phases				
$UO_2(HCO_3)_2 \bullet (H_2O)$	$UO_2(HCO_3)_2 \bullet (H_2O)$			

Table 4c. Thermodynamic properties of Uranium Carbonate Minerals and Synthetic Solid Carbonates: Entropies

Mineral		$S^0_{P_r,T_r}$	Secondary Reference	Primary Reference
Name	Formula	J K^{-1} gfw^{-1}		
Minerals				
Andersonite	$Na_2CaUO_2(CO_3)_3 \cdot 6(H_2O)$			
Andersonite	$Na_2CaUO_2(CO_3)_3$	343.		Van Genderen and Van der Weijden (1984)
Bayleyite	$Mg_2UO_2(CO_3)_3 \cdot 18(H_2O)$			
Bayleyite	$Mg_2UO_2(CO_3)_3$	305.		Van Genderen and Van der Weijden (1984)
Fontanite	$Ca[(UO_2)_3(CO_3)_4] \cdot 3(H_2O)$			
Grimselite	$NaK_3UO_2(CO_3)_3 \cdot (H_2O)$			
Grimselite	$NaK_3UO_2(CO_3)_3$	390.		Van Genderen and Van der Weijden (1984)
Joliotite	$UO_2CO_3 \cdot (H_2O)_{1-2}$			
Liebigite	$Ca_2UO_2(CO_3)_3 \cdot 10(H_2O)$			
Liebigite	$Ca_2UO_2(CO_3)_3$	318.		Van Genderen and Van der Weijden (1984)
Liebigite	$Ca_2UO_2(CO_3)_3 \cdot 11(H_2O)$			Van Genderen and Van der Weijden (1984)
Rabbittite	$Ca_3Mg_3(UO_2)_2(CO_3)_6(OH)_4 \cdot 18(H_2O)$			
Rabbittite	$Ca_3Mg_3(UO_2)_2(CO_3)_6$ (?)	565.		Van Genderen and Van der Weijden (1984)

Table 4c. Thermodynamic properties of Uranium Carbonate Minerals and Synthetic Solid Carbonates: Entropies (Continued)

Mineral		$S^0_{P_r,T_r}$	Secondary Reference	Primary Reference
Name	Formula	J K^{-1} gfw^{-1}		
Rutherfordine*	UO_2CO_3	(142.3)#		Sergeyeva et al. (1972a)
Rutherfordine*	UO_2CO_3	121.	Woods and Garrels (1987)	Sergeyeva et al. (1972b)
		146.44 ± 12.		Naumov et al. (1974)
		146.4	Woods and Garrels (1987)	Naumov et al. (1974)
		139		Cordfunke and O'Hare (1978)
		139	Kubatko et al. (2005)	Cordfunke and O'Hare (1978)
		142.7		Langmuir (1978)
		142.7	Kubatko et al. (2005)	Langmuir (1978)
		194 ± 25		Lemire and Tremaine (1980)
estimated		142.7 ± 2.0		Hemingway (1982)
		142.7 ± 2.0	Kubatko et al. (2005)	Hemingway (1982)
		138.1	Woods and Garrels (1987)	Wagman et al. (1982)
		144.2 ± 0.3		Gurevich et al. (1987)
		144.2 ± 0.3	Kubatko et al. (2005)	Gurevich et al. (1987)
Schröckingerite	$NaCa_3(UO_2)(CO_3)_3(SO_4)\cdot F\bullet 10(H_2O)$			
Sharpite *estimated*	$UO_2CO_3\bullet(H_2O)$	192. ± 10.		Hemingway (1982)
Sharpite	$Ca[(UO_2)_6(CO_3)_5(OH)_4]\bullet 6(H_2O)$			
Swartzite	$CaMgUO_2(CO_3)_3\bullet 12(H_2O)$			
Swartzite	$CaMgUO_2(CO_3)_3$	314.		Van Genderen and Van der Weijden (1984)
Urancalcarite	$Ca_2[(UO_2)_3(CO_3)(OH)_6]\bullet 3(H_2O)$			

Table 4c. Thermodynamic properties of Uranium Carbonate Minerals and Synthetic Solid Carbonates: Entropies (Continued)

Mineral		$S^0_{P_r,T_r}$	Secondary Reference	Primary Reference
Name	Formula	J K^{-1} gfw^{-1}		
Voglite	$Ca_3Cu(UO_2)(CO_3)_4 \bullet 6(H_2O)$			
Voglite	$Ca_3Cu(UO_2)(CO_3)_4$	414.		Van Genderen and Van der Weijden (1984)
Widenmannite	$Pb_2(UO_2)(CO_3)_3$	372.		Van Genderen and Van der Weijden (1984)
Zellerite	$Ca_2(UO_2)_2(CO_3)_2 \bullet 3(H_2O)$			
Zellerite	$Ca_2(UO_2)_2(CO_3)_2$	230.		Van Genderen and Van der Weijden (1984)
Synthetic Phases				
$UO_2(HCO_3)_2 \bullet (H_2O)$	$UO_2(HCO_3)_2 \bullet (H_2O)$			

*****Recent spectroscopic data (Frost and Cejka, 2009) have revealed the presence of H_2O and (OH) groups in natural samples of rutherfordine (UO_2CO_3), thus forming limited solid solutions $UO_2(CO_3)_{1-x}(OH)_{2x} \bullet y(H_2O)$, where x, y ≥ 0.

Entropy of formation?

Table 5. Crystallographic Properties of Uranium Carbonate Minerals and Synthetic Solid Carbonates

	Name	Formula	Reference
	Minerals		
1	Albrechtschraufite	$Ca_4Mg(UO_2)_2(CO_3)_6F_2•17(H_2O)$	Gaines et al. (1997), Ondrus et al. (1997)
2	Andersonite	$Na_2CaUO_2(CO_3)_3•6(H_2O)$	Gaines et al. (1997)
3	Andersonite	$Na_2CaUO_2(CO_3)_3•6(H_2O)$	Coda et al. (1981)
4	Astrocyanite-(Ce)	$Cu_2(Ce,Nd,La)_2(\mathbf{U}O_2)(CO_3)_5(OH)_2•1.5(H_2O)$	Gaines et al. (1997), Deliens and Piret (1990)
5	Bayleyite	$Mg_2UO_2(CO_3)_3•18(H_2O)$	Gaines et al. (1997)
6	Bayleyite	$Mg_2UO_2(CO_3)_3•18(H_2O)$	Mayer and Mereiter (1986)
7	Bijvoetite-(Y)	$(Y,REE)_2O_3(UO_3)_4(CO_2)_4•≈14(H_2O)$	Gaines et al. (1997), Deliens and Piret (1982)
8	Bijvoetite-(Y)	$(Y,REE)_8(H_2O)_{25}(\mathbf{U}O_2)_{16}O_8(OH)_8(CO_3)_{16}•14(H_2O)$	Li et al. (2000)
9	Blatonite	$UO_2CO_3•(H_2O)$	Vochten and Deliens (1998)
10	Cejkaite	$Na_4UO_2(CO_3)_3$	Mineralogy Database (http://webmineral.com/)
11	Cejkaite	$Na_4UO_2(CO_3)_3$	Ondrus et al. (2003)

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
	Minerals									
1	Albrechtschraufite	13.562(3)	13.406(3)	11.636(3)	115.75(2)	107.66(2)	92.86(2)	2	P_1	534.36
2	Andersonite	18.009		23.838				18	R-3	224.01
3	Andersonite	17.902		23.734				18	R-3m	220.39
4	Astrocyanite-(Ce)	14.96		26.86				12	P 6/mmm	261.26
5	Bayleyite	26.65	15.3	6.53		93.1		4	$P2_1/c$	
6	Bayleyite	26.650	15.256	6.505		92.90		4	$P2_1/a$	397.67
7	Bijvoetite-(Y)	21.22(3)	45.30(7)	13.38(2)				16	C2ma, Cm2b or Cmma	484.10
8	Bijvoetite-(Y)	21.234(3)	12.958(2)	44.911(7)		90.00(2)		4	B1211 (pseudo orthorh)	1860.43
9	Blatonite	15.79		23.93(3)				36	Hex - unk	96.434
10	Cejkaite	9.28	9.295	12.864	90.293	91.124	119.548	4	P1 or P-1	145.29
11	Cejkaite	9.291	9.292	12.895	90.73	90.82	120.00	4	P-1	145.10

	Name	Formula	Reference
12	Fontanite	$Ca[(UO_2)_3(CO_3)_4•(H_2O)_3$	Gaines et al. (1997),
13	Fontanite	$Ca[(UO_2)_3(CO_3)_2O_2•6(H_2O)$	Hughes and Burns (2003)
14	Fontanite	$Ca[(UO_2)_3(CO_3)_4•6(H_2O)$	Kubatko (2005)
15	Grimselite	$NaK_3UO_2(CO_3)_3•(H_2O)$	Gaines et al. (1997)
16	Grimselite	$NaK_3UO_2(CO_3)_3•(H_2O)$	Li and Burns (2001)
17	Joliotite	$(UO_2)(CO_3)•n(H_2O)$,(n=2?)	Gaines et al. (1997), Walenta (1976)
18	Lepersonnite-(Gd)	$CaOGd_2O_3(UO_3)_{24}(CO_2)_8(SiO_2)_4•60(H_2O)$	Gaines et al. (1997), Deliens and Piret (1982)
19	Liebigite	$Ca_2UO_2(CO_3)_3•10(H_2O)$	Gaines et al. (1997)
20	Liebigite	$Ca_2UO_2(CO_3)_3•10(H_2O)$	Gaines et al. (1997), Mereiter (1982)
21	Metazellerite	$Ca(UO_2)(CO_3)_2•3(H_2O)$	Coleman et al. (1966)

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
12	Fontanite	15.337	17.051	6.931				4	Pmnm, $Pmn2_1$ or $P2_1nm$	272.88
13	Fontanite	6.968(3)	17.276(7)	15.377(6)		90.064(6)		4	$P2_1/n$	278.69
14	Fontanite	6.968(3)	17.276(7)	15.377(6)		90.064(6)		4	$P2_1/n$	278.69
15	Grimselite	9.30		8.26				2	P-62c	186.93
16	Grimselite	9.302		8.260				2	P-62c	186.37
17	Joliotite	8.16	10.35	6.32				4	P222, Pmm2 or Pmmm	80.360
18	Lepersonnite-(Gd)	16.23(3)	38.74(9)	11.73(3)				2	Pnnm,, Pnnn or Pnn2	2220.74
19	Liebigite	16.703	17.513	13.741				8	Bba2	302.58
20	Liebigite	16.699	17.5567	13.697				8	Bba2	302.29
21	Metazellerite	9.718	18.226	4.965				4	$Pbn2_1$ or Pbnm	132.40

	Name	Formula	Reference
22	Oswaldpeetersite	$(UO_2)_2CO_3(OH)_2•4(H_2O)$	Vochten et al. (2001)
23	Rabbittite	$Ca_3Mg_3(UO_2)_2(CO_3)_6(OH)_4•18(H2O)$	Gaines et al. (1997)
24	Roubaultite	$Cu_2(UO_2)_3(CO_3)_2O_2(OH)_2•4(H_2O)$	Gaines et al. (1997), Ginderow and Cesbron (1985)
25	Roubaultite	$Cu_2(UO_2)_3(CO_3)_2O_2(OH)_2•4(H_2O)$	RRUFF ID: R080131.9, Mineralogy Database (http://webmineral.com/)
26	Rutherfordine*	UO_2CO_3	Gaines et al. (1997), Christ et al. (1955)
27	Rutherfordine*	UO_2CO_3	Finch et al. (1999)
28	Schröckingerite	$NaCa_3(UO_2)(CO_3)_3(SO_4)F•10(H_2O)$	Mineralogy Database (http://webmineral.com/)
29	Schröckingerite	$NaCa_3(UO_2)(CO_3)_3(SO_4)F•10(H_2O)$	Gaines et al. (1997), Mereiter (1986b)
30	Sharpite	$Ca[(UO_2)_6(CO_3)5(OH)_4]•6(H_2O)$	Gaines et al. (1997), Cějka et al. (1984)
31	Swartzite	$CaMgUO_2(CO_3)_3•12(H_2O)$	Gaines et al. (1997)
32	Swartzite	$CaMgUO_2(CO_3)_3•12(H_2O)$	Mereiter (1986a)

	Name	Cell Constants							Space Group	$V^{o\#}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		$cm^3\ gfw^{-1}$
22	Oswaldpeetersite	4.1425(6)	14.098(3)	18.374(5)		103.62(1)		4	$P2_1/c$	157.01
23	Rabbittite	32.6	23.8	9.45		90.		8	mono	551.93
24	Roubaultite	7.767	6.942	7.850	92.16	90.89	93.48	1	P-1	254.20
25	Roubaultite	7.765(2)	6.915(2)	7.840(2)	92.31(2)	90.89(2)	93.48(2)	1	triclin	252.80
26	Rutherfordine*	4.845(10)	9.205(10)	4.296(6)				2	$Pm2_1n$ or Pmmn	57.690
27	Rutherfordine*	4.840	9.273	4.298				2	Imm2	58.084
28	Schröckingerite	9.69	16.83	14.26				4	Cmmm	350.12
29	Schröckingerite	9.634(1)	9.635(1)	14.391(2)	91.41(1)	92.33(1)	120.26(1)	2	P-1	346.67
30	Sharpite	21.99(2)	15.63(2)	4.487(4)				2	Ortho	464.37
31	Swartzite	11.12	14.72	6.47		99.5		2	$P2_1/m$	314.58
32	Swartzite	11.080	14.634	6.439		99.43		2	$P2_1/m$	310.12

	Name	Formula	Reference
33	Urancalcarite	$Ca_2[(UO_2)_3(CO_3)(OH)_6]•3(H_2O)$	Gaines et al. (1997), Deliens and Piret (1984)
34	Voglite	$Ca_3Cu(UO_2)(CO_3)_4•6(H_2O)$	Gaines et al. (1997), Piret (1979)
35	Widenmannite	$Pb_2(UO_2)(CO_3)_3$	Gaines et al. (1997)
36	Widenmannite	$Pb_2(UO_2)(CO_3)_3$	Plasil et al. (2010)
37	Wyartite	$Ca_3U(IV)(UO_2)_6(CO_3)_2(OH)_{18}•3\text{-}5(H_2O)$	Gaines et al. (1997)
38	Wyartite	$CaU(V)(UO_2)_2(CO_3)O_4(OH)•7(H_2O)$	Burns and Finch (1999)
39	Wyartite, dehydrated (ideal)	$CaU(V)(UO_2)_2(CO_3)O_4(OH)•3(H_2O)$	Hawthorne and Finch (2006)
40	Zellerite	$Ca_2(UO_2)(CO_3)_2•5(H_2O)$	Gaines et al. (1997), Coleman et al. (1966)
41	Znucalite	$CaZn_{12}(UO_2)(CO_3)_3(OH)_{22}•4(H_2O)$	Gaines et al. (1997), Ondruš et al. (1990), Jambor and Puziewicz (1991)
42	Znucalite	$CaZn_{11}(UO_2)(CO_3)_3(OH)_{20}•4(H_2O)$	Chiappero and Sarp (1993), Jambor et al. (1994)

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
33	Urancalcarite	15.42(3)	16.08(4)	6.970(6)				4	Pbnm or Pbn21	260.19
34	Voglite	25.97	24.50	10.70		104.		16	$P2_1$ or $P2_1/m$	248.63
35	Widenmannite	8.99	9.36	4.95				2	Pnnm, $Pnm2_1$ or $P22_12_1$	125.42
36	Widenmannite	8.964(4)	9.378(6)	5.007(4)				2	Pnnm, $Pnm2_1$ or $P22_12_1$	126.74
37	Wyartite	11.25	7.08	20.98				2	$P2_12_12_1$	503.17
38	Wyartite	11.2706(8)	7.1055(5)	20.807(1)				4	$P2_12_12_1$	250.87
39	Wyartite, dehydrated (ideal)	11.2610(6)	7.0870(4)	16.8359(10)				4	Pmcn	202.29
40	Zellerite	11.220	19.252	4.933				4	Pbnm or Pbn21	160.42
41	Znucalite	12.692(4)	25.096(6)	11.685(5)	89.08(2)	91.79(2)	90.37(3)	4	P1 or P-1	559.99
42	Znucalite	10.72(1)	25.16(1)	6.324(4)				2	ortho	513.59

	Name	Formula	Reference
	Synthetic Phases		
43	bright yellow ppt.	$Ba[UO_2(OO)CO_3•2(H_2O)]$	Gurevich and Polozenskaya (1963)
44		$Ba_2[UO_2(OO)(CO_3)_2]$ •x(H_2O)	Gurevich and Polozenskaya (1963)
45		$Ba_2[(UO_2)_2(OO)_3CO_3$• 4(H_2O)]	Gurevich and Polozenskaya (1963)
46		$(CN_3H_6)_4[UO_2(OO)(CO_3)_2]$•2($H_2O$)	Mikhailov et al. (1981)
47	*bright-yellow am. ppt.*	$K_2[UO_2(OO)CO_3(H_2O)_2]$•3($H_2O$)	Gurevich and Polozenskaya (1963)
48		$K_2Ca_3(UO_2)_2(CO_3)_6$•5(H_2O)	Kubatko (2005)
49	*red-orange ? am. ppt.*	$K_3[UO_3(OOH)(CO_3)_2$•(H_2O)]	Gurevich and Polozenskaya (1963)
50	*red-orange ? am. ppt.*	$K_4[UO_2(OO)(CO_3)_2]$	Gurevich and Polozenskaya (1963)
51		$K_4[(UO_2)(O_2)(CO_3)_2]$•3(H_2O)	Kubatko (2005)

	Name	Cell Constants							Space Group	$V_o^{\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
	Synthetic Phases									
43	bright yellow ppt.									
44										
45										
46		15.883(1)	8.788(2)	16.155(1)				4	Orthorh Pca21	339.48
47	*bright-yellow am. ppt.*									
48		17.015(2)	18.048(2)	18.394(2)				8	Pnnm	425.20
49	*red-orange am. ppt.?*									
50	*red-orange am. ppt. ?*									
51		6.9038(4)	9.2157(5)	21.8144(13)		91.061(1)		4	P21/n	330.98

	Name	Formula	Reference
54	*orange am. ppt.*	$K_4[(UO_2)_2(OO)_3CO_3(H_2O)_4]\bullet(H_2O)$	Gurevich and Polozenskaya (1963)
55	*am. at 420-640°C*	$K_4[(UO_2)_2(O)_3CO_3]$	Gurevich and Polozenskaya (1963)
56	*dark-orange xtllne ppt.*	$K_8[(UO_2)_2(OO)(CO_3)_5]\bullet 3(H_2O)$	Gurevich and Polozenskaya (1963)
57		$K_8[(UO_2)(O_2)(CO_3)_2]_2\bullet 3(H_2O)$	Kubatko (2005)
58		$Na_4(UO_2)(CO_3)_3$	Li et al. (2001)
59		$Rb_2(UO_2)(CO_3)_3\bullet 5(H_2O)$	Kubatko (2005)
60		$Rb_6Na_2[(UO_2)(CO_3)_3]_2\bullet(H_2O)$	Kubatko (2005)

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
54	*orange am. ppt.*									
55	*am. at 420-640°C*									
56	*dark-orange xtllne ppt.,*									
57		6.938(1)	9.225(2)	20.006(3)	83.612(3)	89.914(3)	89.632(3)	2	P-1	383.15
58		9.3417(6)		2.824(1)				4	P-3c1	145.91
59		10.774(4)	9.334(3)	12.483(4)		94.845(8)		8	C2/c	188.32
60		9.4316(7)		8.3595(8)				1	P-62c	387.82

Note discrepant formulas for Zellerite: $Ca(UO_2)(CO_3)_2\bullet 5(H_2O)$, Fontanite: $Ca[(UO_2)_3(CO_3)_2O_2]\bullet 6(H_2O)$, Urancalcarite: $Ca[(UO_2)_3(CO_3)(OH)_6]\bullet 3(H_2O)$

[#]Calculated from cell constants, this work

Table 6. Carbonate Minerals containing greater than 10 wt.% Uranium*

Name	Formula	Uranium, wt.%	gfw	Thermodynamic Data	
				Est.	Meas.
Albrechtschraufite	$Ca_4Mg(UO_2)_2(CO_3)_6F_2•17(H_2O)$	33.31	1428.98	no	no
Andersonite	$Na_2Ca(UO_2)(CO_3)_3•6(H_2O)$	36.95	644.20	yes	yes
Astrocyanite-(Ce)	$Cu_2(Ce,Nd,La)_2(UO_2)(CO_3)_5(OH)_2•1.5(H_2O)$	25.02	951.38	no	no
Bayleyite	$Mg_2(UO_2)(CO_3)_3•18(H_2O)$	28.92	822.94	yes	yes
Bijvoetite-(Y)	$(Y,REE)_8(H_2O)_{25}(UO_2)_{16}O_8(OH)_8(CO_3)_{16}•14(H_2O)$	53.88	7068.68	no	no
Blatonite	$UO_2CO_3•(H_2O)$	68.39	348.05	yes?	yes?
Cejkaite	$Na_4(UO_2)(CO_3)_3$	44.87	546.35	no	yes
Fontanite	$Ca[(UO_2)_3(CO_3)_2O_2]•6(H_2O)$	64.32	1110.27	yes	no
Grimselite	$K_3Na(UO_2)(CO_3)_3•(H_2O)$	39.13	608.36	yes	yes
Joliotite	$(UO_2)(CO_3)•n(H_2O),(n=2?)$	65.02	366.07	yes	no
Kamotoite-(Y)	$(Y,Nd,Gd)_2U(VI)_4(CO_3)_3O_{12}•14.5(H_2O)$	53.19	1790.08	no	no
Lepersonnite-(Gd)	$CaGd_2(UO_3)_{24}(CO_3)_8(SiO_4)_4O_4•60(H_2O)$	63.99	8909.01	no	no
Liebigite	$Ca_2(UO_2)(CO_3)_3•11(H_2O)$	32.68	728.38	yes	yes
Metazellerite	$Ca(UO_2)(CO_3)_2•3(H_2O)$	49.16	484.17	no	no
Oswaldpeetersite	$(UO_2)_2CO_3(OH)_2•4(H_2O)$	67.42	706.14	no	no
Rabbittite	$Ca_3Mg_3(UO_2)_2(CO_3)_6(OH)_4•18(H_2O)$	32.05	1485.56	yes	yes
Roubaultite	$Cu_2(UO_2)_3(CO_3)_2O_2(OH)_2•4(H_2O)$	59.74	1195.27	no	no
Rutherfordine	$UO_2(CO_3)$	72.12	330.04	-	yes
Schröckingerite	$NaCa_3(UO_2)(CO_3)_3(SO_4)F•10(H_2O)$	26.79	888.49	yes	yes
Shabaite-(Nd)	$Ca(Nd,Sm,Y)_2(UO_2)(CO_3)_4(OH)_2•6(H_2O)$	24.54	969.96	no	no
Sharpite	$Ca(UO_2)_6(CO_3)_5(OH)_4•6(H_2O)$	66.85	2136.41	yes	yes
Swartzite	$CaMg(UO_2)(CO_3)_3•12(H_2O)$	32.58	730.62	yes	yes
Urancalcarite	$Ca(UO_2)_3(CO_3)(OH)_6•3(H_2O)$	66.97	1066.26	yes	no
Voglite	$Ca_2Cu(UO_2)(CO_3)_4•6(H_2O)$	31.24	761.86	yes	yes
Widenmannite	$Pb_2(UO_2)(CO_3)_3$	27.54	864.46	no	no
Wyartite	$Ca_3U(IV)(UO_2)_6(CO_3)_2(OH)_{18}•3\text{-}5(H_2O)$	67.77	2458.63	?	?
Zellerite	$Ca(UO_2)(CO_3)_2•5(H_2O)$	45.76	520.20	yes	no
Znucalite	$CaZn_{11}(UO_2)(CO_3)_3(OH)_{20}•4(H_2O)$	14.68	1621.63	no	no

*Data taken primarily from a compilation given by the Mineralogy Database (http://webmineral.com).

References

Aas, W., Moukhamet-Galeev, A. and Grenthe, I. (1998). Complex formation in the ternary U(VI)-F-L system (L=Carbonate, oxalate and picolinate). Radiochimica Acta, 82, 77-82.

Allen, P.G., Bucher, J.J., Clark, D.L., Edelstein, N.M., Ekberg, S.A., Godhes, J.W., Hudson, E.A., Kaltsoyannis, N., Lukens, W.W., Neu, M.P., Palmer, P.D., Reich, T., Shuh, D.K., Tait, C.D. and Zwick, B.D. (1995). Multinuclear NMR, Raman, EXAFS, and X-ray structure of $[C(NH_2)_3]_6[(UO_2)_3(CO_3)_6]\bullet 6.5H_2O$. Inorganic Chemistry, 34, 4797-4807.

Almagro, V., Garcia, F.S. and Suncho, J. (1973), Polarographic study of the uranyl ion in sodium carbonate medium. Anales de Quimica (1968-1979), 69(6), 709-716.

Alwan, A.K. and Williams, P.A. (1980). The aqueous chemistry of uranium minerals: Part II. Minerals of the liebigite group. Mineralogical Magazine, 43, 665-667.

Amayri, S., Bernhard, G. and Nitsche, H. (1999). Solubility of $Ca_2[UO_2(CO_3)_3]\bullet 10H_2O$, Liebigite. Annual Report 1998 (FZR-247, January 1999), p. 12, Forschungszentrum Dresden-Rossendorf, Institute of Radiochemistry, Dresden, Germany.

Amayri, S., Geipel, G., Schuster, G., Baraniak, L., Bernhard, G. and Nitsche, H. (1998). Synthesis and characterization of calcium uranyl carbonate: $Ca_2[UO_2(CO_3)_3]\bullet 10H_2O$ (Liebigite). Annual Report 1997 (FZR- 218, May 1998), p. 14-15, Forschungszentrum Dresden-Rossendorf, Institute of Radiochemistry, Dresden, Germany.

Babko, A.K. and Kodenskaya, V.S. (1960). Equilibrium in solutions of complex uranyl carbonates. Russ. Journal of Inorg. Chemistry (Engl. Transl.) 5, 1241-1244. Also in Zhurnal Neorganicheskoi Khimii (1960), 5, 2568-2574 [In Russian].

Bernhard, G., Geipel, G., Brendler, V. and Nitsche, H. (1996). Speciation of uranium in seepage waters of a mine tailing pile studied by time-resolved laser-induced fluorescence spectroscopy (TRLFS). Radiochimica Acta, 74, 87-91.

Bernhard, G., Geipel, G., Brendler, V., Reich, T. and Nitsche, H. (1998). Validation of complex formation of Ca^{2+}, UO_2^{2+} and CO_3^{2-}. Annual Report 1997 (FZR- 218, May 1998), p. 16-17, Forschungszentrum Dresden-Rossendorf, Institute of Radiochemistry, Dresden, Germany.

Bernhard, G., Geipel, G., Reich, T., Brendler, V., Amayri, S. and Nitsche, H. (2001). Uranyl(VI) carbonate complex formation: Validation of the $Ca_2UO_2(CO_3)_3(aq)$ species. Radiochimica Acta, 89, 511-518.

Berto, S., Crea, F., Daniele, P. G., Gianguzza, A., Pettignano, A. and Sammartano, S. (2012). Advances in the investigation of dioxouranium (VI) complexes of interest for natural fluids. Coordination Chemistry Reviews, 256(1), 63-81.

Bidoglio, G., Cavalli, P., Grenthe, I., Omenetto, N., Qi, P. and Tanet, G. (1991). Studies on metal carbonate equilibria, Part 21: Study of the U(VI)-H_2O-CO_2(g) system by thermal lensing spectrophotometry. Talanta, 38, 433-437.

Blake, C.A., Colman, C.F., Brown, K.B., Hill, D.G., Lowie, R.S. and Schmitt, J.M. (1956). Studies in the carbonate-uranium system. Journal of the American Chemical Society, 78, 5978-5983.

Babinets, A.E., Zhorov, V.A,, Mitropol'skii, A.Yu and Bezborodov, A.A. (1977). Forms in which uranium is found in Black Sea water. Geologicheskii Zhurnal, 37(5), 109-114. [In Russian].

Brücher, E., Glaser, J. and Toth, I. (1991). Carbonate exchange for the complex $UO_2(CO_3)_3^{4-}$ in aqueous solution as studied by ^{13}C NMR spectroscopy. Inorganic Chemistry, 30, 2239-2241.

Bruno, J., Grenthe, I. and Robouch, P. (1989). Studies of metal carbonate equilibria. 20. Formation of tetra (carbonato) uranium (IV) ion, $U(CO_3)_4^{4-}$ in hydrogen carbonate solutions. Inorganica Chimica Acta, 158(2), 221-226.

Bullwinkel, E.P. (1954). The chemistry of uranium in carbonate solutions. U.S. Atomic Energy Commission Report RMO-2614, 59 p.

Burns, P.C. and Finch, R J. (1999). Wyartite: Crystallographic evidence for the first pentavalent-uranium mineral. American Mineralogist, 84, 1456-1460.

Capdevila, H. and Vitorge, P. (1990). Temperature and ionic strength influence on U(VI/V) and U(IV/III) redox potentials in aqueous acidic and carbonate solutions. Journal of Radioanalytical and Nuclear Chemistry, 143, 403-414.

Capdevila, H. and Vitorge, P. (1999). Redox potentials of M(VI)/M(V) limiting carbonate complexes (M = U or Pu) at different ionic strengths and temperatures. Entropy and heat capacity. Czech Journal of Physics, 49, 603-609.

Carroll, S. A. and Bruno, J. (1991). Mineral-solution interactions in the U(VI)-CO_2-H_2O system, Radiochimica Acta, 52, 187-193.

Čejka, J., Mŕazek, Z. and Urbanec, Z. (1984). New data on sharpite, a calcium uranyl carbonate. Neues Jahrbuch für Mineralogie, Monatshefte, 109-117.

Chen, F., Ewing, R.C. and Clark, S.B. (1999). The Gibbs free energies and enthalpies of formation of U^{6+} phases: An empirical method of prediction. American Mineralogist, 84, 650-664.

Christ, C.L., Clark, J.R. and Evans, H.T. (1955). Crystal structure of rutherfordine, UO_2CO_3. Science, 121(3144), 472-473.

Ciavatta, L., Ferri, D., Grimaldi, M., Palombari, R. and Salvatore, F. (1979). Dioxouranium(VI) carbonate complexes in acid solution. Journal of Inorganic and Nuclear Chemistry, 41, 1175-1182.

Ciavatta, L., Ferri, D., Grenthe, I. and Salvatore, F. (1981). The first acidification step of the tris(carbonato)dioxouranate(VI) Ion, $UO_2(CO_3)_3^{4-}$. Inorganic Chemistry, 20, 463-467.

Chiappero, P. and Sarp, H. (1993). New data on znucalite and 2nd occurrence-Le-Mas-Dalary, Lodeve (Herault, France). Archives des Sciences, 46(3), 291-301.

Cinnéide, S.O., Scanlan, J.P. and Hines, M.J. (1975). Equilibria in uranyl carbonate systems – 1.

The overall stability constant of $UO_2(CO_3)_3^{4-}$. Journal of Inorganic and Nuclear Chemistry, 37, 1013-1018.

Cleveland, J. M. (1970). The Chemistry of Plutonium. Gordon and Breach, New York.

Coda, A., Della Giusta, A. and Tazzoli, V. (1981). The structure of synthetic andersonite, $Na_2Ca[UO_2(CO_3)_3].x(H_2O)$ (x~5.6). Acta Crystallographica, B37, 1496-1500.

Coleman, R.G., Ross, D.R. and Meyrowitz, R. (1966). Zellerite and metazellerite, new uranyl carbonates. American Mineralogist, 51, 1567-1578.

Cordfunke, E.H.P. and O'Hare, P.A.G. (1978). The chemical thermodynamics of actinide elements and

compounds: Part 3. Miscellaneous actinide compounds. International Atomic Energy Agency, Vienna, 83 p.

Deliens, M. and Piret, P. (1982). Bijvoetite and Lepersonnite, uranyl and rare-earth hydrated carbonates at Shinkolobwe, Zaire. Canadian Mineralogist, 20. 231-238.

Deliens, M. and P. Piret (1984). L'urancalcarite, $Ca(UO_2)_3(CO_3)(OH)_6 \cdot 3H_2O$, nouveau minéral de Shinkolobwe, Shaba, Zaire. Bulletin de Mineralogie, 107, 21-24.

Deliens, M. and Piret, P. (1990). L'astrocyanite-(Ce), $Cu_2(TR)_2(UO_2)(CO_3)_5(OH)_2.1{,}5H_2O$, nouvelle espèce minérale de Kamoto, Shaba, Zaire. European Journal of Mineralogy, 2(3), 407-411.

Deliens, M. and Piret, P. (1992). La fontanite, carbonate hydrate d'uranyle et de calcium, nouvelle espèce minerale de Rabejac, Herault, France. European Journal of Mineralogy, 4, 1271-1274.

Devina, 0.A. Khodakovsky, I.L. Efimov, M.E. and Medvedev, V.A. (1977). 7th All Union Conference on Calorimetry, 231. [As cited in Lemire and Tremaine (1980)].

Djogić, R. and M. Branica, M. (1991). Dissolved uranyl complexed species in artificial seawater. Marine Chemistry, 36, 121-135.

Dong, W and Brooks, S.C. (2006). Determination of the formation constants of ternary complexes of uranyl and carbonate with alkaline earth metals (Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) using anion exchange method. Environmental Science and Technology, 40, 4689-4695.

Duro, L., Grivé, M., Cera, E., Domènech, C. and Bruno, J. (2006). Update of a thermodynamic database for radionuclides to assist solubility limits calculation for performance assessment. Swedish Nuclear Fuel and Waste Management Co., Stockholm, Sweden. 128 p.

Ferri, D., Grenthe, I. and Salvatore, F. (1981). Dioxouranium (VI) carbonate complexes in neutral and alkaline solutions. Acta Chemica Scandinavica, Ser. A, 35A, 165-168.

Ferri, D., Grenthe, I. and Salvatore, F. (1983). Studies on metal carbonate equilibria. 7. Reduction of tris(carbonato)dioxouranate(VI) ion, $UO_2(CO_3)_3^{4-}$, in carbonate solutions. Inorganic Chemistry, 22, 3162-3165.

Finch, F.R. (1997). Thermodynamic stabilities of U(VI) minerals: Estimated and observed relationships. In Scientific Basis for Nuclear Waste Management XX, (W.J. Gray and I.R. Triay, Eds.), Materials Research Society Proceedings, 465, 1185-1192.

Finch R.J., Cooper, M.A., Hawthorne, F.C. and Ewing, R.C. (1999). Refinement of the crystal structure of rutherfordine. Canadian Mineralogist, 37, 929-938.

Frost, R.L. and Cejka, J. (2009). A Raman spectroscopic study of the uranyl mineral rutherfordine – revisited. Journal of Raman Spectroscopy, 40(9). 1096-1103.

Fuger, J. (1983). Uranium: chemical thermodynamic properties-selected values, Gmelin Handbook of Inorganic Chemistry, Suppl. A6, 165-192, Springer-Verlag, Berlin.

Gaines, R.V., Skinner, H.C.W., Foord, E.E., Mason, B., Rosenzweig, A. King, V.T. and Dowty, E. (1997). Dana's New Mineralogy (Eighth edition). John Wiley and Sons, Inc., New York. 1819 p.

Garrels, R.M. (1957). Some free energy values from geologic relations. American Mineralogist, 42(11-2), 780-791.

Garrels, R.M. (1960). Some free energy values from geologic correlations. In Thermodynamics of

Geochemical Processes, 122-136. [In Russian]. See Garrels (1957).

Geipel, G., Reich, T., Brendler, V., Bernhard, G. and Nitsche, H. (1997). Laser and X-ray spectroscopic studies of uranium-calcite interface phenomena. Journal of Nuclear Materials, 248, 408-411.

Geipel, G., Bernhard, G., Brendler, V. and Nitsche, H. (1998a). Complex formation between UO_2^{2+} and CO_3^{2-}: Studied by laser-induced photoacoustic spectroscopy (LIPAS). Annual Report 1997 (FZR - 218, May 1998), p. 22-23, Forschungszentrum Dresden-Rossendorf, Institute of Radiochemistry, Dresden, Germany.

Geipel, G., Bernhard, G., Brendler, V. and Nitsche, H. (1998b). Complex formation between UO_2^{2+} and CO_3^{2-}: Studied by laser-induced photoacoustic spectroscopy (LIPAS). Radiochimica Acta, 82, 59-62.

Geipel, G., Bernhard, G., Brendler, V. and Nitsche, H. (1998c). Uranyl hydroxo carbonate complexes by laser-induced spectroscopy. Annual Report 1997 (FZR - 218, May 1998), p. 23-25, Forschungszentrum Dresden-Rossendorf, Institute of Radiochemistry, Dresden, Germany.

Geipel, G., Bernhard, G. and Nitsche, H. (1999). Validation of the complex formation between UO_2^{2+} and CO_3^{2-} using EDTA adjust the Ca^{2+} concentration. Annual Report 1998 (FZR - 247, January 1999), p. 11, Forschungszentrum Dresden-Rossendorf, Institute of Radiochemistry, Dresden, Germany.

Ginderow, D.A.R.I.A. and Cesbron, F. (1985). Structure de la roubaultite, $Cu_2(UO_2)_3(CO_3)_2O_2(OH)_2.4H_2O$. Acta Crystallographica Section C: Crystal Structure Communications, 41(5), 654-657.

Golovnya, V.A., Pospelova, L.A. and Bolotova, G.T. (1960). Acido complexes of cerium(IV) and uranium(IV). Zhurnal Neorganicheskoi Khimii, 5, 2204-2210. [In Russian].

Gorman-Lewis, D., Burns, P.C. and Fein, J.B. (2008). Review of uranyl mineral solubility measurements. Journal of Chemical Thermodynamics, 40, 335-352.

Götz, C., Geipel, G. and Bernhard, G. (2011). The influence of the temperature on the carbonate complexation of uranium (VI): a spectroscopic study. Journal of Radioanalytical and Nuclear Chemistry, 287(3), 961-969.

Grenthe, I. and Lagerman, B. (1991). Studies on metal carbonate equilibria. 22. A coulometric study of the uranium (VI)-carbonate system, the composition of the mixed hydroxide carbonate species. Acta Chemica Scandinavica, 45, 122-128.

Grenthe, I., Ferri, D., Salvatore, F. and Riccio, G. (1984a). Studies on metal carbonate equilibria. Part 10. A solubility study of the complex formation in the uranium (VI)–water–carbon dioxide (g) system at 25° C. Journal of Chemical Society, Dalton Transactions, (11), 2439-2443.

Grenthe, I., Spahiu, K. and Olofsson, G. (1984b). Studies on metal carbonate equilibria. 9. Calorimetric determination of the enthalpy and entropy changes for the formation of uranium (IV and VI) carbonate complexes at 25° C in a 3 *M* $(Na,H)ClO_4$ ionic medium. Inorganica Chimica Acta, 95(2), 79-84.

Grenthe, I., Robouch, P. and Vitorge, P. (1986). Chemical equilibria in actinide carbonate systems. Journal of the Less Common Metals, 122, 225-231.

Grenthe, I., Fuger, J., Konings, R.J.M., Lemire, R.J., Muller, A.B., Nguyen-Trung, C., Wanner, H. and Forest, I. (1992). Chemical Thermodynamics of Uranium. Nuclear Energy Agency, Organisation for Economic Co-operation, Development, Eds., vol. 1, Chemical Thermodynamics, North Holland Elsevier Science Publishers B. V., Amsterdam, The Netherlands, 715 p.

Guillaumont, R., Fanghanel, T., Fuger, J., Grenthe, I., Neck, V., Palmer, D. and Rand, M.H. (2003). Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technecium. Elsevier: Amsterdam.

Gurevich, A.M. and Polozenskaya, L.D., 1963. The solid phase in the $UO_2(NO_3)_2$-K_2CO_3-H_2O_2-H_2O system. Radiokhimiya, 5, 592-602 [In Russian].

Gurevich, V.M., Seregeyeva, E.I., Gavrichev, K.S., Gorbunov, V.E. and Khodakovsky, I.L. (1987). Low temperature specific heat of UO_2CO_3. Russian Journal of Physical Chemistry, 61, 856-857.

Hála, J. and Navratil, J.D. (2001). IUPAC-NIST solubility data series. 74. Actinide carbon compounds. Journal of Physical and Chemical Reference Data, 30(2), 531-698.

Hawthorne, F.C., Finch, R.J. and Ewing, R.C. (2006). The crystal structure of dehydrated wyartite, $Ca(CO_3)[U^{5+}(U^{6+}O_2)_2O_4(OH)]\,(H_2O)_3$. Canadian Mineralogist, 44, 1379-1385.

Hemingway, B.S. (1982). Thermodynamic properties of selected uranium compounds and aqueous species at 298.15 K and I bar and at higher temperatures. Preliminary models for the origin of coffinite deposits, U.S. Geological Survey, Open File Report 82-619, (1982), 89 p.

Hietanen, S. and Sillen, L.G. (1959). Studies on the hydrolysis of metal ions. 22. Equilibrium studies in self-medium; Application to the hydrolysis of Th^{4+}. Acta Chemica Scandinavica, 13, 533-550.

Hughes, K-A, and Burns, P C. (2003). A new uranyl carbonate sheet in the crystal structure of fontanite, $Ca[(UO_2)_3(CO_3)_2O_2](H_2O)_6$. American Mineralogist, 88, 962-966.

Hummel, W., Berner, U., Curti, E., Pearson, F.J. and Thoenen, T. (2002). Nagra / PSI Chemical Thermodynamic Data Base 01/01. Universal Publishers/uPublish.com, Parkland, Florida, 565 p.

Jambor, J.L. and Puziewicz, J. (1991). New Mineral Names. American Mineralogist, 76, 1728-1735.

Jambor, J.L., Grew, E.S. and Roberts, A.C. (1994). New Mineral Names. American Mineralogist, 79, 1210-1214.

Kalmykov, S.N. and Choppin, G.R. (2000). Mixed $Ca^{2+}/UO_2^{2+}/CO_3^{2-}$ complex formation at different ionic strengths. Radiochimica Acta, 88, 603-606.

Karpov, I.K., Kashik, S.A. and Pampura, V.D. (1968). Thermodynamic Constants for Calculations in Geochemistry and Petrology. Izdva, Nauka, 143 p. [In Russian].

Kato, Y., Kimura, T., Yoshida, Z. and Nitani, N. (1996). Solid-liquid phase equilibria of Np(VI) and of U(VI) under controlled CO_2 partial pressures. Radiochimica Acta, 74, 21-25.

Kelly, S.D., Kemner, K.M. and Brooks, S.C. (2007). X-ray absorption spectroscopy identifies calcium-uranyl-carbonate complexes at environmental concentrations. Geochimica et Cosmochimica Acta, 71(4), 821-834.

Kimura, T., Serrano, J., Nakayama, S., Takahashi, K. and Takeishi, H. (1992). Speciation of uranium in aqueous-solutions and in precipitates by photoacoustic-spectroscopy. Radiochimica Acta, 58, 173-178.

Klygin, A.E. and Smirnova, Y.D. (1959). Instability constant of $UO_2(CO_3)_3^{4-}$. Russian Journal of Inorganic Chemistry (English Translation), 4, 16.

Komarov, E.V. (1959). Complex formation in the system uranyl nitrate-potassium bicarbonate-hydrogen peroxide-water. Zhurnal Neorganicheskoi Khimii, 4, 1313-23. [in Russian].

Komarov, E.V., Preobrazhenskaya, L.D. and Gurevich, A.M., 1959. Compounds formed in the $UO_2(NO_3)_2$-K_2CO_3-H_2O_2-H_2O system. Zhurnal Neorganicheskoi Khimii, 4, 1667-1673. [in Russian].

Kramer-Schnabel, U., Bischoff, H., Xi, R.H. and Marx, G. (1992). Solubility products and complex formation equilibria in the systems uranyl hydroxide and uranyl carbonate at 25 C and I= 0.1 M. Radiochimica Acta, 56(4), 183-188.

Krishnamurty, K.V. Harris, G.M. and Sastri, V.S. (1970). The chemistry of the metal carbonato complexes. Chemical Reviews, 70(2), 171-197.

Kubatko, K.A. (2005). Crystallography, Hierarchy of Crystal Structures and Chemical Thermodynamics of Select Uranyl Phases, Doctoral dissertation, University of Notre Dame.

Kubatko, K-A., Helean, K.B., Navrotsky, A. and Burns, P.C. (2005). Thermodynamics of uranyl minerals: Enthalpies of formation of rutherfordine, UO_2CO_3, andersonite, $Na_2CaUO_2(CO_3)_3(H_2O)_5$, and grimselite, $K_3NaUO_2(CO_3)_3H_2O$. American Mineralogist, 90(8-9), 1284-1290

Langmuir, D. (1978). U solution mineral equilibria at low temperatures with applications to sedimentary ore deposits. Geochimica et Cosmochimica Acta, 42, 547-569.

Lemire, R.J. and Tremaine, P.R. (1980). Uranium and plutonium equilibria in aqueous solutions to 200°C. Journal of Chemical and Engineering Data, 25(4), 361-370.

Lemire, R.J. (2001). Chemical Thermodynamics of Neptunium and Plutonium. Organisation for Economic Co-operation and Development (OECD)/Nuclear Energy Agency (NEA): Elsevier. New York, New York.

Li, Y., Burns, P.C. and Gault, R.A. (2000). A new rare-earth-element uranyl carbonate sheet in the structure of bijvoetite-(Y). Canadian Mineralogist, 38, 153-162

Li, Y., and Burns, P.C. (2001). The crystal structure of synthetic grimselite, $K_3Na[(UO_2)(CO_3)_3](H_2O)$. Canadian Mineralogist, 39, 1147-1151.

Li, Y., Krivovichev, S.V. and Burns, P.C. (2001). The crystal structure of $Na_4(UO_2)(CO_3)_3$ and its relationship to schröckingerite. Mineralogical Magazine, 65(2), 297-304.

Liu, C, Zachara, J.M., Qafoku, O. and Heald, S. (2002). Thermodynamics and dissolution kinetics of uranyl minerals in Hanford Bx-102 sediments. Appendix D.3.5, p. D-188 - D-220. In Appendix D: Digest of Science and Technology Project Evaluations, 306 p. In Field Investigation Report for Waste Management Area B-BX-BYRPP-10098, Rev. 0, CH2M HILL Hanford Group, Inc., Richland, Washington. 2003.

Maya, L. (1982). Hydrolysis and carbonate complexation of dioxouranium (VI) in the neutral-pH range at 25. degree. C. Inorganic Chemistry, 21(7), 2895-2898.

Mayer, H. and Mereiter, K. (1986). Synthetic bayleyite, $Mg_2[UO_2(CO_3)_3].18H_2O$: Thermochemistry, crystallography and crystal structure. Tschermaks mineralogische und petrographische Mitteilungen, 35, 133-146.

McClaine, L.A., Bullwinkel, E.P. and Huggins, J.C. (1956). The carbonate chemistry of uranium: theory and applications. Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva, 8, 26-37.

Meinrath, G., and Kimura, T. (1993a). Carbonate complexation of the uranyl(VI) ion. Journal of Alloys and Compounds, 202, 89-93.

Meinrath, G. and Kimura, T. (1993b). Behaviour of U(VI) solids under conditions of natural aquatic systems. Inorganica Chimica Acta, 204, 79-85.

Meinrath, G., Kato, Y. and Yoshida, Z. (1993). Spectroscopic study of the uranyl hydrolysis species $(UO_2)_2(OH)_2^{2+}$. Journal of Radioanalytical and Nuclear Chemistry, 174(2), 299-314. [Errata reported in Journal of Radioanalytical and Nuclear Chemistry, (1994), 181(2), 253, but not found.]

Meinrath, G., Klenze, R. and Kim, J.I. (1996a). Direct spectroscopic speciation of uranium(VI) in carbonate solutions. Radiochimica Acta, 74, 81-86.

Meinrath, G., Kato, Y., Kimura, T. and Yoshida, Z. (1996b). Solid-aqueous phase equilibria of uranium(VI) under ambient conditions. Radiochimica Acta, v. 75, p. 159-167.

Meinrath, G., Kato, Y., Kimura, T. and Yoshida, Z. (1999). Comparative analysis of actinide(VI) carbonate complexation by Monte Carlo resampling methods. Radiochimica Acta, v. 84, p. 21-29.

Mereiter, K. (1982). The crystal structure of liebigite, $Ca_2UO_2(CO_3)_3.\sim 11H_2O$. Tschermaks mineralogische und petrographische Mitteilungen, 30, 277-288.

Mereiter, K. (1986a). Synthetic swartzite, $CaMg[UO_2(CO_3)_3].12H_2O$, and its strontium analogue, $SrMg[UO_2(CO_3)_3].12H_2O$: Crystallography and crystal structures. Neues Jahrbuch für Mineralogie, Monatshefte, 1986, 481-492.

Mereiter, K. (1986b). Crystal structure and crystallographic properties of a schröckingerite from Joachimsthal. Tschermaks mineralogische und petrographische Mitteilungen, 35, 1-18.

Mikhailov, Yu.N., Lobanova, G.M. and Shchelokov, R.N. (1981). X-ray diffraction study of crystals of guanidinium dicarbonatodioxoperoxouranate dihydrate $(CN_3H_6)_4[UO_2(O_2)(CO_3)_2].2H_2O$. Zhurnal Neorganicheskoi Khimii, 26(3), 718-22. [In Russian].

Mizuguchi, K., Park, Y.Y. and Tomiyasu, H. (1993). Electrochemical and spectroelectrochemical studies on uranyl carbonato and aqua complexes. Journal of Nuclear Science and Technology, 30, 542-548.

Morss, L.R. (1986). Thermodynamic properties, The chemistry of the actinide elements, 2nd ed., Katz, J J., Seaborg, G T., Morss, L.R., Eds., vol. 2, p. 1278-1360, Chapman and Hall, London, (1986).

Naumov, G.B., Ryzhenko, B.N. and Khodakovsky, 1.L. (1974). Handbook of Thermodynamic Data. Natl. Tech. Inf. Service, 722176A, U.S. Dept. Commerce. 328 p.

Nickel, E.H. and Nichols, M.C. (1992). Mineral Reference Manual. Van Norstrand Reinhold (NY), 250 p.

Nikolaeva, N.M. (1976). Solubility product of uranyl carbonate at elevated temperatures. Izvestiya Sibirskogo Otdeleniya Akademii Nauk SSSR, Seriya Khimicheskikh Nauk 6, 30-31. [In Russian]

Nitzsche, O., Meinrath, G. and Merkel, B. (2000). Database uncertainty as a limiting factor in reactive transport prognosis. Journal of Contaminant Hydrology. 44. 223-237.

O'Brien, T.J. and Williams, P.A. (1983). The aqueous chemistry of uranium minerals: 4. Schröckingerite, grimselite, and related alkali uranyl carbonates. Mineralogical Magazine, 47, 69-73.

Ondruš, P., Veselovskí, F. and Rybka, R. (1990). Znucalite, $Zn_{12}(UO_2)Ca(CO_3)_3(OH)_{22}.4H_2O$, a new mineral from Příbram, Czechoslovakia. Neues Jahrbuch fur Mineralogie, Monatshefte, 393-400.

Ondrus, P, Skala, R, Veselovsky, F, Sejkora, J. and Vitti, C. (2003). Cejkaite, the triclinic polymorph of $Na_4(UO_2)$. $p.(CO_3)_3$ - a new mineral from Jachymov, Czech Republic. American Mineralogist, 88, 686-693.

Paramonova, V.I., and Nikolaeva, M.N. (1962). The use of ion exchange for the study of the state of substances in solution. VIII. The study of carbonate solutions of uranyl by an ion-exchange method. Radiokhimiya, 4, 84-89.

Pashalidis, I., Runde, W. and Kim, J.I. (1993). A study of the solid-liquid equilibria of Pu(VI) and U(VI) in aqueous carbonate systems. Radiochimica Acta, 61, 141-146.

Pashalidis, I., Czerwinski, K.R., Fanghanel, T. and Kim, J.I. (1997). Solid-liquid phase equilibria of Pu(VI) and U(VI) in aqueous carbonate systems. Determination of stability constants. Radiochimica Acta, 76, 55-62.

Piret, P. (1979). New crystal data for Ca, Cu, UO_2 hydrated carbonate: voglite. Journal of Applied Crystallography, 12, 616.

Pirozhkov, A.V. and Nikolaeva, N.M. (1976). Determination of the stability constants of uranyl carbonate from 25 to 150°. Izvestiya Sibirskogo Otdeleniya Akademii Nauk SSSR, Seriya Khimicheskikh Nauk, (5), 55-59. [In Russian].

Plášil, J., Cejka, J., Sejkora, J., Škácha, P., Goliáš, V., Jarka, P., Laufek, F., Jehlicka, J., Nemec, I. and Strnad, L. (2010). Widenmannite, a rare uranyl lead carbonate: occurrence, formation and characterization. Mineralogical Magazine, 74, 97-110.

Radha, A.V. and Navrotsky, A. (2013). Thermodynamics of carbonates. Reviews in Mineralogy and Geochemistry, 77(1), 73-121.

Rai, D., Felmy, A.R., Hess, N.J., Moore, D.A. and Yui, M. (1998). A thermodynamic model for the solubility of UO_2(am) in the aqueous K^+-Na^+-HCO_3^--CO_3^{2-}-OH^--H_2O system. Radiochimica Acta, 82, 17-25.

Redkin, A.F. and Wood, S.A. (2007). Uranium(VI) in aqueous solutions at 25°C and a pressure of 1 bar: Insight from experiments and calculations. Geochemistry International, 45(11), 1111-1123.

Rosenheim, A. and Kelmy, M. (1932). Compounds of quadrivalent uranium. Zeitschrift für anorganische und allgemeine Chemie, 206, 31-43.

Scanlan, J.P. (1977). Equilibria in uranyl carbonate systems - II. The overall stability constant of $UO_2(CO_3)_2^{2-}$ and the third formation constant of $UO_2(CO_3)_3^{4-}$. Journal of Inorganic and Nuclear Chemistry, 39, 635-639.

Sergeeva, E.I., Nikitin, A.A., Khodakovskii, I.L. and Naumov, G.B. (1972a). Equilibriums in the uranium trioxide-carbon dioxide-water system at 25-200. Deg. Geokhimiya, 11, 1340-1350 [In Russian].

Sergeyeva, E.I., Nikitin, A.A., Khodakovkiy I.L. and Naumov, G.B. (1972b). Experimental investigation of equilibria in the system UO_3-CO_2-H_2O in 25–200°C temperature interval. Geochemistry

International, 9, 900-910.

Sergeyeva, E.I., Savelyeva, N.I., Red'kin, A.F., Zotov, A.V., Omelyanenko, B.I., Ivanov, I.P. and Khodakovsky, I.L. (1989). Complex formation of U(IV) and U(VI) in aqueous solutions in the range 25-600°C and 1-1000 bars (experimental study). Proceedings of a Workshop, Academy of Sciences of the USSR, Report 3-11, (1989), 1 p.

Shock, E.L., Sassani, D.C. and Betz, H. (1997). Uranium in geologic fluids - estimates of standard partial molal properties, oxidation potentials, and hydrolysis constants at high temperatures and pressures. Geochimica et Cosmochimica Acta, 61, 4245–4266.

Shvareva, T.Y., Fein, J.B. and Navrotsky, A. (2011). Thermodynamic properties of uranyl minerals: constraints from calorimetry and solubility measurements. Industrial and Engineering Chemistry Research, 51(2), 607-613.

Silva, R.J., Bidoglio, G., Rand, M.H., Robouch, P., Wanner, H. and Puigdomenech, I. (1995). Chemical Thermodynamics of Americium. Nuclear Energy Agency, Organisation for Economic Cooperation, Development, Ed., vol. 2, Chemical Thermodynamics, North Holland Elsevier Science Publishers B. V., Amsterdam, The Netherlands, 374 p.

Smith, R.M., Martell, A.E. and Motekaitis, R.J. (1997). NIST Critically Selected Stability Constants of Metal Complexes Database. Version 4.0. NIST Standard Reference Database 46, National Institute of Standards and Technology, Gaithersburg, Maryland. (includes personal computer software database)

Stabrovskii, A.I. (1960). Polarography of uranium compounds in solutions of carbonates and bicarbonates. Zhurnal Neorganicheskoi Khimii, 5, 811-820. [In Russian].

Szabo, Z., Moll, H., Grenthe, I. (2000). Structure and dynamics in the complex ion $(UO_2)_2(CO_3)(OH)_3^-$. Journal of the Chemical Society, Dalton Transactions, 18, 3158-3161.

Tsymball, C. (1969). Contribution to the solution chemistry of uranium (VI). Nuclear Science Abstracts 23(24), abs. 49767.

Tsymball, C. (1970). Commis. Energ. At. (Fr.), Rapp. 1969, CEAR-3476: Chemical Abstracts. 72. 6684j

Van Genderen, A.C.G. and Van der Weijden, C.H. (1984). Prediction of Gibbs energies of formation and stability constants of some secondary uranium minerals containing the uranyl group. Uranium, 1(3), 249-256.

Vochten, R. and Deliens, M. (1998). Blatonite, $UO_2CO_3 \cdot H_2O$, a new uranyl carbonate monohydrate from San Juan County, Utah. Canadian Mineralogist, 36, 1077-1081.

Vochten, R., Deliens, M. and Medenbach, O. (2001). Oswaldpeetersite, $(UO_2)_2CO_3(OH)_2 \cdot 4H_2O$, a new basic uranyl carbonate mineral from the Jomac Uranium Mine, San Juan County, Utah, U.S.A. Canadian Mineralogist, 39, 1685-1689.

Wagman, D.D., Evans, W.H., Parker, V.B., Schumm, R.H., Halow, I., Bailey, S.M., Churney, K.L. and Nuttall, R.L. (1982). The NBS tables of chemical thermodynamic properties: Selected values for inorganic and C_1 and C_2 organic substances in SI units, Journal of Physical and Chemical Reference Data, v. 11, Supplement 2, 1-392.

Woods, T.L. and Garrels, R.M. (1987). Thermodynamic Values at Low Temperature for Natural Inorganic Materials. An Uncritical Summary. Oxford University Press. 242 p. plus references.

Yamamura, T., Kitamura, A., Fukui, A., Nishikawa, S., Yamamoto, T. and Moriyama, H. (1998). Solubility of U(VI) in highly basic solutions. Radiochimica Acta, 83, 139-146.

ZINC

Table 1. Association Constants for Aqueous Carbonate Complexes in the System $ZnO-CO_2-H_2O$

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
$Zn^{2+} + CO_3^{2-} = ZnCO_3(aq)$	4.80	-	Data not found in source reference	Fouillac and Criaud (1984)	Schindler et al. (1968)?
	5.3	-	$I = 0$	Palmer and Van Eldik (1983)	Zirino and Yamamoto (1972)
	5.3	-	Estimate		Zirino and Yamamoto (1972)
	6.3	-	$I = 0.0$	Bilinski et al. (1976)	Zirino and Yamamoto (1972)
	5.3	-		Long and Angino (1977)	Zirino and Yamamoto (1972)
	≈3.5	-	DPP, 0.0001 *M* KNO_3		Bilinski et al. (1976)
	3.9	-		Zachara et al. (1989)	Bilinski et al. (1976)
	6.63		Estimate		Mattigod and Sposito (1977)
	4.80	-0.38	Estimate		Fouillac and Criaud (1984)
	4.35	-		Millero and Hawke (1992)	Stanley and Byrne (1990)
$Zn^{2+} + 2CO_3^{2-} = Zn(CO_3)_2^{2-}$	9.63		Estimate		Mattigod and Sposito (1977)
	6.9 ± 0.1	-	EMF, 3 *M* $NaClO_4$		Ferri et al. (1987)
	7.25	-		Millero and Hawke (1992)	Stanley and Byrne (1990)
$Zn^{2+} + CO_3^{2-} + H^+ = ZnHCO_3^+$	12.4	-	Estimate		Zirino and Yamamoto (1972)
	12.4*	-		Zachara et al. (1989)	Zirino and Yamamoto (1972)
	11.73 ± 0.02*	-	EMF		Ryan and Bauman (1978)
	12.53*	-10.59*	Estimate		Fouillac and Criaud (1984)
	11.13 ± 0.2*	-	EMF, $I = 0.0$		Ferri et al. (1985)
	12.07*	-		Millero and Hawke (1992)	Stanley and Byrne (1990)
$Zn^{2+} + HCO_3^- = ZnHCO_3^+$	2.1	-		Long and Angino (1977)	Zirino and Yamamoto (1972)
	2.1	-	$I = 0$	Palmer and Van Eldik (1983)	Zirino and Yamamoto (1972)
	1.4	-		Palmer and Van Eldik (1983)	Bauman et al. (1975)
	2.07		Estimate		Mattigod and Sposito (1977)
	1.400 ± 0.020	3.57	25°C, $I = 0$		Ryan and Bauman (1978)
		7.3		Palmer and Van Eldik (1983)	Ryan and Bauman (1978)

Table 1. Association Constants for Aqueous Carbonate Complexes in the System ZnO-CO_2-H_2O (Continued)

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	1.4	3.5		Palmer and Van Eldik (1983)	Ryan and Bauman (1978)
	1.4	-		Palmer and Van Eldik (1983)	Bauman (1981)
$Zn^{2+} + H_2O + CO_2(g) = ZnHCO_3^+ + H^+$	-7.70 ± 0.05	-	EMF, 3 *M* $NaClO_4$		Ferri et al. (1985)
$Zn^{2+} + CO_3^{2-} + 2OH^- = ZnCO_3(OH)_2^{2-}$	12.2 ± 0.07	-	EMF, 3 *M* $NaClO_4$		Ferri et al. (1987)
$2Zn^{2+} + H2O + CO_2(g) = Zn_2CO_3^{2+} + 2H^+$	-13.47 ± 0.05	-	EMF, 3 *M* $NaClO_4$		Ferri et al. (1985)
$2Zn^{2+} + CO_3^{2-} = Zn_2CO_3^{2+}$	5.1 ± 0.2	-	EMF, *I* = 0		Ferri et al. (1985)

(1) At standard state (25°C, 1 atm, *I* = 0), unless otherwise noted.

* Corrected using bicarbonate dissociation equation from PHREEQC

Table 2. Solubility Constants of Solid Carbonates in the System $ZnO-CO_2-H_2O$

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
Minerals					
Aurichalcite					
$Zn_{2.73}Cu_{2.27}(CO_3)_2(OH)_6 = 2.73Zn^{2+} + 2.27Cu^{2+} + 2CO_3^{2-} + 6OH^-$	-90.1	-			Alwan et al. (1980)
Hydrozincite					
$Zn_5(CO_3)_2(OH)_6 + 6H^+ = 5Zn^{2+} + 2CO_3^{2-} + 6H_2O$	9.65			Zachara et al. (1989)	Schindler et al. (1969)
	12.94			Zachara et al. (1989)	Sangameshwar and Barnes (1983)
	6.41 ± 0.51		Natural specimen. 22 - 25°C		Zachara et al. (1989)
	8.30		Estimated		Yoder and Rowand (2006)
	2.95		Estimated		Yoder et al. (2010)
$Zn_5(CO_3)_2(OH)_6 = 5Zn^{2+} + 2CO_3^{2-} + 6OH^-$	-73.50		Sol., I = 0.2 ($NaClO_4$)	Clever et al. (1992)	Schindler et al. (1969) citing Sahli (1952)
	-75.8 ± 0.8	-	Sol.		Takahashi (1960)
	-74.25	-	I = 0.3 M	Mercy et al. (1998)	Schindler et al. (1969)
	-70.05	-	I = 0.2 M	Palmer and Van Eldik (1983)	Ryan and Bauman (1978)
	-74.30	-	I = 0	Palmer and Van Eldik (1983)	Ryan and Bauman (1978)
	-74.5 ± 0.5	-			Alwan and Williams (1979)
	-74.65 ± 0.25	-	22°C		Savenko and Shatalov (1999)
$Zn_5(CO_3)_2(OH)_6 + 10H^+ = 5Zn^{2+} + 2CO_2(g) + 8H_2O$	49.00	-			Grauer and Feitnecht (1967)
	45.99 ± 0.25	-			Schindler et al. (1969)
	45.0 ± 0.5	-			Preis and Gamsjager (2001a)
	45.00	-256.5			Preis and Gamsjäger (2001b)
Rosasite					

Table 2. Solubility Constants of Solid Carbonates in the System $ZnO-CO_2-H_2O$ (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
$Cu_{1.16}Zn_{0.84}CO_3(OH)_2 = 1.16Cu^{2+} + 0.84Zn^{2+} + CO_3^{2-} + 2OH^-$	-36.4	-			Alwan et al. (1980)
Smithsonite					
$ZnCO_3(s) = Zn^{2+} + CO_3^{2-}$	-10.68			Latimer (1952)	Ageno and Valla (1911)
	-9.060		25°C, I = 0	Clever et al. (1992)	Ageno and Valla (1911)
	-10.68	-	Uncorrected for complex speciation and Ionic strength		Smith (1918)
	-10.678		25°C, I = 0	Clever et al. (1992)	Smith (1918)
	-10.796		25°C, I = 0	Clever et al. (1992), recalculated from the data of Smith	Smith (1918)
	-10.90 ± 0.04	-		Grauer (1999)	Smith (1918)
			18°C. Solubility = 0.07% and 0.084% at $P(CO_2)$ = 1 and 56 atm., respectively		Haehnel (1924)
	-9.70		25°C, thermodynamic calculations	Latimer (1952)	Kelley and Anderson (1935)
	-10.001		25°C, I = 0	Clever et al. (1992)	Kelley and Anderson (1935)
	-10.780		25°C, I = 0	Clever et al. (1992)	Kelley and Anderson (1935), recalculated from the data of Smith (1918)
	-9.86	-	From thermochemical data.	Grauer (1999)	Kelley and Anderson (1935)
	-10.149		25°C, I = 0	Clever et al. (1992)	Saegusa (1950)
	-9.699		25°C, thermodynamic calculations	Clever et al. (1992)	Latimer (1952)
	-10.84	-		Sillen and Martell (1964)	Sahli (1952)
	-10.839		20°C	Clever et al. (1992)	Sahli (1952), cited in Schindler et al. (1969) as a dissertation, Bern, 1952
	-9.924		25°C, thermodynamic calculations	Clever et al. (1992). Calculated from Gibbs energy data in Wagman et al. (1982).	Wagman et al. (1982)
	-10.00	-		Zhuk (1954)	Goskhimizdat (1952)

Table 2. Solubility Constants of Solid Carbonates in the System ZnO-CO_2-H_2O (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	-10.82	-		Zachara et al. (1989)	Bjerrum et al. (1957)
	-10.68	-		Zachara et al. (1989)	Bjerrum et al. (1957)
	-7.585		25°C, thermodynamic calculations	Clever et al. (1992). Calculated from equation in Egorov and Titova (1962). Authors report 2.1 x 10^{-10}, which may be a printing error.	Egorov and Titova (1962)
	-10.109		50°C, thermodynamic calculations	Clever et al. (1992). Calculated from equation in Egorov and Titova (1962).	Egorov and Titova (1962)
	-10.180		60°C, thermodynamic calculations	Clever et al. (1992). Calculated from equation in Egorov and Titova (1962).	Egorov and Titova (1962)
	-10.415		100°C, thermodynamic calculations	Clever et al. (1992). Calculated from equation in Egorov and Titova (1962).	Egorov and Titova (1962)
	-9.82	-	Natural specimen	Zachara et al. (1989)	Crockett and Winchester (1966)
	-9.72	18.49	Thermodynamic calculations		Helgeson (1969)
	-9.721		25°C, thermodynamic calculations	Clever et al. (1992)	Helgeson (1969)
	-10.050		50°C, thermodynamic calculations	Clever et al. (1992)	Helgeson (1969)
	-10.190		60°C, thermodynamic calculations	Clever et al. (1992)	Helgeson (1969)
	-10.886		100°C, thermodynamic calculations	Clever et al. (1992)	Helgeson (1969)
	-10.8	-		Zachara et al. (1989)	Schindler et al. (1969)
	-9.367		25°C	Clever et al. (1992). Recalculation from data in Schindler et al.(1969) and Wagman et al. (1982) to obtain $\Delta G_{f,P_r,T_r}$ for $ZnCO_3$(s), which was used to calculate K_s.	Schindler et al. (1969), Wagman et al. (1982)

Table 2. Solubility Constants of Solid Carbonates in the System ZnO-CO_2-H_2O (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	-10.793		25°C, *I* = 0.2 ($NaClO_4$)	Clever et al. (1992), who were unable to duplicate this value from data in Schindler et al. (1969)	Schindler et al.(1969)
	-10.79 ± 0.04	-		Grauer (1999)	Schindler et al. (1969)
	-7.585		25°C, *I* = 0.057 (Na_2CO_3.$NaNO_3$)	Clever et al. (1992)	Zhukova and Rachinskii (1972)
	-10.00		*I* = 0	Palmer and Van Eldik (1983)	Smith and Martell (1976)
	-10.347		25°C, thermodynamic calculations	Clever et al. (1992)	Krestov et al. (1977)
	-9.84		*I* = 0	Palmer and Van Eldik (1983)	Balko et al. (1981)
	-10.79		*I* = 0.3	Palmer and Van Eldik (1983)	Balko et al. (1981)
	-9.87	-		Zachara et al. (1989)	Sangameshwar and Barnes (1983)
	-10.53 ± 0.10	-	Natural specimen. 22 - 25°C		Zachara et al. (1989)
	-9.836		25°C, *I* = 0. Tentative value based on linear regression of data by Latimer (1952), Egorov and Titova (1962) and Helgeson (1969)		Clever et al. (1992)
	-10.80 ± 0.10	-	Recommended value		Grauer (1999)
	-10.52		Estimated		Yoder et al. (2010)
$ZnCO_3$(cr) + 2H+ = Zn^{2+} + CO_2(g) + H_2O	7.95	-			Grauer and Feitnecht (1967)
	8.17 ± 0.05	-	25°C, 0.2 *M* $NaClO_4$,		Schindler (1967)
	7.95 ± 0.05	-	25°C, *I* = 0, Thermodynamic cycle		Schindler (1967)
	7.92 ± 0.05	-	25°C, *I* = 0, Davies Eqn.		Schindler (1967)
	7.35 ± 0.04	-			Schindler et al. (1969)
	7.35	-	25°C, *I* = 0,	Gamsjäger (1974)	Schindler et al. (1969)
	7.68 ± 0.04		50°C, 1 *M* $NaClO_4$,	Gamsjäger (1985)	Reiterer (1980)
	7.52	-13.8			Preis and Gamsjäger (2001b)

Table 2. Solubility Constants of Solid Carbonates in the System $ZnO-CO_2-H_2O$ (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
Zaccagnaite, synthesized					
$Zn_2Al^{III}(CO_3)_{0.5}(OH)_6•(H_2O) + 6H^+ = 2Zn^{2+} + Al^{3+} + 0.5CO_3^{2-} + 7H_2O$	21.95 ± 0.46 21.09 ± 1.21 20.30 ± 0.88 19.85 ± 0.02	- - - -	I = 0, corrected using the Davies equation. I = 6.5 mM and 12.8 mM. Equilibration up to 147 days	-	Johnson and Glasser (2003)
$Zn_{0.67}Al_{0.33}(OH)_2(CO_3)_{0.17}•0.30(H_2O) + 2H^+ = 0.67Zn^{2+} + 0.33Al^{3+} + 0.17CO_3^{2-} + 2.30H_2O$	3.73	-	Calculated from thermochemical data.	-	Allada et al. (2006)
Synthetic Phases					
$Zn_{25}(CO_3)_9(OH)_{32}$		-			
$Zn_{25}(CO_3)_9(OH)_{32} = 25Zn^{2+} + 9CO_3^{2-} + 32OH^-$	-360.5	-		Sillen and Martell (1964)	Sahli (1952)
$Zn_2CO_3(OH)_2$					
$Zn_2CO_3(OH)_2 + 2H^+ = 2Zn^{2+} + CO_3^{2-} + 2H_2O$	-2.52	-	Estimated		Yoder et al. (2010)
$Zn_3CO_3(OH)_4$					
$Zn_3CO_3(OH)_4 + 4H^+ = 3Zn^{2+} + CO_3^{2-} + 4H_2O$	5.48	-	Estimated		Yoder et al. (2010)
$Zn_4CO_3(OH)_6$					
$Zn_4CO_3(OH)_6 + 6H^+ = 4Zn^{2+} + CO_3^{2-} + 6H_2O$	13.48	-	Estimated		Yoder et al. (2010)
$Zn_5CO_3(OH)_8$					
$Zn_5CO_3(OH)_8 + 8H^+ = 5Zn^{2+} + CO_3^{2-} + 8H_2O$	21.48	-	Estimated		Yoder et al. (2010)
$Zn_3(CO3)_2(OH)_2$					
$Zn_3(CO3)_2(OH)_2 + 2H^+ = 3Zn^{2+} + 2CO_3^{2-} + 2H_2O$	-13.05	-	Estimated		Yoder et al. (2010)

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Table 3a. Association Constants of Aqueous Carbonate Complexes in the System ZnO-CO_2-H_2O extracted from Databases of Distribution-of-Species Codes

Association Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Database	Source
$Zn^{2+} + CO_3^{2-} = ZnCO_3(aq)$			MinteqA2	
			Wateq4f	
			V8.R6+	
	+5.9	0	Minteq (2009)	Not cited
	+4.76	0	Minteq (2006)	NIST46.4, MTQ3.11
	+5.3	-	Phreeqc (2009)	Not cited
	+5.3	-	Wateq4f (2005)	Not cited
	-	-	ThermoChimie v.7.b	
	-	-	NAGRA/PSI (2001)	
	+3.9000	-	Data0.YMP.R5	89zac/kit
	-	-	Thermoddem (2009)	
$Zn^{2+} + 2CO_3^{2-} = Zn(CO_3)_2^{2-}$			MinteqA2	
			Wateq4f	
			V8.R6+	
	+9.63	0	Minteq (2009)	Not cited
	+11.829	0	Minteq (2006)	NIST46.4, MTQ3.11
	+9.63	-	Phreeqc (2009)	Not cited
	+9.63	-	Wateq4f (2005)	Not cited
	-	-	ThermoChimie v.7.b	
	-	-	NAGRA/PSI (2001)	
	-	-	Data0.YMP.R5	
	-	-	Thermoddem (2009)	
$Zn^{2+} + CO_3^{2-} + H^+ = ZnHCO_3^+$			MinteqA2	
			Wateq4f	
			V8.R6+	
	+12.4	0	Minteq (2009)	Not cited
			Minteq (2006)	
	+12.43	-	Phreeqc (2009)	Not cited
	+12.43	-	Wateq4f (2005)	Not cited
	-	-	ThermoChimie v.7.b	
	-	-	NAGRA/PSI (2001)	
	+11.7488	-	Data0.YMP.R5	87bou/bar
	-	-	Thermoddem (2009)	

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Table 3b. Solubility Constants of Solid Carbonates in the System ZnO-CO_2-H_2O extracted from Databases of Distribution-of-Species Codes

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Database	Source
Smithsonite				
$ZnCO_3(s) = Zn^{2+} + CO_3^{2-}$			MinteqA2	
			Wateq4f	
			V8.R6+	
	-10.	-18.24	Minteq (2009)	Not cited
	-10.	-15.84	Minteq (2006)	Not cited
	-10.000	-18.24	Phreeqc (2009)	Not cited
	-10.0	-18.24	Wateq4f (2005)	Not cited
			ThermoChimie v.7.b	
	-	-	NAGRA/PSI (2001)	
	-9.8655	-	Data0.YMP.R5	78hel/del
	-9.8801	-	Thermoddem (2009)	78hel/del
Hydrozincite				
$Zn_5(CO_3)_2(OH)_6 + 6H^+ = 5Zn^{2+} + 2CO_3^{2-} + 6H_2O$			MinteqA2	
			Wateq4f	
			V8.R6+	
	-	-	Minteq (2009)	
	-	-	Minteq (2006)	
	-	-	Phreeqc (2009)	
	-	-	Wateq4f (2005)	
	-	-	ThermoChimie v.7.b	
	-	-	NAGRA/PSI (2001)	
	+9.6500	-	Data0.YMP.R5	69sch/rei
			Thermoddem (2009)	
$ZnCO_3 \cdot (H_2O)$				
$ZnCO_3 \cdot (H_2O) = Zn^{+2} + H_2O + CO_3^{-2}$	-10.26	0	Minteq (2009)	Not cited
	-10.26	0	Minteq (2006)	Not cited
			Phreeqc (2009)	
	-10.260	-	Wateq4f (2005)	Not cited
			ThermoChimie v.7.b	
	-	-	NAGRA/PSI (2001)	
	-10.1890	-	Data0.YMP.R5	82wag/eva
			Thermoddem (2009)	

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Table 3c. Distribution-of-Species Codes: Database References

Database	Reference
Data0.com.VR.R6+	Wolery, T.J. (1994). EQ3NR, Letter report: EQ3/6 version 8.0. Differences from version 7. UCRL-ID-129749. Lawrence Livermore National Laboratory, Livermore, California. USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/LLNL.DAT
Data0.YMP.R5	BSC (Bechtel SAIC Company) (2007). Qualification of Thermodynamic Data for Geochemical Modeling of Mineral–Water Interactions in Dilute Systems. ANL-WIS-GS-000003 REV 01. Las Vegas, Nevada: Bechtel SAIC Company.DOC.20070619.0007.
MinteqA2	HydroGeoLogic, Inc. and Allison Geoscience Consultants, Inc. (1999). MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: User Manual Supplement for Version 4.0, Appendix A: thermodynamic database for MINTEQA2 V4.0, p. 44-74.
Minteq (2009)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/MINTEQ.DAT
Minteq (2006)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/minteq.v4.dat
NAGRA/PSI (2001)	Hummel, W., Berner, U., Curti, E., Pearson, F.J. and Thoenen, T. (2002). Nagra/PSI Chemical Thermodynamic Data Base 01/01. Universal Publishers/uPublish.com, Parkland, Florida. 565 p.
Phreeqc (2009)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/PHREEQC.DAT
ThermoChimie v.7.b	Duro, L., Grivém M. and Giffaut, E. (2010). ThermoChimie, the ANDRA thermodynamic database In Buckau G, Kienzler B, Duro L, Grivé M, Montoya V (eds). 2nd Annual Workshop Proceedings of the Collaborative Project “Redox Phenomena Controlling Systems” (7th EC FP CP Recosy) Larnaca (Cyprus) 16–19 March 2010. Karlsruhe: KIT Scientific Publishing, 275–283.
Thermoddem (2009)	Blanc P., Lassin A. and Piantone P. (2007) THERMODDEM a database devoted to waste minerals. BRGM (Orléans, France). For updates: http://thermoddem.brgm.fr
Wateq4f	Ball, J. W., & Nordstrom, D. K. (1991). User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters. U.S. GEOLOGICAL SURVEY, Open-File Report 91-183, Revised and reprinted - April, 2001. p. 81-94
Wateq4f (2005)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/WATEQ4F.DAT

Table 4a. Thermodynamic properties of Zinc Carbonate Minerals and Synthetic Solid Carbonates: Gibbs Free Energies of Formation

Mineral		$\Delta G^0_{f,P_r,T_r}$ kJ/gfw $^{-1}$	Secondary Reference	Primary Reference
Name	Formula			
Minerals				
Aurichalcite	$(Zn,Cu)_5(CO_3)_2(OH)_6$	-2765.8		Alwan et al. (1980)
Hydrozincite	$Zn_5(CO_3)_2(OH)_6$	-3168.5 ± 4.		Takahashi (1960)
		-3159.8 ± 0.5		Schindler et al. (1969)
		-3161.5	Mercy et al. (1998). Calculated from hydrozincite solubility product of by:	Alwan and Williams (1979)
		-3141.2	Woods and Garrels (1987)	Sangameshwar and Barnes (1983)
		-3163.3 ± 4.		Mercy et al. (1998)
		-3164.6 ± 3.0		Preis and Gamjager (2001a)
Rosasite	$(Cu,Zn)_2(CO_3)(OH)_2$	-1100.5		Alwan et al. (1980)
Sclarite	$(Zn,Mg,Mn{+}{+})_4Zn_3(CO_3)_2(OH)_{10}$			
Smithsonite	$ZnCO_3$	-7332.87	Naumov et al. (1974)	Roth and Chall (1928)
		-732.48	Karpov et al. (1968)	Saegusa (1950)
		-732.480	Karapet'yants and Karapet'yants (1970)	Saegusa (1950)
		-731.36	Latimer (1952)	Rossini et al. (1952)?
		-731.36	Zhuk (1954)	Rossini et al. (1952), Karapet'yantz (1953)
		-731.28 ± 4.18	Robie (1962, 1966)	Rossini et al. (1952)
		-731.36	Karpov et al. (1968)	Rossini et al. (1952)
		-731.4	Woods and Garrels (1987)	Rossini et al. (1952)
calculated		-732.37		Zhuk (1954)
		-732.37	Karpov et al. (1968)	Zhuk (1954)
		-732.37	Karapet'yants and Karapet'yants (1970)	Zhuk (1954)
		-733.87	Karpov et al. (1968)	Karaptet'yantz (1957)

Table 4a. Thermodynamic properties of Zinc Carbonate Minerals and Synthetic Solid Carbonates: Gibbs Free Energies of Formation (Continued)

Mineral		$\Delta G^0_{f,P_r,T_r}$ kJ/gfw $^{-1}$	Secondary Reference	Primary Reference
Name	Formula			
		-733.87	Karapet'yants and Karapet'yants (1970)	Karaptet'yantz (1957)
		-736.8 ± 0.17		Schindler et al. (1969)
		-731.480 ± 2.970	Robie et al. (1979)	Parker et al. (1971)
		-731.48 ± 2.97	Radha and Navrotsky (2013)	Parker et al. (1971), Robie et al. (1978)
		-733.9	Woods and Garrels (1987)	Naumov et al. (1974)
		-731.6	Woods and Garrels (1987)	Helgeson et al. (1978)
		-731.5	Woods and Garrels (1987)	Robie et al. (1978)
		-731.5	Woods and Garrels (1987)	Wagman et al. (1982)
		-735.3 ± 3.1	Robie and Hemingway (1995)	Haselton and Goldsmith (1987)
		-731.5	Woods and Garrels (1987)	Sangameshwar and Barnes (1983)
		-735.3		Robie and Hemingway (1995)
		-837.35	Stern (2000)	Barin et al. (1993)
		-737.3		Dobrydiev et al. (2005)
Zaccagnaite, 3R1 polytype *calculated*	$Zn_{2/3}Al_{1/3}(OH)_2(CO_3)_{1/6}•4/6(H_2O)$	-38.66[(1)]		Costa et al. (2010)
Synthetic Phases				
$Zn_2(CO_3)(OH)_2•(H_2O)$	$Zn_2(CO_3)(OH)_2•(H_2O)$			
$Zn_4(CO_3)_3(OH)_2•4(H_2O)$	$Zn_4(CO_3)_3(OH)_2•4(H_2O)$			
$\underline{CdZn(CO_3)_2}$				
$CdZn(CO_3)_2$	$CdZn(CO_3)_2$	-1406.7 ± 1.1		Tareen et al. (1995)

Table 4b. Thermodynamic properties of Zinc Carbonate Minerals and Synthetic Solid Carbonates: Enthalpies of Formation

Mineral		$\Delta H^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
Minerals				
Aurichalcite	$(Zn,Cu)_5(CO_3)_2(OH)_6$			
Hydrozincite	$Zn_5(CO_3)_2(OH)_6$	-3465.4	Woods and Garrels (1987)	Sangameshwar and Barnes (1983)
		-3584. ± 15.		Preis and Gamjager (2001a)
Rosasite	$(Cu,Zn)_2(CO_3)(OH)_2$			
Smithsonite	$ZnCO_3$	-815.04	Naumov et al. (1974)	Roth and Chall (1928)
		-810.74	Karpov et al. (1968)	Saegusa (1950)
		-810.742	Karapet'yants and Karapet'yants (1970)	Saegusa (1950)
		-812.53	Latimer (1952)	Rossini et al. (1952)?
		-812.53	Zhuk (1954)	Rossini et al. (1952), Karapet'yantz (1953)
		-812.53 ± 2.93	Robie (1962, 1966)	Rossini et al. (1952)
		-812.53	Karpov et al. (1968)	Rossini et al. (1952)
		812.5	Woods and Garrels (1987)	Rossini et al. (1952)
		-811.95	Karpov et al. (1968)	Gerasimov (1960)
		-810.86	Karpov et al. (1968)	Karapet'yantz and Karapet'yants (1961)
		-812.780 ± 2.930	Robie et al. (1979)	Parker et al. (1971)
		-812.78 ± 2.93	Radha and Navrotsky (2013)	Parker et al. (1971), Robie et al. (1979)
		-815.0	Woods and Garrels (1987)	Naumov et al. (1974)
		-812.8	Woods and Garrels (1987)	Robie et al. (1978)
		-812.8	Woods and Garrels (1987)	Helgeson et al. (1978)
		-812.8	Woods and Garrels (1987)	Wagman et al. (1982)
		-812.8	Woods and Garrels (1987)	Sangameshwar and Barnes (1983)
		-817.0 ± 3.1	Robie and Hemingway (1995)	Haselton and Goldsmith (1987)
		-812.78	Stern (2000)	Barin et al. (1993)
		-817.0		Robie and Hemingway (1995)

Table 4b. Thermodynamic properties of Zinc Carbonate Minerals and Synthetic Solid Carbonates: Enthalpies of Formation (Continued)

Mineral		$\Delta H^0_{f,P_r,T_r}$ kJ/gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
		-818.6		Dobrydiev et al. (2005)
Zaccagnaite, synthesized	$Zn_{0.67}Al_{0.33}(OH)_2(CO_3)_{0.17}$•0.30($H_2O$)	-993.04 ± 0.96		Allada et al. (2006)
3R1 polytype *experimental*	$Zn_{2/3}Al_{1/3}(OH)_2(CO_3)_{1/6}$•4/6($H_2O$)	-45.31 ± 0.92[(1)]	Costa et al. (2010)	Allada et al. (2006)
calculated		-42.09[(1)]		Costa et al. (2010)
Synthetic Phases				
$Zn(HCO_3)_2$	$Zn(HCO_3)_2$	-1543.90 ± 62.76	Estimated value for fictive compound	Wilcox and Bromley (1963)
		-1543.90	Karapet'yants and Karapet'yants (1970)	Wilcox and Bromley (1963)
$CdZn(CO_3)_2$	$CdZn(CO_3)_2$	-1566.3 ± 1.1		Tareen et al. (1995)

Table 4c. Thermodynamic properties of Zinc Carbonate Minerals and Synthetic Solid Carbonates: Entropies

Mineral		$S^0_{P_r,T_r}$ J K^{-1} gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
Minerals				
Aurichalcite	$(Zn,Cu)_5(CO_3)_2(OH)_6$			
Hydrozincite	$Zn_5(CO_3)_2(OH)_6$	+436. ± 50		Preis and Gamjager (2001a)
Rosasite	$(Cu,Zn)_2(CO_3)(OH)_2$			
Sclarite	$(Zn,Mg,Mn{+}{+})_4Zn_3(CO_3)_2(OH)_{10}$			
Smithsonite *graphical*	$ZnCO_3$	82.4 ± 1.3		Anderson (1934),
calculated		82.0		Anderson (1934)
		82.42 ± 1.26	Kelley and King (1961)	Anderson (1934)
		82.42 ± 1.3	Naumov et al. (1974)	Anderson (1934)
		82.42 ± 1.26	Karpov et al. (1968)	Britske et al. (1949)
		92.47	Karpov et al. (1968)	Saegusa (1950)
		92.47	Karapet'yants and Karapet'yants (1970)	Saegusa (1950)
		82.42	Latimer (1952)	Rossini et al. (1952)?
		82.42	Zhuk (1954)	Rossini et al. (1952), Karapet'yants (1953)
		82.42	Karpov et al. (1968)	Rossini et al. (1952)
		82.4	Woods and Garrels (1987)	Rossini et al. (1952)
calculated		86.19		Zhuk (1954)
		86.19	Karpov et al. (1968)	Zhuk (1954)
		86.19	Karapet'yants and Karapet'yants (1970)	Zhuk (1954)
		82.42 ± 1.26	Robie (1962, 1966)	Kelley and King (1961)
		82.42 ± 1.25	Robie et al. (1979)	Kelley and King (1961)
		79.71	Karapet'yants and Karapet'yants (1970)	Kelley and King (1961)

Table 4c. Thermodynamic properties of Zinc Carbonate Minerals and Synthetic Solid Carbonates: Entropies (Continued)

Mineral		$S^0_{P_r,T_r}$ J K^{-1} gfw^{-1}	Secondary Reference	Primary Reference
Name	Formula			
		82.4	Woods and Garrels (1987)	Naumov et al. (1974)
		82.4	Woods and Garrels (1987)	Helgeson et al. (1978)
		82.4	Woods and Garrels (1987)	Robie et al. (1978)
		82.4	Woods and Garrels (1987)	Wagman et al. (1982)
		82.40	Stern (2000)	Barin et al. (1993)
		81.2 ± 0.2	Robie and Hemingway (1995)	Robie et al. (1989)
		81.19		Robie and Hemingway (1995)
Synthetic Phases				

Table 5. Crystallographic Properties of Zinc Carbonate Minerals and Synthetic Solid Carbonates

	Name	Formula	Reference
	Minerals		
1	Aurichalcite	$Zn_{2.73}Cu_{2.27}(CO_3)_2(OH)_6$	Gaines et al. (1997)
2	Aurichalcite	$Zn_{2.73}Cu_{2.27}(CO_3)_2(OH)_6$	Harding et al. (1994)
3	Aurichalcite	$Zn_{2.38}Cu_{2.62}(CO_3)_2(OH)_6$	Giester and Rieck. (2014
4	Brianyoungite	$Zn_3(CO_3)_{0.75}(SO_4)_{0.25}(OH)_4$	Gaines et al. (1997), Livingstone and Champness (1993)
5	Claraite	$(Cu,Zn)_3(CO_3)(OH)_4 \bullet 4(H_2O)$	Gaines et al. (1997)
6	Claraite	$Cu_2Zn(CO_3)(OH)_4 \bullet 4(H_2O)$	Mineralogy Database (http://webmineral.com/)
7	Claraite	$(Cu_{2.6}Zn_{0.4})(CO_3)(OH)_4 \bullet 4(H_2O)$	Walenta and Dunn (1982), Walenta (1999)
8	Hauckite	$Mg_{14}Mn^{2+}{}_{10}Zn_{18}Fe^{3+}{}_3(SO_4)_4(CO_3)_2(OH)_{81}$	Gaines et al. (1997)
9	Hauckite	$Fe_{3.1}Al_{0.4}Mg_{13.5}Mn_{9.9}Zn_{18.2}(SO_4)_{3.8}(CO_3)_2(OH)_{80.8}$	Dunn et al. (1980)
10	Hydrozincite	$Zn_5(CO_3)_2(OH)_6$	Gaines et al. (1997)

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
	Minerals									
1	Aurichalcite	13.82	6.419	5.29		101.04		2	$P2_1/m$	138.69
2	Aurichalcite	13.82	6.419	5.29		101.04		2	$P2_1/m$	138.69
3	Aurichalcite	13.790(2)	6.414(2)	5.266(1)		100.99(1)		2	$P2_1/m$	
4	Brianyoungite	15.724	6.256	5.472		90		4	Ortho or mono, C2/m	81.040
5	Claraite	26.22		21.56				66	P1 or P-1	117.13
6	Claraite	14.28	8.03	7.27	79.16	107.9	99.68	4	P1 or P-1	116.48
7	Claraite	14.28	8.03	7.27	79.16	107.9	99.68	4	P1 or P-1	116.54
8	Hauckite	9.17		30.21				1	P6/mmm	1324.9
9	Hauckite	9.17(4)		30.21(9)				1	P6/mmm	1324.9
10	Hydrozincite	13.58	6.28	5.41		95.51		2	C 2/m	138.28

	Name	Formula	Reference
11	Hydrozincite	$Zn_5(CO_3)_2(OH)_6$	Mineralogy Database (http://webmineral.com/)
12	Hydrozincite	$Zn_5(CO_3)_2(OH)_6$	Ghose (1964)
13	Hydrozincite	$Zn_5(CO_3)_2(OH)_6$	Jambor (1964)
14	Loseyite	$(Mn_{0.75}Zn_{0.25})_7(CO_3)_2(OH)_{10}$	Gaines et al. (1997)
15	Loseyite	$(Mn_{3.5}Zn_{3.0}Mg_{0.5})(CO_3)_2(OH)_{10}$	Hill (1981)
16	Minrecordite	$CaZn(CO_3)_2$	Gaines et al. (1997)
17	Minrecordite	$CaZn(CO_3)_2$	Garavelli et al. (1983)
18	Rosasite	$Cu_{1.16}Zn_{0.84}CO_3(OH)_2$	Gaines et al. (1997)
19	Rosasite	$Cu_{1.16}Zn_{0.84}CO_3(OH)_2$	Mineralogy Database (http://webmineral.com/)
20	Rosasite	$Cu_{1.16}Zn_{0.84}CO_3(OH)_2$ (assumed)	Perchiazzi (2006)

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
11	Hydrozincite	13.479	6.32	5.368		95.6		2	C 2/m	137.04
12	Hydrozincite	13.479	6.32	5.368		95.6		2	C 2/m	137.04
13	Hydrozincite	13.53	6.30	5.41		95.85		2		138.13
14	Loseyite	16.23	5.51	14.95		95.37		4	A 2/a	200.39
15	Loseyite	16.408(7)	5.540(3)	15.150(4)		95.48(3)		4	A 2/a	206.39
16	Minrecordite	4.8183		16.0295				3	R-3	64.695
17	Minrecordite	4.8183(4)		16.0295(10)				3	R-3	64.695
18	Rosasite	9.366	12.116	3.127		90.06		4	$P2_1/m$ or $P2_1$	53.423
19	Rosasite	12.873	9.354	3.156		110.36		4	$P2_1/a$	53.641
20	Rosasite	12.8976(3)	9.3705(1)	3.1623(1)		110.262(3)		4	$P2_1/a$	53.980

	Name	Formula	Reference
21	Sclarite	$(Zn,Mg,Mn{+}{+})_4Zn_3(CO_3)_2(OH)_{10}$	Grice and Dunn (1989)
22	Sclarite	$Zn_{2.4}Mg_{1.2}Mn^{2+}{}_{0.4}Zn_3(CO_3)_2(OH)_{10}$	Gaines et al. (1997)
23	Skorpionite	$Ca_3Zn_2(PO_4)_2CO_3(OH)_2{\bullet}(H_2O)$	Krause et al. (2008)
24	Smithsonite	$ZnCO_3$	Graf (1961)
25	Smithsonite	$ZnCO_3$	Gaines et al. (1997)
26	Undescribed	$Zn_5(CO_3)_2(OH)_6{\bullet}(H_2O)$	Jambor (1964)
27	Zaccagnaite	$Zn_4Al_2(OH)_{12}(CO_3){\bullet}3(H_2O)$	Gaines et al. (1997), Merlino and Orlandi (2001)
28	Zincrosasite	$(Zn)_{1.25}(Cu)_{0.75}(CO_3)(OH)_2$	Mineralogy Database (http://webmineral.com/)
29	Schulenbergite	$(Zn,Cu)_7(SO_4)_{1.5}(CO_3)_{0.5}(OH)_{10}{\bullet}3(H_2O)$	Gaines et al. (1997)
30	Zn-Schulenbergite	$Zn_5Cu_2(SO_4)_{1.5}(CO_3)_{0.5}(OH)_{10}{\bullet}3(H_2O)$	Mineralogy Database (http://webmineral.com/)

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
21	Sclarite	16.110(7)	5.432(1)	15.041(10)		95.490(4)		4	A 2/a	197.25
22	Sclarite	16.11	5.432	15.041		95.49		4	A 2/a	197.25
23	Skorpionite	19.045	9.32	6.525		92.73		4	C 2/c	174.17
24	Smithsonite	4.6528		15.025				6	R3c	28.273
25	Smithsonite	4.653		15.028				6	R3c	28.281
26	Undescribed	13.76	6.35	5.38		96.00		2?	mono	140.77
27	Zaccagnaite	3.0725		15.1135				1/3	$P6_3/mmc$	223.25
28	Zincrosasite	-	-	-	-	-	-	-	$P2_1/a$(mono)	-
29	Schulenbergite	8.249		7.183				1	P3 or P-3	254.91
30	Zn-Schulenbergite	8.292		7.271				1	hex	260.73

	Name	Formula	Reference
31	Zn-Schulenbergite	$Zn_5Cu_2(SO_4)_{1.5}(CO_3)_{0.5}(OH)_{10}•3(H_2O)$	Ohnishi et al. (2007)
32	Znucalite	$CaZn_{12}(UO_2)(CO_3)_3(OH)_{22}•4(H_2O)$	Ondruš et al. (1990), Jambor and Puziewicz (1991)
33	Znucalite	$CaZn_{11}(UO_2)(CO_3)_3(OH)_{20}•4(H_2O)$	Chiappero and Sarp (1993), Jambor et al. (1994)
	Synthetic Phases		
34	$Zn_2(CO_3)(OH)_2•(H_2O)$	$Zn_2(CO_3)(OH)_2•(H_2O)$	Feitknecht and Oswald (1966)
35	$Zn_4(CO_3)_3(OH)_2•4(H_2O)$	$Zn_4(CO_3)_3(OH)_2•4(H_2O)$	Feitknecht and Oswald (1966)

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o, Å	b_o, Å	c_o, Å	α, °	β, °	γ, °	Z		
31	Zn-Schulenbergite	8.292		7.271				1	hex	260.73
32	Znucalite	12.692(4)	25.096(6)	11.685(5)	89.08(2)	91.79(2)	90.37(3)	4	P1 or P-1	559.99
33	Znucalite	10.72(1)	25.16(1)	6.324(4)				2	orthorh	513.59
	Synthetic Phases									
34	$Zn_2(CO_3)(OH)_2•(H_2O)$	9.36_8	3.13	6.06_8				1?	Orthorh.	106.92
35	$Zn_4(CO_3)_3(OH)_2•4(H_2O)$	13.32		7.53				1/3?	Hex.	2090.5

[#]Calculated from cell constants, this work

Table 6. Carbonate Minerals containing greater than 10 wt.% Zinc*

Name	Formula	Lead, wt.%	gfw	Thermodynamic Data	
				Est.	Meas.
Aurichalcite	$(Zn,Cu)_5(CO_3)_2(OH)_6$	44.85	546.71	no	no
Brianyoungite	$Zn_3(CO_3,SO_4)(OH)_4$	58.87	333.22	no	no
Claraite	$(Cu,Zn)_3(CO_3)(OH)_4 \bullet 4(H_2O)$	16.66	392.58	no	no
Hauckite	$(Mg,Mn^{II})_{24}Zn_{18}Fe^{III}{}_3(SO_4)_4(CO_3)_2(OH)_{81}$	29.47	3993.55	no	no
Hydrozincite	$Zn_5(CO_3)_2(OH)_6$	59.55	549.01	no	yes
Loseyite	$(Mn,Zn)_7(CO_3)_2(OH)_{10}$	16.51	692.95	no	no
Minrecordite	$CaZn(CO_3)_2$	29.00	225.49	no	no
Rosasite	$(Cu,Zn)_2(CO_3)(OH)_2$	14.72	222.04	no	yes
Schulenbergite	$(Cu,Zn)_7(SO_4,CO_3)_2(OH)_{10} \bullet 3(H_2O)$	15.45	846.73	no	no
Sclarite	$(Zn,Mg,Mn{+}{+})_4Zn_3(CO_3)_2(OH)_{10}$	50.85	694.34	no	yes
Skorpionite	$Ca_3Zn_2(PO_4)_2CO_3(OH)_2 \bullet (H_2O)$	23.21	552.09	no	no
Smithsonite	$ZnCO_3$	52.15	125.4	no	yes
Zaccagnaite	$Zn_4Al_2(OH)_{12}(CO_3) \bullet 3(H_2O)$	40.49	629.83	no	yes
Zincrosasite	$(Zn,Cu)_2(CO_3)(OH)_2$	36.58	223.42	no	no
Znucalite	$CaZn_{11}(UO_2)(CO_3)_3(OH)_{20} \bullet 4(H_2O)$	44.36	1621.63	no	no
Zn-Schulenbergite	$(Zn,Cu)_7(SO4,CO_3)_2(OH)_{10} \bullet 3(H_2O)$	38.36	852.26	no	no

*Data taken primarily from a compilation given by the Mineralogy Database (http://webmineral.com).

References

Ageno, F. and Valla, E. (1912). Hydrolysis. I. Hydrolysis of Carbonates. Atti della Accademia Nazionale dei Lincei, Classe di Scienze Fisiche, Matematiche e Naturali, Rendiconti, 20(II), 706-12 [In Italian].

Allada, R.K., Peltier, E., Navrotsky, A., Casey, W.H., Johnson, A., Thompson-Berbeco, H. and Sparks, D.L. (2006). Calorimetric determination of the enthalpies of formation of hydrotalcite-like solids and their use in the geochemical modeling of metals in natural waters. Clays and Clay Minerals, 54(4), 409-417.

Alwan, A.K. and Williams, P.A. (1979). Mineral formation from aqueous solution. Part I. The deposition of hydrozincit, $(Zn_5(OH)_6(CO_3)_2$, from natural waters. Transition Metal Chemistry, 4, 128-132.

Alwan, A.K., Thomas, J.H. and Williams, P.A. (1980). Mineral formation from aqueous solution. Part III. The stability of aurichalcite, $(Zn,Cu)_5(CO_3)_2(OH)_6$, and rosasite $(Cu,Zn)_2(CO_3)(OH)_2$. Transition Metal Chemistry, 5, 3-5.

Anderson, C.T. (1934). The heat capacities of magnesium, zinc, lead, manganese and iron carbonates at low temperatures1. Journal of the American Chemical Society, 56(4), 849-851.

Balko, B., Bowen, P., Berger, R.L. and Anderson, K. (1981). Fast stopped-flow microcalorimeter. Journal of biochemical and biophysical methods, 4(1), 1-28.

Barin I., Sauert, F., Schultze-Rhonhof, E. and Wang, S.-S. (1993). Thermochemical Data of Pure Substances Part I Ag -Kr/Part II La-Zr). VCH Velagsgesellschaft, Weinheim, Germany.

Bauman, J.E., Jr. (1981). Thermodynamic measurements of carbonate equilibriums involving metal ions. US. Bureau of Mines, Information Circular No. 8853, 268-274.

Bauman, J.E., Jr., Siebert, R.M., Almon, W.R. and Hostetler, P.B. (1975). Thermodynamics of carbon dioxide interactions in electrolyte solutions. In Chemical Physics of Aqueous Gas Solutions, [Proc. Symp.] (W.A Adams, Galen Greer, Jacques E. Desnoyers, Eds.), 77-84.

Bilinski, H., Huston, R., and Stumm, W. (1976). Determination of the stability constants of some hydroxo and carbonato complexes of Pb(II), Cu(II), Cd(II), and Zn(II) in dilute solutions by anodic stripping voltammetry and differential pulse polarography. Analytica Chimica Acta, 84, 157-164.

Bjerrum J., Schwarzenbach, G. and Sillen, L.G. (1957). Stability constants of metal ion complexes with solubility products of inorganic substances. Part II. Inorganic Ligands. Chemical Society. (London), Spec. Pub. No. 7. (Cited by Zachara et al., 1989)

Britske, E.V., Kapustinskii, A.F., Veselovskii, B.K., Shamovskii, L.M., Chentsova, L.G. and Anvaer, B.I. (1949). Termicheskie konstanty neorganicheskikh veshchestv (Thermal Constants of Inorganic Substances). Ied-vo AN SSR, 1010 p. [In Russian].

Chiappero, P.J., and Sarp, H. (1993). Nouvelles données sur la znucalite et seconde occurrence: Le Mas d'Alary, Lodève (Hérault, France). Archives des Sciences, Genève, 46, 291-301.

Clever, H.L., Derrick, M.E. and Johnson, S.A. (1992). The solubility of some sparingly soluble salts of zinc and cadmium in water and in aqueous electrolyte solutions. Journal of Physical and Chemical Reference Data, 21(5), 941-1004.

Costa, D.G., Rocha, A.B., Diniz, R., Souza, W.F., Chiaro, S.S.X. and Leitão, A.A. (2010). Structural model proposition and thermodynamic and vibrational analysis of hydrotalcite-like compounds by DFT calculations. Journal of Physical Chemistry C, 114(33), 14133-14140.

Crockett, J.H. and Winchester, J.W. (1966). Co-precipitation of zinc with calcium carbonate. Geochimica et Cosmochimica Acta, 30, l093-1109.

Dobrydiev, S.V., Nilova, E.V. and Beskov, V.S. (2005). Calculation of $\Delta_f G^0(298)$ and $\Delta_f H^0(298)$ for sparingly soluble metal carbonates and oxalates in the solid state. Zhurnal Neorganicheskoi Khimii, 50(12), 2015-2018. [In Russian].

Dunn, P.J., Peacor, D.R. and Sturman, B.D. (1980). Hauckite, $Fe_3^{3+}(Mg,Mn)_{24}Zn_{18}(SO_4)_4(CO_3)_2(OH)_{81}$, a new mineral from Sterling Hill, New Jersey. American Mineralogist, 65, 192-195.

Egorov, A.M. and Titova, Z.P. (1962). Solubility products of salts with polyatomic ions as a function of the temperature. Zhurnal Neorganicheskoi Khimii, 7, 275-8 [In Russian]. Russian Journal of Inorganic Chemistry. (English Translation) 7, 141. (cited by Clever et al., 1992).

Feitnecht, W. and Oswald, H.R. (1965). Uber die Hydroxidcarbonate des Zinks. Helvetica Chimica Acta, 49(1), 334-344.

Ferri, D., Grenthe, I., Hietanen, S., Neher-Neumann, E. and Salvatore, F. (1985). Studies on metal carbonate equilibria. 12. Zinc(II) carbonate complexes in acid solutions. Acta Chemica Scandinavica, A 39, 347-353.

Ferri, D., Grenthe, I., Hietanen, S. and Salvatore, F. (1987). Studies on metal carbonate equilibria. 17. Zinc(II) carbonate complexes in alkaline solutions. Acta Chemica Scandinavica, A 41, 190-196.

Fouillac, A. and Criaud, A. (1984). Carbonate and bicarbonate trace metal complexes: Critical reevaluation of stability constants. Geochemical Journal, 18, 297-303.

Gaines, R.V., Skinner, H.C.W., Foord, E.E., Mason, B., Rosenzweig, A. King, V.T. and Dowty, E. (1997). Dana's New Mineralogy (Eighth edition). John Wiley and Sons, Inc., New York. 1819 p.

Gamsjäger, H. (1974). Wechselwirkung von Metalloxiden, -hydroxiden, -carbonaten und -sulfiden mit Wasser. Radex-Rundschau, 4, 274-285.

Gamsjäger, H. (1985). Solid state chemical model for the solubility behavior of homogeneous solid cobalt manganese carbonate mixtures. Berichte der Bunsen-Gesellschaft, 89(12), 1318-22.

Garavelli, C.G., Vurro, F. and Fioravanti, G.C. (1982). Minrecordite, a new mineral from Tsumeb. Mineral Record, 13, 131-136.

Gerasimov, Ya.I., Krestovnikov, A.N. and Shakhov, A.S. (1960). Khimicheskaya termodinamika v tsvetno.crn.i metallurgii, Tom I. (Chemical Thermodynamics in Nonferrous Metallurgy. Volume 1), 23 p. [In Russian]

Giester, G. and Rieck, B. (2014). Crystal structure refinement of aurichalcite, $(Cu,Zn)_5(CO_3)_2(OH)_6$, from the Lavrion Mining District, Greece. Neues Jahrbuch für Mineralogie-Abhandlungen: Journal of Mineralogy and Geochemistry, 191(2), 225-232.

Ghose, S. (1964). The crystal structure of hydrozincite, $Zn_5(OH)_6(CO_3)_2$. Acta Crystallographica, 17(8), 1051-1057.

Goskhimizdat. (1952). Chemical Reference, vol. 3. [In Russian]. (As cited in Zhuk, 1954).

Graf, D.L. (1961). Crystallographic tables for the rhombohedral carbonates. American Mineralogist, 46, 1283-1316.

Grauer, R. (1999). Solubility products of M(II) – Carbonates. [Edited and translated by U. Berner]. Paul Scherrer Institute, Waste Management laboratory, PSI Bericht Nr. 99-04, ISSN 1019-0643, 24 p.

Grauer, R. and Feitknecht, W. (1967). Thermodynamische Grundlagen der Zinkkorrosion in carbonathaltigen Lösungen. Corrosion Science, 7, 629–644.

Grice, J.D. and Dunn, P.J. (1989). Sclarite, a new mineral from Franklin, New Jersey, with essential octahedrally and tetrahedrally coordinated zinc; description and structure refinement. American Mineralogist, 74(11-12), 1355-1359.

Haehnel, O. (1924). Über die Löslichkeit der Carbonate des Strontiums, des Bariums und der Schwermetalle in Wasser unter hohen Kohlendioxyddrucken sowie über die Eigenschaften solcher Lösungen. Journal für praktische Chemie (Leipzig), 108, 187-193

Harding, M.M., Kariuki, B.M., Cernik, R. and Cressey, G. (1994). The structure of aurichalcite, $(Cu,Zn)_5(OH)_6(CO_3)_2$, determined from a microcrystal. Acta Crystallographica, B50, 673-676.

Haselton, H.T. and Goldsmith, J.R. (1987). The decarbonation and heat capacity of $ZnCO_3$. Geochimica et Cosmochimica Acta, 51(2), 261-265.

Helgeson, H.C. (1969). Thermodynamics of hydrothermal systems at elevated temperatures and pressures. American Journal of Science, 267, 729-804.

Helgeson, H.C., Delany, J.M., Nesbitt, H.W. and Bird, D.K. (1978). Summary and critique of the thermodynamic properties of rock forming minerals. American Journal of Science, 278-A, 229 p.

Hill, R.J. (1981). The structure of loseyite. Acta Crystallographica, B37, 1323-1328.

Johnson, C.A., and Glasser, F.P. (2003). Hydrotalcite-like minerals ($M_2Al(OH)_6(CO_3)_{0.5}.XH_2O$, where M = Mg, Zn, Co, Ni) in the environment: synthesis, characterization and thermodynamic stability. Clays and Clay Minerals, 51(1), 1-8.

Jambor, J.L. (1964). Basic copper and zinc carbonates. I. Synthetic zinc carbonates and their relation to hydrozincite. Canadian Mineralogist, 8(1), 92-108.

Jambor, J.L. and Puziewicz, J. (1991). New mineral names. American Mineralogist, 76, 1728-1735.

Jambor, J.L., Grew, E.S. and Roberts, A.C. (1994). New mineral names. American Mineralogist, 79, 1210-1214.

Karapet'yants, M. Kh. (1953). Khimicheskaya Termodinamika (Chemical Thermodynamics). 2nd Edition. Goshkhimizdat. 611 p. [In Russian].

Karapet'yants, M. Kh. (1955). Approximate method for the calculation of the isobaric potential and heat of formation of different substances. Trudy Instituta - Moskovskii Khimiko-Tekhnologicheskii Institut imeni D. I. Mendeleeva, (No. 20), 10-28. [In Russian].

Karapet'yants, M.Kh. (1954b). Approximate method of calculation of entropy. Trudy Instituta - Moskovskii Khimiko-Tekhnologicheskii Institut imeni D. I. Mendeleeva, (No. 18), 27-34. [In Russian].

Karapet'yants, M. Kh. (1957). Investigation of specific methods for the comparative calculation of physico-chmical properties of different substances. Author's dissertation for a degree in chemical sciences, MKhTI im D.I. Mendeleeva. [In Russian].

Karapet'yants, M.Kh. and Karapet'yants, M.L. (1961). Tablitsy nekotorykh termodinamicheskikh svoistv razlichnykh veshestv (Tables of Certain thermodynamic Parameters of different Substances). Trudy MKhTI im D.I. Mendeleeva, vol. 34. [In Russian].

Karapet'yants, M.Kh. and Karapet'yants, M.L. (1970). Thermodynamic constants of Inorganic and Organic Compounds (trans. By J. Schmorak). Humphrey Science Publishers, Ann Arbor, Michigan. 461 p.

Karpov, I.K., Kashik, S.A. and Pampura, V.D. (1968). Thermodynamic Constants for Calculations in Geochemistry and Petrology. Izdva, Nauka, 143 p. [In Russian].

Kelley, K.K. and Anderson, C.T. (1935). Theoretical metallurgy. IV. Metal carbonates-correlations and applications of thermodynamic properties. U.S. Bureau of Mines Bulletin No. 384, 73 p.

Kelley, K.K. and King, E.G. (1961). Contributions to the data on theoretical metallurgy XIV. Entropies of the elements and inorganic compounds. U.S. Bureau of Mines Bulletin No. 592. United States Government Printing Office, Washington, D.C., 149 p.

Krause, W., Effenberger, H., Bernhardt, H.J. and Medenbach, O. (2008). Skorpionite, $Ca_3Zn_2(PO_4)_2CO_3(OH)_2 \cdot H_2O$, a new mineral from Namibia: description and crystal structure. European Journal of Mineralogy, 20(2), 271-280.

Krestov, G.A., Kobenin, V.A. and Sokolov, V.N. (1977). Method for calculating the solubility product at 273-373°K. Zhurnal Neorganicheskoi Khimii, 22(10), 2864-7 [In Russian]. Russ. Journal of Inorganic Chemistry (English Translation), 22, 1556 (cited by Clever et al., 1992).

Latimer, W.M. (1952). The Oxidation States of the Elements and their Potentials in Aqueous Solutions. Second edition. Prentice Hall, New York, 392 p.

Livingstone, A. and Champness, P.E. (1993). Brianyoungite, a new mineral related to hydrozincite, from the north of England orefield. Mineralogical Magazine, 57, 665-670.

Long, D.T. and Angino, E.E. (1977). Chemical speciation of Cd, Cu, Pb, and Zn in mixed freshwater, seawater, and brine solutions. Geochimica et Cosmochimica Acta, 41(9), 1183-1191.

Mattigod, S.V. and Sposito, G. (1977). Estimated association constants for some complexes of trace metals with inorganic ligands. Soil Science Society of America Journal, 41(6), 1092-1097.

Mercy, M.A., Rock, P.A., Casey, W.H., and Mokarram, M.M. (1998). Gibbs energies of formation for hydrocerussite $[Pb(OH)_2 \cdot (PbCO_3)_2(s)]$ and hydrozincite $\{[Zn(OH)_2]_3 \cdot (ZnCO_2(s)\}$ at 298 K and 1 bar from electrochemical cell measurements. American Mineralogist, 83, 739-745.

Merlino, S. and Orlandi, P. (2001). Carraraite and zaccagnaite, two new minerals from the Carrara marble quarries: their chemical compositions, physical properties, and structural features. American Mineralogist, 86(10), 1293-1301.

Millero, F.J. and Hawke, D.J. (1992). Ionic interactions of divalent metals in natural waters. Marine Chemistry, 40, 19-48.

Naumov, G.B., Ryzhenko, B.N. and Khodakovsky, I.L. (1974). Handbook of Thermodynamic Data. Natl. Tech. Inf. Service, 722176A, U.S. Dept. Commerce. 328 p.

Neczaj-Hruzewicz, J., Janusz, W. and Szczypa, J. (1977). Some remarks on the preparation of zinc carbonate. Gazzetta Chimica Italiana, 107(9-10), 461-466.

Ohnishi, M., Kusachi, I., Kobayashi, S. and Yamakawa, J. (2007). Mineral chemistry of schulenbergite and its Zn-dominant analogue from the Hirao mine, Osaka, Japan. Journal of Mineralogical and Petrological Sciences, 102(4), 233-239.

Ondruš, P., Veselovskí, F. and Rybka, R. (1990). Znucalite, $Zn_{12}(UO_2)Ca(CO_3)_3(OH)_{22}.4H_2O$, a new mineral from Příbram, Czechoslovakia. Neues Jahrbuch fur Mineralogie, Monatshefte, 393-400.

Palmer, D.A. and van Eldik, R. (1983). The chemistry of metal carbonato and carbon dioxide complexes. Chemical Reviews, 83, 651-731.

Perchiazzi, N. (2006). Crystal structure determination and Rietveld refinement of rosasite and mcguinnessite. Zeitschrift für Kristallographie, Supplement, 23, 505-510.

Preis, W. and Gamsjäger, H. (2001a). (Solid + solute) phase equilibria in aqueous solution. XIII. Thermodynamic properties of hydrozincite and predominance diagrams for (Zn^{2+} + H_2O + CO_2). Journal of Chemical Thermodynamics, 33, 803-819.

Preis, W., and Gamsjäger, H. (2001b). Thermodynamic investigation of phase equilibria in metal carbonate-water-carbon dioxide systems (Invited Review). Monatshefte für Chemie, 132, 1327-1346.

Radha, A.V. and Navrotsky, A. (2013). Thermodynamics of carbonates. Reviews in Mineralogy and Geochemistry, 77(1), 73-121.

Reiterer, F. (1980). Lös1ichkeitskonstanten und freie Bildungsenthalpien neutraler Übergangsmetallcarbonate: $MnCO_3$, $FeCO_3$, $CoCO_3$, $NiCO_3$, $CuCO_3$, $ZnCO_3$. PhD thesis, Montanuniversität, Leoben, Austria.

Robie, R.A. (1962). Thermodynamic properties of minerals. U.S. Geological Survey Open File Report TEI-816. 31 p.

Robie, R.A. (1966). Section 20: Thermodynamic properties of minerals. Handbook of Physical Constants, Geological Society of America Memoirs, 97, 437-458.

Robie, R.A. and Hemingway, B.S. (1995). Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 Pascals) pressure and at higher temperatures. U.S. Bureau of Mines Bulletin No. 2131, 461 p.

Robie, R.A., Hemingway, B.S., and Fisher, J.R. (1978). Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 Pa) pressure and at higher temperatures. U.S. Bureau of Mines Bulletin No. 1452. U.S. Government Printing Office, Washington, DC. 456 p.

Robie, R.A., Hemingway, B.S. and Fisher, J.R. (1979). Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 Pa) pressure and at higher temperatures. U.S. Bureau of Mines Bulletin No. 1452. (Reprinted with corrections). U.S. Government Printing Office, Washington, DC. 456 p.

Robie, R.A., Haselton, H.T., Jr. and Hemingway, B.S. (1989). Heat capacities and entropies at 298.15 K of $MgTiO_3$ (geikielite), ZnO (zincite), and $ZnCO_3$ (smithsonite). The Journal of Chemical Thermodynamics, 21(7), 743-749.

Rossini, F.D., Wagman, D.D., Evans, W.H., Levine, S. and Jaffe, I. (1952). Selected values of chemical tbermodynamical properties. NBS Circular 500. 1268 p., Washington, D.C.

Roth, W.A. and Chall, P. (1928). Die thermische Verfolgung einiger metallurgisch wichtiger Reaktionen in einem bei höherer Temperatur arbeitenden Kalorimeter. Zeitschrift für Elektrochemie und angewandte physikalische Chemie, 34(4), 185-199.

Ryan, M.P., and Bauman, J.E., Jr. (1978). Thermodynamics of the zinc bicarbonate ion pair. Inorganic Chemistry, 17(12), 3329-3331.

Saegusa, F. (1950). Thermodynamic studies on carbonates. Part I. Thermodynamic studies of cadmium, zinc, lead, mercurous, and thallous carbonates. Science Reports. Tohoku University, First Series, vol. 34(1), 55-65.

Sangameshwar, S.R. and Barnes, H.L. (1983). Supergene processes in zinc-lead-silver sulfide ores in carbonates. Economic Geology, 78, 1379-1397.

Savenko, V.S. and Shatalov, I.A. (1999). Hydrozincite solubilities and the physicochemical state of zinc in seawater. Geochemistry International, 37, 1021-1023.

Sahli, M. (1952). Cited by Sillen and Martell (1964).

Schindler, P. (1967). Heterogeneous equilibria involving oxides, hydroxides, carbonates, and hydroxide carbonates Advances in Chemistry Series, No. 67, 196-222.

Schindler, P., Reinert, M. and Gamsjäger, H. (1968). Zur Thermodynamik der Metallcarbonate 2: Löslichkeitskonstanten und Freiebildungsenthalpien von $Cu_2(OH)_2CO_3$ (Malachit) und $Cu_3(CO_3)_2(OH)_2$ (Azurit) bei 25°C. Helvetica Chimica Acta, 51, 1845-1856.

Schindler, P., Reinert, M. and Gamsjäger, H. (1969). Zur Thermodynamik der Metallcarbonate III. Loslichkeitskonstanten und Freie Bildungsenthalpien von $ZnCO_3$ und $Zn_5(OH)_6(CO_3)_2$ bei 25º. Helvetica Chimica Acta, 52(8), 2327-2332.

Sillen. L.G. and Martell, A.E. (1964). Stability Constants of Metal-ion Complexes. Special Publication No. 17, The Chemical Society, London. 754 p.

Smith, H.J. (1918). On equilibrium in the system: Zinc carbonate, carbon dioxide and water. Journal of the American Chemical Society, 40, 883-885.

Smith, R.M. and Martell, A.E. (1976). Critical Stability Constants, Volume 4, Inorganic Complexes. Plenum Press: New York.

Stanley, Jr. J.K., and Byrne, R.H. (1990). Inorganic complexation of Zinc (II) in seawater. Geochimica et Cosmochimica Acta, 54, 753-760.

Stern, K.H. (2000). High Temperature Properties and Thermal Decomposition of Inorganic Salts with Oxyanions. 256 p. CRC Press LLC, 2000 N.W. Corporate Blvd., Boca Raton Florida 33431.

Takahashi, T. (1960). Supergene alteration of zinc and lead deposits in limestone. Economic Geology, 55(6), 1083-1115

Tareen, J.A.K., Fazeli, A.R., Basavalingu, B. and Bhandige, G.T. (1995). Decarbonation curves and associated thermodynamic data for synthetic Cd-dolomites $CdMg(CO_3)_2$, $CdMn(CO_3)_2$ and $CdZn(CO_3)_2$. Journal of Thermal Analysis and Calorimetry, 44(4), 937-954.

Wagman, D.D., Evans, W.H., Parker, V.B., Schumm, R.H., Halow, I., Bailey, S.M., Churney, K.L. and Nuttall, R.L. (1982). The NBS Tables of Chemical Thermodynamic Properties: Selected Values for Inorganic and C1 and C2 Organic Substances in SI Units. American Chemical Society and the

American Institute of Physics for the National Bureau of Standards (Journal of Physical Chemical Reference Data, 11, supp. 2, 392 p.).

Walenta, K. (1999). On the lattice constants of claraite. Der Erzgräber, 13, 20-22 [in German].

Walenta, K. and Dunn, P.J. (1982). Claraite, a new carbonate mineral from the Clara Mine. (Central Black Forest). Chemie der Erde, 41, 97-102.

Wilcox. D.E. and Bromley, L.A. (1963). Computer Estimation of heat and free energy for simple inorganic compounds. Industrial and Engineering Chemistry, 55(7), 32-39.

Woods, T.L. and Garrels, R.M. (1987). Thermodynamic Values at Low Temperature for Natural Inorganic Materials. An Uncritical Summary. Oxford University Press. 242 p. plus references.

Yoder, C.H. and Rowand, J.P. (2006). Application of the simple salt lattice energy approximation to the solubility of minerals. American Mineralogist, 91(5-6), 747-752.

Yoder, C.H., Gotlieb, N.R. and Rowand, A.L. (2010). The relative stability of stoichiometrically related natural and synthetic double salts. American Mineralogist, 95(1), 47-51.

Zachara, J.M., Kittrick, J.A., Dake, L.S. and Harsh, J.B. (1989). Solubility and surface spectroscopy of zinc precipitates on calcite. Geochimica et Cosmochimica Acta, 53(1), 9-19.

Zhuk, N.P. (1954). Thermodynamic constants of sulfates, carbonates, chromates, bromates, iodates, oxalates, and other salts slightly soluble in water. Zhurnal Fizicheskoi Khimii, 28, 1690-1697. [In Russian].

Zirino, A. and Yamamoto, S. (1972). A pH-dependent model for the chemical speciation of copper, zinc, cadmium, and lead in seawater. Limnology and Oceanography, 17, 661-671.

Zhukova, L.A. and Rachinskii, V.V. (1972). Precipitation of calcium and zinc carbonates. Izvestiya Timiryazevskoi Sel'skokhozyaistvennoi Akademii, (6), 204-8 [In Russian] (cited by Clever et al., 1992).

Supplementary Data

ALKALI AND ALKALI EARTH METALS

Table 1. Solubility Constants of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
Minerals					
Aragoniite					
	-8.16		calculated		Latimer (1952)
$CaCO_3 = Ca^{2+} + CO_3^{2-}$	-8.336 ± 0.020	-			Plummer and Busenberg (1982)
	-8.34	-		Palmer and Van Eldik (1983)	Plummer and Busenberg (1982)
Burkeite					
$Na_6CO_3(SO_4)_2 = 6Na^+ + CO_3^{2-} + 2SO_4^{2-}$					Bialik et al. (2008), Picot et al. (2012). See also Frederick et al. (2004)
Artinite					
$MgCO_3.Mg(OH)_2•3(H_2O) = Mg^{2+} + CO_3^{2-} + 2OH^-$	-17.2	-	25ºC, based on soly equilibrium with brucite	Langmuir (1965)	Kazakov et al. (1959)
Calcite					
$CaCO_3 = Ca^{2+} + CO_3^{2-}$	-7.90		16ºC		Stieglitz (1908)
	-7.90			McCoy and Smith (1911)	Stieglitz (1908)
	-8.03	-			McCoy and Smith (1911)
	Not computed	-	Solubility measurements under $P(CO_2)$ = to 65 atm, T 18 to 65°C		Haehnel (1924a)
	-8.32			Latimer (1952)	Frear and Johnston (1929)
	-8.31	-		Zhuk (1954)	Goskhimizdat (1952)
	-8.33		calculated		Latimer (1952)
	-8.33		Not reported	Jensen et al. (2002)	Latimer (1952)

Table 1. Solubility Constants of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	-8.00				
			Soly. of Iceland spar (calcite) in H_2O and in $CaCl_2$ soln. at 150-225°C and P(CO_2) ≤ 400 kg./cm^2.		Malinin (1963)
			Activity product of $CaCO_3$ up to 300°C in water and NaCl solns.		Malinin (1963)
	-8.30		Not reported	Jensen et al. (2002)	Garrels and Christ (1965)
	-8.31		Precipitation from supersaturated solutions	Jensen et al. (2002)	Nakayama (1968)
	-8.40		Theoretically determined from other studies	Jensen et al. (2002)	Langmuir (1968)
	-8.47		Resuspension of crystals and precipitation from supersaturated solutions	Jensen et al. (2002)	Jacobson and Langmuir (1974)
	-8.42	-10.1		Palmer and Van Eldik (1983)	Jacobsen and Langmuir (1974)
	-8.47	-10.8		Palmer and Van Eldik (1983)	Jacobsen and Langmuir (1974)
	-8.48 ± 0.02	8.4		Palmer and Van Eldik (1983)	Smith and Martell (1976)
	-8.480 ± 0.020				Plummer and Busenberg (1982)
	-8.35 ± 0.1			Palmer and Van Eldik (1983)	Plummer and Busenberg (1982)
	-8.48		Resuspension of dry crystals	Jensen et al. (2002)	Plummer and Busenberg (1982)
	-8.46 ± 0.03				Millero et al. (1984)
	-8.305	-	Calculated from thermodynamic data		Meng et al. (1995)
	-8.58		Precipitation from supersaturated solutions		Jensen et al. (2002)
Dawsonite					

Table 1. Solubility Constants of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
$NaAlCO_3(OH)_2 + 2H_2O = Al(OH)_4^- + HCO_3^- + Na^+ + H^+$	-17.88	-	25ºC. Extrapolated from high temperature measurements		Bénézeth et al. (2007)
Dolomite (ordered)					
$CaMg(CO_3)_2(cr) = Ca^{2+} + Mg^{2+} + 2CO_3^{2}$	-18.6	-	Literature compilations	Sherman and Barak (2000)	Rossini et al. (1952)
	-17.8	-	Based on Ca, Mg and alk.	Halla (1962c)	Yanat'eva (1952)
	-18.4	-		Sherman and Barak (2000)	Yanat'eva (1952)
	-18.5	-	Based on pH and CO_2	Halla (1962c)	Yanat'eva (1952)
	-19.3	-		Sherman and Barak (2000)	Yanat'eva (1952)
	-16.8	-			Kramer (1959)
	-17.2	-		Sherman and Barak (2000)	Kramer (1959)
	-19.3	-	pH = 5.7		Garrels et al. (1960)
	-19.4	-	pH = 6.2 (after grinding)	Sherman and Barak (2000)	Garrels et al. (1960)
	-17.0	-	21ºC. Based on Ca and Alk	Halla and Van Tassel (1965)	Halla (1962c)
	-16.6	-	21ºC. Based on pH and CO_2	Halla and Van Tassel (1965)	Halla (1962c)
	-16.7	-	22-27ºC, Field data		Hsu (1963)
	-17.1	-	22-27ºC, Field data	Sherman and Barak (2000)	Hsu (1963)
	-18.7	-	From bomb calorimetry		Stout and Robie (1963)
	-16.5	-			Barnes and Back (1964)
	-17.5	-		Sherman and Barak (2000)	Halla and Van Tassel (1965)
	-17.7	-		Sherman and Barak (2000)	Halla and Van Tassel (1965)
	-17.0	-	Solubility, field data	Pokrovsky and Schott (2001)	Langmuir (1965, 1971), Berner (1967), Lippmann (1973)
	-18.7	-	Literature compilations	Sherman and Barak (2000)	Karpov et al. (1971)
	-15.6	-	Literature compilations	Sherman and Barak (2000)	Naumov et al. (1971)
	-18.3	-	Phase equilibria data	Sherman and Barak (2000)	Helgeson et al. (1978)
	-17.5	-	27ºC. Calorimetry, HCl soln	Hemingway and Robie (1994)	Robie et al. (1978)
	-17.09	-	Based on calorimetric data	Pokrovsky and Schott (2001)	Robie et al. (1978)
	-17.6	-	Literature compilations	Sherman and Barak (2000)	Wagman et al. (1982)

Table 1. Solubility Constants of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	-17.38	-	Solubility, laboratory	Pokrovsky and Schott (2001)	Konigsberger and Gamsjäger (1987)
	-18.2	-	85ºC, Calorimetry, HCl soln	Morrow et al. (1994) and Sherman and Barak (2000)	Navrotsky and Capobianco (1987)
	-17.4	-	Phase equilibria data	Sherman and Barak (2000)	Chernosky and Berman (1989)
	-17.4	-	Phase equilibria data	Sherman and Barak (2000)	Holland and Powell (1990)
	-17.8	-	Literature compilations	Sherman and Barak (2000)	Knacke at al. (1991)
	-17.6	-	Literature compilations	Sherman and Barak (2000)	Barin (1993)
	-18.5	-	700ºC. PbO-B_2O_3 melt	Sherman and Barak (2000)	Chai and Navrotsky (1993)
	-17.2	-	27ºC. Calorimetry, HCl soln	Robie and Hemingway (1995)	Hemingway and Robie (1994)
	-17.2 ± 0.2	-	Solubility measurements		Sherman and Barak (2000)
	-17.40		Estimate		Yoder and Rowand (2006)
	-17.95 ± 0.1	-	80ºC (est by author to be ≈ -16.7 at 25ºC)		Gautelier et al. (2007)
Eitelite					
$NaMg_{0.5}CO_3 + 2H^+ = 0.5Mg^{2+} + Na^+ + CO_2(g) + H_2O$	14.67		25ºC, 3 *m* $NaClO_4$		Konigsberger et al. (1992)
	14.18		25ºC, *I* = 0		Konigsberger et al. (1992)
Hydromagnesite (I)					
$3MgCO_3.Mg(OH)_2 \bullet 3(H_2O) = 4Mg^{2+} + 3CO_3^{2-} + 2OH^- + 3H_2O$	-30.6		25ºC, soly of natural occurrence	Langmuir (1965)	Von der Borch (1962, 1965)
	-30.6		25ºC, approximate value		Langmuir (1965)
	-30.1		25ºC		Langmuir (1965)
Hydromagnesite (II)					
$Mg(OH)_{0.4}(CO_3)_{0.8} \bullet 0.8(H_2O) + 2H^+ = Mg^{2+} + 0.8CO_2(g)^- + 2H_2O$	12.56		25ºC, 3 *m* $NaClO_4$	Konigsberger et al. (1992)	Riesen (1969)
	12.34		25ºC, *I* = 0	Konigsberger et al. (1992)	Riesen (1969)

Table 1. Solubility Constants of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
$5MgO•4CO_2•5(H_2O) = 5Mg^{2+} + 4CO_3^{2-} + 2OH^- + 4H_2O$	-37.08 ± 0.45		Calculated from calorimetric data		Robie and Hemingway (1973)
Hydrotalcite-CO_3 (-Pyroaurite)					
$Mg_2Al^{III}(CO_3)_{0.5}(OH)_6•(H_2O) + 6H^+ = 2Mg^{2+} + Al^{3+} + 0.5CO_3^{2-} + 7H_2O$	24.98 ± 0.49 24.94 ± 0.18 25.70 ± 0.32 26.10 ± 0.21	- - - -	I = 0, corrected using the Davies equation. I = 6.5 m*M* and 12.8 m*M*. Equilibration up to 147 days		Johnson and Glasser (2003)
$Mg_4Al_2(OH)_{12}(CO_3)•2(H_2O)(s) = 4Mg^{2}+ + 2Al(OH)_4^- + CO_3^{2-} + 4OH^- + 2H_2O$	-51.14	-		Lothenbach and Winnefeld (2006)	Johnson and Glasser (2003)
$Mg_4Al_2(OH)_{12}(CO_3)•2(H_2O) + 13H^+ = 2Al^{+++} + HCO_3^- + 4Mg^{++} + 14H_2O$	61.19	-	Solubility	Blanc et al. (2010)	Johnson and Glasser (2003)
$Mg_{0.74}Al_{0.26}(CO_3)_{0.13}(OH)_2•0.39(H_2O) + 1.22H^+ = 0.74Mg^{2+} + 0.26Al(OH)_3(s) + 0.13CO_3^{2-} + 1.61H_2O$	7.65	-	Log K retrieved from Figure 2 of cited reference.		Allada et al. (2005b)
$Mg_{0.73}Al_{0.27}(CO_3)_{0.16}(OH)_{1.95}•0.83(H_2O) + 1.14H^+ = 0.73Mg^{2+} + 0.27Al(OH)_3(s) + 0.16CO_3^{2-} + 1.97H_2O$	10.16	-	Log K retrieved from Figure 2 of cited reference.		Allada et al. (2005b)
$Mg_{0.74}Al_{0.26}(OH)_2(CO_3)_{0.13}•0.39(H_2O) + 2H^+ = 0.74Mg^{2+} + 0.26Al^{3+} + 0.13CO_3^{2-} + 2.39H_2O$	9.82	-	Calculated from thermochemical data.		Allada et al. (2006)
$Mg_3Al_{1.019}(CO_3)_{0.472}(OH)_{8.114}•2.53(H_2O) = 3Mg^{2+} + 1.019Al^{3+} + 0.472CO_3^{2-} + 8.114(OH)^- = 2.53H_2O$	−68.92 ± 3.50	-	Solubility		Rozov et al. (2010)
$Mg_3Al_{1.021}(CO_3)_{0.666}(OH)_{7.730}•2.46(H_2O) = 3Mg^{2+} + 1.021Al^{3+} + 0.666CO_3^{2-} + 7.730(OH)^- + 2.46H_2O$	−69.52 ± 3.54	-	Solubility		Rozov et al. (2010)
$Mg_3Al_{0.896}Fe_{0.097}(CO_3)_{0.336}(OH)_{8.305}•2.51(H_2O) = 3Mg^{2+} + 0.896Al^{3+} + 0.097Fe^{3+} + 0.336CO_3^{2-} + 8.305(OH)^- + 2.51H_2O$	−68.76 ± 3.55	-	Solubility		Rozov et al. (2010)
$Mg_3Al_{0.827}Fe_{0.192}(CO_3)_{0.536}(OH)_{7.987}•2.62(H_2O) = 3Mg^{2+} + 0.827Al^{3+} + 0.192Fe^{3+} + 0.536CO_3^{2-} + 7.987(OH)^- + 2.62H_2O$	−67.79 ± 3.62	-	Solubility		Rozov et al. (2010)
$Mg_3Al_{0.802}Fe_{0.205}(CO_3)_{0.537}(OH)_{7.946}•2.67(H_2O) = 3Mg^{2+} + 0.802Al^{3+} + 0.205Fe^{3+} + 0.537CO_3^{2-} + 7.946(OH)^- + 2.67H_2O$	−71.61 ± 3.75	-	Solubility		Rozov et al. (2010)

Table 1. Solubility Constants of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
$Mg_3Al_{0.695}Fe_{0.304}(CO_3)_{0.481}(OH)_{8.034}\bullet 2.52(H_2O) = 3Mg^{2+} + 0.695Al^{3+} + 0.304Fe^{3+} + 0.481CO_3^{2-} + 8.034(OH)^- + 2.52H_2O$	−70.83 ± 3.61	-	Solubility		Rozov et al. (2010)
$Mg_3Al_{0.625}Fe_{0.394}(CO_3)_{0.553}(OH)_{7.95}\bullet 2.50(H_2O) = 3Mg^{2+} + 0.625Al^{3+} + 0.394Fe^{3+} + 0.553CO_3^{2-} + 7.950(OH)^- + 2.50H_2O$	−68.7 ± 3.65	-	Solubility		Rozov et al. (2010)
$Mg_3Al_{0.502}Fe_{0.496}(CO_3)_{0.361}(OH)_{8.276}\bullet 2.45(H_2O) = 3Mg^{2+} + 0.502Al^{3+} + 0.496Fe^{3+} + 0.361CO_3^{2-} + 8.276(OH)^- + 2.45H_2O$	−69.25 ± 3.63	-	Solubility		Rozov et al. (2010)
$Mg_3Al_{0.415}Fe_{0.619}(CO_3)_{0.531}(OH)_{8.039}\bullet 2.47(H_2O) = 3Mg^{2+} + 0.415Al^{3+} + 0.619Fe^{3+} + 0.531CO_3^{2-} + 8.039(OH)^- + 2.47H_2O$	−69.51 ± 3.74	-	Solubility		Rozov et al. (2010)
$Mg_3Al_{0.299}Fe_{0.703}(CO_3)_{0.248}(OH)_{8.509}\bullet 2.55(H_2O) = 3Mg^{2+} + 0.299Al^{3+} + 0.619Fe^{3+} + 0.248CO_3^{2-} + 8.509(OH)^- + 2.55H_2O$	−70.09 ± 3.68	-	Solubility	-	Rozov et al. (2010)
$Mg_3Al_{0.207}Fe_{0.839}(CO_3)_{0.491}(OH)_{8.157}\bullet 2.55(H_2O) = 3Mg^{2+} + 0.207Al^{3+} + 0.839Fe^{3+} + 0.491CO_3^{2-} + 8.157(OH)^- + 2.55H_2O$	−70.23 ± 3.81	-	Solubility	-	Rozov et al. (2010)
$Mg_3Al_{0.108}Fe_{0.902}(CO_3)_{0.342}(OH)_{8.344}\bullet 2.64(H_2O) = 3Mg^{2+} + 0.108Al^{3+} + 0.902Fe^{3+} + 0.342CO_3^{2-} + 8.334(OH)^- + 2.64H_2O$	−70.38 ± 3.53	-	Solubility	-	Rozov et al. (2010)
$Mg_3Fe_{1.086}(CO_3)_{0.343}(OH)_{8.570}\bullet 2.15(H_2O) = 3Mg^{2+} + 1.086Fe^{3+} + 0.343CO_3^{2-} + 8.570(OH)^- + 2.15H_2O$	−72.36 ± 3.99	-	Solubility	-	Rozov et al. (2010)
<u>Kalicinite</u>					
$KHCO_3 = K^+ + HCO_3^-$	-	21.76		Naumov et al. (1974)	Rossini et al. (1952)
	1.146		Calculated from thermodynamic data		Meng et al. (1995)
<u>Magnesite</u>					
$MgCO_3 = Mg^{2+} + CO_3^{2-}$	-9.88	-	Room temp., $P(CO_2)$ ≈1 atm. “Amorphous” magnesite	Langmuir (1965)	Leitmeier (1915)
	-8.00	-	20ºC, air	Langmuir (1965)	Wells (1915)
		-	Solubility measurements under $P(CO_2)$ to 34 atm, T to 60°C		Haehnel (1924b)

Table 1. Solubility Constants of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	-5.59	-	Probably a minimal value.	Langmuir (1965)	Haehnel (1924b)
	-10.30	-	17ºC, $P(CO_2)$ ≈1 atm. Run for 55 days	Langmuir (1965)	Bär (1932)
	-6.26	-	25ºC, air?	Langmuir (1965)	Leick (1932)
	-7.02	-	25ºC, $P(CO_2)$ ≈1 atm.	Langmuir (1965)	Halla and Ritter (1935)
	-7.69	-	25ºC, $P(CO_2)$ ≈1 atm. "Gel" magnesite	Langmuir (1965)	Halla and Ritter (1935)
	-5.00	-		Zhuk (1954)	Goskhimizdat (1952)
	-8.10		calculated		Latimer (1952)
	-7.69	-	25ºC, $P(CO_2)$ ≈1 atm.	Langmuir (1965)	Yanat'yeva (1954)
	-8.00	-	25ºC, $P(CO_2)$ ≈1 atm.	Langmuir (1965)	Garrels et al. (1960), quoted in Zen (1960)
	-7.46	-	25ºC	Halla (1962a)	Yanatyeva and Rassonskaya (1961), Halla and Ritter (1935)
	-9.42	-	25ºC, $P(CO_2)$ ≈1 atm.	Langmuir (1965)	Morey (1962)
	-8.12	-	25ºC	Langmuir (1965)	Stout and Robie (1963)
	-9.90	-	21 ± 2ºC, $P(CO_2)$ ≈1 atm. Run for 534 days, synthetic magnesite.	Langmuir (1965)	Halla and Van Tasse (1964)
	-8.167		Calculated from thermodynamic data		Meng et al. (1995)
	-6.00	-	Estimate		Yoder et al. (2010)
$MgCO_3 + 2H^+ = Mg^{2+} + CO_2(g) + H_2O$	9.54	-	25ºC, 3 *m* $NaClO_4$, prep. after Jantsch and Zemek (1949)	Konigsberger et al. (1992)	Horn (1969)
	9.41	-	25ºC, *I* = 0, prep. after Jantsch and Zemek (1949)	Konigsberger et al. (1992)	Horn (1969)
	9.42	-	25ºC, 3 *m* $NaClO_4$, natural	Konigsberger et al. (1992)	Riesen (1969)
	9.24	-	25ºC, *I* = 0, natural	Konigsberger et al. (1992)	Riesen (1969)
	10.04	-	3 *m* $NaClO_4$ at 25ºC, prep. after Marc and Simek (1913)	Konigsberger et al. (1992)	Riesen (1969)
	9.86	-	25ºC, *I* = 0, prep. after Marc and Simek (1913)	Konigsberger et al. (1992)	Riesen (1969)

Table 1. Solubility Constants of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
Nahcolite					
$NaHCO_3 = Na^+ + HCO_3^-$		-18.66 ± 0.21			Rupert et al. (1965)
	-	-18.66 ± 0.21		Naumov et al. (1974)	Rupert et al. (1965)
	-0.407		Calculated from thermodynamic data		Meng et al. (1995)
Natrite					
$Na_2CO_3 = 2Na^+ + CO_3^{2-}$	-	-26.61 ± 0.33			Rupert et al. (1965)
	-	-26.61 ± 0.33		Naumov et al. (1974)	Rupert et al. (1965)
	1.258		Calculated from thermodynamic data		Meng et al. (1995)
Nesquehonite					
$MgCO_3•3(H_2O) = Mg^{2+} + CO_3^{2-} + 3H_2O$	≈ -5.0			Latimer (1952)	Kline (1929)
	-4.67		25ºC	Halla (1962a)	Yanatyeva and Rassonskaya (1961), Halla and Ritter (1935)
	-5.07		25ºC. complexing neglected, survey of prior literature	Robie and Hemingway (1973)	Langmuir (1965)
	-5.59		25ºC. Solubility study		Langmuir (1965)
	-5.59 ± 0.10			Robie and Hemingway (1973)	Langmuir (1965)
	-5.59			Naumov et al. (1974)	Langmuir (1965)
	-5.42 ± 0.10			Robie and Hemingway (1973)	Hostetler (1970) (1965)
$MgCO_3•3(H_2O) + 2H^+ = Mg^{2+} + CO_2(g)^- + 4H_2O$	13.14		3 *m* $NaClO_4$ at 25ºC	Konigsberger et al. (1992)	Riesen (1969)
	12.83		25ºC, *I* = 0	Konigsberger et al. (1992)	Riesen (1969)
Strontianite					
$SrCO_3(cr) = Sr^{2+} + CO_3^{2-}$	-8.805				McCoy and Smith (1911)

Table 1. Solubility Constants of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
	-9.03			Latimer (1952)	McCoy and Smith (1911), Kelley and Anderson (1935)
		-	Solubility measurements under $P(CO_2)$ = to 65 atm/		Haehnel (1924c)
	-9.963		Calc. from solubility		Townley et al. (1937)
	-9.03			Zhuk (1954)	Goskhimizdat (1952)
	-9.15		calculated		Latimer (1952)
	-9.32		25ºC, *I* = 0, calculated from thermodynamic data by Rossini et al. (1950)		Helz and Holland (1965)
	-9.48 ± 0.03		50ºC, *I* = 0		Helz and Holland (1965)
	-9.48 ± 0.03		100ºC, *I* = 0		Helz and Holland (1965)
	-9.48 ± 0.03		150ºC, *I* = 0		Helz and Holland (1965)
	-9.48 ± 0.03		200ºC, *I* = 0		Helz and Holland (1965)
	-9.271 ± 0.020		25ºC, *I* = 0		Busenberg et al. (1984)
	-9.13 ± 0.03				Millero et al. (1984)
Thaumasite					
$CaSiO_3 \cdot CaSO_4 \cdot CaCO_3 \bullet 15(H_2O) + 3H^+ = 3Ca^{++} + H_4SiO_4 + SO_4^{2-} + HCO_3^- + 14H_2O$	10.30			Blanc et al. (2010)	Macphee and Barnett (2004)
Trona					
$Na_2CO_3.NaHCO_3 \bullet 2(H_2O) = 3Na^+ + CO_3^{2-} + HCO_3^- + 2H_2O$		23.64 ± 0.21			Rupert et al. (1965)
Vaterite					
$CaCO_3 = Ca^{2+} + CO_3^{2-}$	-7.913 ± 0.020				Plummer and Busenberg (1982)
	-7.91			Palmer and Van Eldik (1983)	Plummer and Busenberg (1982)

Table 1. Solubility Constants of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
Synthetic Phases					
K_2CO_3					
$K_2CO_3 = 2K^+ + CO_3^{2-}$	-	-31.80 ± 2.09		Naumov et al. (1974)	Stull and Prophet (1965), *et seq*. (-1968)
	5.405		Calculated from thermodynamic data		Meng et al. (1995)
$MgCO_3$•$5(H_2O)$					
$MgCO_3$•$5(H_2O) = Mg^{2+} + CO_3^{2-} + 5H_2O$	-4.56		25ºC	Halla (1962a)	Yanatyeva and Rassonskaya (1961)
$Mg_2CO_3(OH)_2$					
$Mg_2CO_3(OH)_2 + 2H^+ = 2Mg^{2+} + CO_3^{2-} + 2H_2O$	6.90		Estimate		Yoder et al. (2010)
$Mg_3CO_3(OH)_4$					
$Mg_3CO_3(OH)_4 + 4H^+ = 3Mg^{2+} + CO_3^{2-} + 4H_2O$	19.70		Estimate		Yoder et al. (2010)
$Mg_3(CO_3)_2(OH)_2$					
$Mg_3(CO_3)_2(OH)_2 + 2H^+ = 3Mg^{2+} + 2CO_3^{2-} + 2H_2O$	1.00		Estimate		Yoder et al. (2010)
$Mg_5(CO_3)_4(OH)_2$					
$Mg_5(CO_3)_4(OH)_2 + 2H^+ = 5Mg^{2+} + 4CO_3^{2-} + 2H_2O$	-10.70		Estimate		Yoder et al. (2010)
$Mg_5(CO_3)_4(OH)_2$•$4(H_2O)$					
$Mg_5(CO_3)_4(OH)_2$•$4(H_2O) + 2H^+ = 5Mg^{2+} + 4CO_3^{2-} + 6H_2O$	-5.04		55ºC	Halla (1962a)	Yanatyeva and Rassonskaya (1961)
$Mg_5(CO_3)_4(OH)_2$•$4(H_2O) + 10H^+ = 5Mg^{2+} + 4CO_2 + 10`H_2O$	62.80		25ºC, 3 *m* $NaClO_4$	Gamsjäger (1974)	Gamsjäger et al. (1973), Schindler et al. (1970)

Table 1. Solubility Constants of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
$\underline{Mg_7(CO_3)_5(OH)_4}$					
$Mg_7(CO_3)_5(OH)_4 + 4H_+ = 7Mg^{2+} + 3CO_3^{2-} + 4H_2O$	-4.00		Estimate		Yoder et al. (2010)
$\underline{Ca_2(CO_3)(OH)_2}$					
$Ca_2(CO_3)(OH)_2 + 2H^+ = 2Ca^{2+} + CO_3^{2-} + 2H_2O$	11.30		Estimate		Yoder et al. (2010)
$\underline{Ca_3(CO_3)_2(OH)_2}$					
$Ca_3(CO_3)_2(OH)_2 + 2H^+ = 3Ca^{2+} + 2CO_3^{2-} + 2H_2O$	3.48		Estimate		Yoder et al. (2010)
$\underline{Ca_4(CO_3)_3(OH)_2}$					
$Ca_4(CO_3)_3(OH)_2 + 2H^+ = 4Ca^{2+} + 3CO_3^{2-} + 2H_2O$	-4.52		Estimate		Yoder et al. (2010)
$\underline{Ca_5(CO_3)_4(OH)_2}$					
$Ca_5(CO_3)_4(OH)_2 + 2H^+ = 5Ca^{2+} + 4CO_3^{2-} + 2H_2O$	-12.52		Estimate		Yoder et al. (2010)
Hemicarboaluminate					
$3CaO.Al_2O_3.0.5CaCO_3.0.5Ca(OH)_2 \bullet 10.5(H_2O) + 13H^+ = 4Ca^{2+} + 2Al^{3+} + 0.5CO_3^{2-} + 17.5H_2O$	85.728	-			Damidot et al. (1994)
$Ca_4Al_2(CO_3)_{0.5}(OH)_{13} \bullet 5.5(H_2O) = 4Ca^{2+} + 2Al(OH)_4^- + 0.5CO_3^{2-} + 5OH^- + 5.5H_2O$	-29.13	-	Solubility	-	Matschei et al. (2007)
$6CaO \cdot 2Al_2O_3 \cdot CaCO_3 \cdot Ca(OH)_2 \bullet 21(H_2O) + 27H^+ = 4Al^{+++} + HCO_3^- + 8Ca^{++} + 37H_2O$	183.66				Blanc et al. (2010)

Table 1. Solubility Constants of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O (Continued)

Solubility Constant Reaction	Log $K^{(1)}$	$\Delta H^0_{R,P_r,T_r}$ kJ	Comments	Secondary Reference	Primary Reference
Monocarboaluminate					
$3CaO.Al_2O_3.CaCO_3 \bullet 10(H_2O) + 12H^+ = 4Ca^{2+} + 2Al^{3+} + CO_3^{2-} + 16H_2O$	69.99	-			Damidot et al. (1994)
$Ca_4Al_2(CO_3)(OH)_{12} \bullet 5(H_2O) = 4Ca^{2+} + 2Al(OH)_4^- + CO_3^{2-} + 4OH^- + 5H_2O$	-31.47	-	Solubility	-	Matschei et al. (2007)
$3CaO \cdot Al_2O_3 \cdot CaCO_3 \bullet 10.68(H_2O) + 13H^+ = 2Al^{+++} + HCO_3^- + 4Ca^{++} + 16.68H_2O$	80.55				Blanc et al. (2010)
Tricarboaluminate					
$3CaO.Al_2O_3.3CaCO_3 \bullet 30(H_2O) + 12H^+ = 6Ca^{2+} + 2Al^{3+} + 3CO_3^{2-} + 36H_2O$	54.595	-			Damidot et al. (1994)
$Ca_6Al_2(CO_3)_3(OH)_{12} \bullet 26(H_2O) = 6Ca^{2+} + 2Al(OH)_4- + 3CO_3^{2-} + 4OH^- + 26H_2O$	-46.5	-	Solubility	-	Matschei et al. (2007)

(1) At standard state (25°C, 1 atm, I = 0), unless otherwise noted.

Table 2a. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Gibbs Free Energies of Formation

Mineral Name	Formula	$\Delta G^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
Minerals				
Aragonite	$CaCO_3$	-1127.38	Naumov et al. (1974)	Backstrom (1925); Kelley and Anderson (1935)
		-1127.71	Latimer (1952)	Rossini et al. (1952)?
		-1127.71	Karpov et al. (1968)	Latimer (1952)
		-1127.88 ± 0.84	Robie (1962, 1966)	Rossini et al. (1952), Garrels et al. (1960)
		-1127.7	Woods and Garrels (1987)	Rossini et al. (1952)
		-1127.7	La Iglesia and Felix (1994)	Rossini et al. (1952)
		-1128.05		Garrels et al. (1960)
		-1126.37	Karpov et al. (1968)	Garrels et al. (1960)
		-128.99[(1)]	Karpov et al. (1968)	Kireev (1964)
		-1128.5	Woods and Garrels (1987)	Karpov et al. (1971)
		-1126.5	La Iglesia and Felix (1994)	Karpov et al. (1971)
		-1127.80		Parker et al. (1971)
		-1127.793 ± 1.464	Robie et al. (1979)	Parker et al. (1971)
		-1127.79 ± 1.46	Radha and Navrotsky (2013)	Parker et al. (1971), Robie et al. (1978)
		-1129.4	Woods and Garrels (1987)	Christ et al. (1974)
		-1127.4	Woods and Garrels (1987)	Naumov et al. (1974)
		-1127.4	La Iglesia and Felix (1994)	Naumov et al. (1974)
		-1128.35	BSC (2007)	Helgeson et al. (1978)
		-1129.2	Woods and Garrels (1987)	Helgeson et al. (1978)
		-1129.4	La Iglesia and Felix (1994)	Helgeson et al. (1978)
		-1127.8	Woods and Garrels (1987)	Robie et al. (1978)
		-1127.5	La Iglesia and Felix (1994)	Robie et al. (1979)
		-1127.4 ± 1.5	Robie and Hemingway (1995)	Plummer and Busenberg (1982)
		-1130.1	Woods and Garrels (1987)	Robinson et al. (1982)
		-1127.8	Woods and Garrels (1987)	Wagman et al. (1982)

Table 2a. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Gibbs Free Energies of Formation (Continued)

Mineral Name	Formula	$\Delta G^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
		-1128.2	Woods and Garrels (1987)	Harvie et al. (1984)
		-1128.2	La Iglesia and Felix (1994)	Harvie et al. (1984)
		-1127.7 ± 1.0		La Iglesia and Felix (1994)
		-1127.4		Robie and Hemingway (1995)
		-1128.03		Holland and Powell (1998)
		-1128.306		Hummel et al. (2002)
Artinite	$Mg_2CO_3(OH)_2$•3(H_2O)	-2562.62 ± 4.60		Langmuir (1965)
		-2562.62	Karpov et al. (1968)	Langmuir (1965)
		-2568.66 ± 0.75		Hemingway and Robie (1973)
		-2568.346 ± 0.750	Robie et al. (1979)	Hemingway and Robie (1973)
		-2568.4 ± 0.8	Robie and Hemingway (1995)	Hemingway and Robie (1973)
		-2568.35 ± 0.75	Radha and Navrotsky (2013)	Hemingway and Robie (1973), Robie et al. (1978)
		-2568.62	BSC (2007)	Helgeson et al. (1978)
		-2568.6	Woods and Garrels (1987)	Helgeson et al. (1978)
		-2568.6	La Iglesia and Felix (1994)	Helgeson et al. (1978)
		-2568.3	Woods and Garrels (1987)	Robie et al. (1978)
		-2568.3	La Iglesia and Felix (1994)	Robie et al. (1979)
		-2568.2	La Iglesia and Felix (1994)	Wagman et al. (1982)
Predicted		-2568.3 ± 3.7		La Iglesia and Felix (1994)
Burkeite	$Na_6CO_3(SO_4)_2$	-3592.99	BSC (2007)	Harvie et al. (1984)
		-3592.99	Radha and Navrotsky (2013)	Johnson et al. (1992)
Calcite	$CaCO_3$	-1128.34	Naumov et al. (1974)	Kelley and Anderson (1935); Wells and Taylor (1937)
		-1128.76	Latimer (1952)	Rossini et al. (1952)?

Table 2a. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Gibbs Free Energies of Formation (Continued)

Mineral Name	Formula	$\Delta G^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
		-1128.76	Zhuk (1954)	Rossini et al. (1952), Karapet'yants (1953)
		-1128.93 ± 0.84	Robie (1962, 1966)	Rossini et al. (1952), Garrels et al. (1960)
		-1128.76	Karpov et al. (1968)	Rossini et al. (1952)
		-1128.8	Woods and Garrels (1987)	Rossini et al. (1952)
		-1128.0	La Iglesia and Felix (1994)	Rossini et al. (1952); Wagman et al. (1982); Robie et al. (1979); Sangarmeshwar and Barnes (1983)
calculated		-1128.63		Zhuk (1954)
		-1128.63	Karpov et al. (1968)	Zhuk (1954)
		-1128.63	Karapet'yants and Karapet'yants (1970)	Zhuk (1954)
		-1128.34		Garrels et al. (1960)
		-1129.09	Karpov et al. (1968)	Garrels et al. (1960)
		-1128.93 ± 0.84	Karpov et al. (1968)	Robie (1962)
		-1127.88 ± 0.84	Karpov et al. (1968)	Robie (1962)
		-1128.84		Parker et al. (1971)
		-1128.842 ± 1.381	Robie et al. (1979)	Parker et al. (1971)
		-1128.84 ± 1.38	Radha and Navrotsky (2013)	Parker et al. (1971), Robie et al. (1978)
		-1130.3	Woods and Garrels (1987)	Christ et al. (1974)
		-1130.3	La Iglesia and Felix (1994)	Christ et al. (1974)
		-1128.3	Woods and Garrels (1987)	Naumov et al. (1974)
		-1128.3	La Iglesia and Felix (1994)	Naumov et al. (1974)
		-1129.18	BSC (2007)	Helgeson et al. (1978)
		-1130.1	Woods and Garrels (1987)	Helgeson et al. (1978)
		-1130.1	La Iglesia and Felix (1994)	Helgeson et al. (1978)
		-1128.8	Woods and Garrels (1987)	Robie et al. (1978)
		-1128.5 ± 1.4	Robie and Hemingway (1995)	Plummer and Busenberg (1982), Ko et al. (1982)

Table 2a. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Gibbs Free Energies of Formation (Continued)

Mineral Name	Formula	$\Delta G^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
		-1130.6	Woods and Garrels (1987)	Robinson et al. (1982)
		-1130.8	La Iglesia and Felix (1994)	Robinson et al. (1982)
		-1128.8	Woods and Garrels (1987)	Wagman et al. (1982)
		-1128.79	Meng et al. (1995)	Wagman et al. (1982)
		-1128.8	Woods and Garrels (1987)	Sangameshwar and Barnes (1983)
		-1129.3	Woods and Garrels (1987)	Harvie et al. (1984)
		-1129.3	La Iglesia and Felix (1994)	Harvie et al. (1984)
				Holland and Powell (1990)
		-1234.62	Stern (2000)	Barin (1993)
predicted		-1128.0 ± 0.8		La Iglesia and Felix (1994)
		-1128.5		Robie and Hemingway (1995)
		-1128.81		Holland and Powell (1998)
		-1129.127		Hummel et al. (2002)
Dawsonite	$NaAlCO_3(OH)_2$	-1785.990 ± 2.950	Robie et al. (1979)	Ferrante et al. (1976)
		-1786.0 ± 3.0	Robie and Hemingway (1995)	Ferrante et al. (1976)
		-1786 ± 4	Bénézeth et al. (2007)	Ferrante et al. (1976)
		-1785.99 ± 2.95	Radha and Navrotsky (2013)	Ferrante et al. (1976), Robie et al. (1978)
		-1786.0	Woods and Garrels (1987)	Robie et al. (1978)
		-1785.99	BSC (2007)	Robie et al. (1979)
		-1786.0		Robie and Hemingway (1995)
		-1782 ± 2		Bénézeth et al. (2007)
Dolomite	$CaMg(CO_3)_2$	-2169.3	Woods and Garrels (1987)	Rossini et al. (1952)
		-2169.3	La Iglesia and Felix (1994)	Rossini et al. (1952)
		-2169.3	Sherman and Barak (2000)	Rossini et al. (1952)
		-2175.68	Karapet'yants and Karapet'yants (1970)	Karapet'yants (1955)

Table 2a. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Gibbs Free Energies of Formation (Continued)

Mineral Name	Formula	$\Delta G^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
		-2170.14 ± 3.77	Robie (1962)	Robie (1957)
		-2175.68		Garrels et al. (1960)
		-2175.68	Karpov et al. (1968)	Garrels et al. (1960)
		-2177.8	Woods and Garrels (1987)	Garrels et al. (1960)
		-2170.14 ± 3.77	Karpov et al. (1968)	Robie (1962)
		-2170.14 ± 3.77	Robie (1966)	Stout and Robie (1963)
		-11.30(2?)	Karpov et al. (1968)	Stout and Robie (1963)
		-7.20 ± 1.17(2?)	Karpov et al. (1968)	Halla (1965)
		-2148.48	Karpov et al. (1968)	Halla (1965)
		-2149.32	Karpov et al. (1968)	(reference 87a not listed)
		-2151.91	Naumov et al. (1974)	Stout and Robie (1963)
		-2170.0	Woods and Garrels (1987)	Karpov et al. (1971)
		-2170.0	Sherman and Barak (2000)	Karpov et al. (1971)
		-2151.9	Woods and Garrels (1987)	Naumov et al. (1974)
		-2151.9	Sherman and Barak (2000)	Naumov et al. (1974)
		-2161.672 ± 1.670	Robie et al. (1979)	Robie and Hemingway (1977)
		-2166.31	BSC (2007)	Helgeson et al. (1978)
		-2167.2	Woods and Garrels (1987)	Helgeson et al. (1978)
		-2167.2	Sherman and Barak (2000)	Helgeson et al. (1978)
		-2161.7	Woods and Garrels (1987)	Robie et al. (1978)
		-2151.9	La Iglesia and Felix (1994)	Naumov et al. (1974)
		-2161.7	La Iglesia and Felix (1994)	Robie et al. (1979)
		-2167.2	La Iglesia and Felix (1994)	Helgeson et al. (1978)
		-2163.4	Woods and Garrels (1987)	Wagman et al. (1982)
		-2163.4	La Iglesia and Felix (1994)	Wagman et al. (1982)
		-2163.4	Sherman and Barak (2000)	Wagman et al. (1982)
		-2162.4	Sherman and Barak (2000)	Chernosky and Berman (1989)
		-2168.59 ± 2.07		Tareen et al. (1992)

Table 2a. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Gibbs Free Energies of Formation (Continued)

Mineral Name	Formula	$\Delta G^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
		-2163.6	Sherman and Barak (2000)	Barin (1993)
predicted		-2157.0 ± 1.4		La Iglesia and Felix (1994)
		-2161.3 ± 1.7	Robie and Hemingway (1995)	Hemingway and Robie (1994)
		-2161.7 ± 1.7	Radha and Navrotsky (2013)	Hemingway and Robie (1994)
		-2161.3		Robie and Hemingway (1995)
		-2161.51		Holland and Powell (1998)
		-2147.82		Rock et al. (2001)
		-2147.82 ± 2.20	Radha and Navrotsky (2013)	Rock et al. (2001)
		-2161.565		Hummel et al. (2002)
(Gaylussite)	$CaNa_2(CO_3)_2$•5(H_2O)	-3371.09		Alekseev, and Barinova (1981)
Gaylussite		N/A	BSC (2007)	Harvie et al. (1984)
		–3372.61	Radha and Navrotsky (2013)	Johnson et al. (1992)
Huntite	$CaMg_3(CO_3)_4$	-4216.22		Garrels et al. (1960)
		-4216.22 ± 4.18	Robie (1962, 1966)	Garrels et al. (1960)
		-4216.22	Karpov et al. (1968)	Garrels et al. (1960)
		-4216.2	Woods and Garrels (1987)	Garrels et al. (1960)
		-4216.2	La Iglesia and Felix (1994)	Garrels et al. (1960)
		-4216.2	Walling et al. (1995)	Garrels et al. (1960)
		-4203.425 ± 1.630	Robie et al. (1979)	Hemingway and Robie (1972),
		-4203.1 ± 1.6	Robie and Hemingway (1995)	Hemingway and Robie (1972), Königsberger and Gamsjäger (1987)
		-4203.69 ± 1.63		Hemingway and Robie (1973)
		-4203.4 ± 1.6	Walling et al. (1995)	Hemingway and Robie (1973)
		-4203.42 ± 1.63	Radha and Navrotsky (2013)	Hemingway and Robie (1973), Robie et al. (1978)
		-4203.707	Walling et al. (1995)	Schott and Dandurand (1975)

Table 2a. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Gibbs Free Energies of Formation (Continued)

Mineral Name	Formula	$\Delta G^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
		-4203.707	Walling et al. (1995)	Helgeson et al. (1978)
		-4203.71	BSC (2007)	Helgeson et al. (1978)
		-4203.4	Woods and Garrels (1987)	Robie et al. (1978)
		-4203.4	La Iglesia and Felix (1994)	Robie et al. (1979)
		-4203.7	La Iglesia and Felix (1994)	Wagman et al. (1982)
		-4180 ± 9.6	Walling et al. (1995)	Königsberger and Gamsjäger (1987)
		-4188.63 ± 1.0	Walling et al. (1995)	Gamsjäger (1989)
Predicted		-4215.0 ± 3.2		La Iglesia and Felix (1994)
		-4195.6 ± 6.4		Walling et al. (1995)
Hydromagnesite (I)	$3Mg(CO_3).Mg(OH)_2•3(H_2O)$	-4637.13		Garrels et al. (1960)
		-4637.13	Karpov et al. (1968)	Garrels et al. (1960), (reference 359a not listed)
		-4637.13	Robie and Hemingway (1973)	Garrels et al. (1960)
		-4637.1	Woods and Garrels (1987)	Garrels et al. (1960)
	$3Mg(CO_3).Mg(OH)_2•3(H_2O)$	-4602.82 ± 8.37		Langmuir (1965)
		-4602.82 ± 8.37	Karpov et al. (1968)	Langmuir (1965)
		-4602.82 ± 8.37	Robie and Hemingway (1973)	Langmuir (1965)
		-4603.66		Parker et al. (1971)
		-4603.3	Woods and Garrels (1987)	Wagman et al. (1982)
Hydromagnesite (II)	$Mg_5(CO_3)_4(OH)_2•4(H_2O)$	-5864.75 ± 1.05		Robie and Hemingway (1973)
		-5864.166 ± 1.090	Robie et al. (1979)	Robie and Hemingway (1973)
		-5864.2 ± 1.1	Robie and Hemingway (1995)	Robie and Hemingway (1973)
		-5864.17 ± 1.09	Radha and Navrotsky (2013)	Robie and Hemingway (1973), Robie et al. (1978)
		-5864.66	BSC (2007)	Helgeson et al. (1978)
		-5864.6	Woods and Garrels (1987)	Helgeson et al. (1978)

Table 2a. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Gibbs Free Energies of Formation (Continued)

Mineral Name	Formula	$\Delta G^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
		-5864.2	Woods and Garrels (1987)	Robie et al. (1978)
Hydrotalcite-CO_3	$Mg_4Al_2(OH)_{12}(CO_3)$ •2(H_2O)	-6342.97	Lothenbach and Winnefeld (2006)	Johnson and Glasser (2003)
	$Mg_{0.74}Al_{0.26}(OH)_2(CO_3)_{0.13}$•0.39($H_2O$)	-1043.08 ± 2.07		Allada et al. (2005a)
	$Mg_3Al(OH)_8(CO_3)_{0.5}$•n(H_2O), n = 0	-3773.3 ± 51.4		Rozov et al. (2010)
	$Mg_3Al(OH)_8(CO_3)_{0.5}$•n(H_2O), n = 0	-3294.5 ± 95.8		Rozov et al. (2010)
	$Mg_4Al_2(OH)_{12}(CO_3)$ •2(H_2O)	-6295.37		Blanc et al. (2010)
3R1 polytype *calculated*	$Mg_{2/3}Al_{1/3}(OH)_2(CO_3)_{1/6}$•4/6($H_2O$)	-59.83[(1)]		Costa et al. (2010)
	$Mg_3Al_{1.019}(CO_3)_{0.472}(OH)_{8.114}$•2.53($H_2O$)	−3773.43 ± 124.15		Rozov et al. (2010)
	$Mg_3Al_{1.021}(CO_3)_{0.666}(OH)_{7.730}$•2.46($H_2O$)	−3818.71 ± 118.97		Rozov et al. (2010)
Hydrotalcite-CO_3 (-Pyroaurite)	$Mg_3Al_{0.896}Fe_{0.097}(CO_3)_{0.336}(OH)_{8.305}$•2.51($H_2O$)	−3671.87 ± 112.49		Rozov et al. (2010)
	$Mg_3Al_{0.827}Fe_{0.192}(CO_3)_{0.536}(OH)_{7.987}$•2.62($H_2O$)	−3690.29 ± 112.49		Rozov et al. (2010)
	$Mg_3Al_{0.802}Fe_{0.205}(CO_3)_{0.537}(OH)_{7.946}$•2.67($H_2O$)	−3701.77 ± 111.44		Rozov et al. (2010)
	$Mg_3Al_{0.695}Fe_{0.304}(CO_3)_{0.481}(OH)_{8.034}$•2.52($H_2O$)	−3623.89 ± 104.99		Rozov et al. (2010)
	$Mg_3Al_{0.625}$ $Fe_{0.394}(CO_3)_{0.553}$ $OH)_{7.95}$•2.50(H_2O)	−3604.44 ± 103.58		Rozov et al. (2010)
	$Mg_3Al_{0.502}Fe_{0.496}(CO_3)_{0.361}(OH)_{8.276}$•2.45($H_2O$)	−3499.21 ± 95.95		Rozov et al. (2010)
	$Mg_3Al_{0.415}Fe_{0.619}(CO_3)_{0.531}(OH)_{8.039}$•2.47($H_2O$)	−3513.97 ± 95.17		Rozov et al. (2010)
	$Mg_3Al_{0.299}Fe_{0.703}(CO_3)_{0.248}(OH)_{8.509}$•2.55($H_2O$)	−3387.14 ± 85.67		Rozov et al. (2010)

Table 2a. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Gibbs Free Energies of Formation (Continued)

Mineral Name	Formula	$\Delta G^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
	$Mg_3Al_{0.207}Fe_{0.839}(CO_3)_{0.491}OH)_{8.157}$•2.55($H_2O$)	−3418.14 ± 86.37		Rozov et al. (2010)
	$Mg_3Al_{0.108}Fe_{0.902}(CO_3)_{0.342}(OH)_{8.344}$•2.64($H_2O$)	−3323.14 ± 71.95		Rozov et al. (2010)
	$Mg_3Fe_{1.086}(CO_3)_{0.343}(OH)_{8.570}$•2.15($H_2O$)	−3321.52 ± 78.70		Rozov et al. (2010)
Ikaite	$CaCO_3$•6(H_2O)	-2540.9 ± 5.0	Robie and Hemingway (1995)	Marland (1975)
		-2540.9	Radha and Navrotsky (2013)	Robie and Hemingway (1995)
Kalicinite	$KHCO_3$	-860.65	Karpov et al. (1968)	Latimer (1952)
		-860.65	Karapet'yants and Karapet'yants (1970)	Latimer (1952)
		-860.65	Latimer (1952)	Rossini et al. (1952)?
		-866.76	Naumov et al. (1974)	Rossini et al. (1952)
		-876.34	Karapet'yants and Karapet'yants (1970)	Karapet'yants (1955)
		-867.34	Karpov et al. (1968)	Karapet'yants and Karapet'yants (1961)
		-863.5	Meng et al. (1995)	Wagman et al. (1982)
		-867.783	BSC (2007)	Harvie et al. (1984)
Lansfordite	$MgCO_3$•5(H_2O)	-2200.24 ± 2.51		Langmuir (1965)
		-2200.24 ± 2.51	Karpov et al. (1968)	Langmuir (1965)
		-2200.99	Mel'nik (1972)	Langmuir (1965)?
		-2200.24	Naumov et al. (1974)	Langmuir (1965)
		+16.53	Karapet'yants and Karapet'yants (1970)	Halla (1962)
		-2199.53		Parker et al. (1971)
		-2200.99		Mel'nik (1972) Recommended
		-2201.0	Woods and Garrels (1987)	Mel'nik (1972)
		-2201.0	La Iglesia and Felix (1994)	Mel'nik (1972)
		-2200.2	Woods and Garrels (1987)	Naumov et al. (1974)

Table 2a. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Gibbs Free Energies of Formation (Continued)

Mineral Name	Formula	$\Delta G^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
		-2200.2	La Iglesia and Felix (1994)	Helgeson et al. (1978)
		-2199.2	BSC (2007)	Wagman et al. (1982)
		-2199.2	Woods and Garrels (1987)	Wagman et al. (1982)
		-2199.2	La Iglesia and Felix (1994)	Wagman et al. (1982)
		-2199.2	Radha and Navrotsky (2013)	Woods and Garrels (1987)
predicted		-2197.0 ± 5.1		La Iglesia and Felix (1994)
Magnesite	$MgCO_3$	-1029.26	Latimer	Rossini et al. (1952)?
		-1029.26	Zhuk (1954)	Rossini et al. (1952), Karapet'yants (1953)
		-1029.26	Karpov et al. (1968)	Rossini et al. (1952)
		-1029.0	Woods and Garrels (1987)	Rossini et al. (1952)
		-1029.0	La Iglesia and Felix (1994)	Rossini et al. (1952)
		-1029.3	Saldi (2009)	Rossini et al. (1952)
calculated		-1012.65		Zhuk (1954)
		-1012.65	Karpov et al. (1968)	Zhuk (1954)
		-1012.65	Karapet'yants and Karapet'yants (1970)	Zhuk (1954)
		-1029.59 ± 1.88	Robie (1962)	Robie (1957)
		-1029.59 ± 1.88	Karpov et al. (1968)	Robie (1962)
		-1029.59 ± 1.88	Robie (1966)	Stout and Robie (1963)
		-1012.19 ± 2.30		Langmuir (1965)
		-1012.19 ± 2.30	Karpov et al. (1968)	Langmuir (1965)
		-1012.28	Naumov et al. (1974)	Langmuir (1965)
		-1012.2 ± 2.3	Saldi (2009)	Langmuir (1965)
		-65.96 ± 1.13[(1)]		Robie (1965)
		-58.84[(1)]	Karpov et al. (1968)	Robie (1965)
		-1029.480 ± 1.381	Robie et al. (1979)	Robie (1965)
		-1029.5 ± 1.4	Robie and Hemingway (1995)	Robie (1965)
		-1029.5 ± 1.4	Saldi (2009)	Robie (1965)

Table 2a. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Gibbs Free Energies of Formation (Continued)

Mineral Name	Formula	$\Delta G^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
		-1029.48 ± 1.38	Radha and Navrotsky (2013)	Robie (1965)
		-1029.360	Karapet'yants and Karapet'yants (1970)	Stull and Prophet (1965)
		-1031.90	Karpov et al. (1968)	Gerasimov et al. (1966)
		-1029.7 ± 1.4	Saldi (2009)	Robie and Waldbaum (1968)
		-1030.52	Mel'nik (1972)	Horn (1969), Christ and Hostetler (1970)
		-1029.6	Woods and Garrels (1987)	Karpov et al. (1971)
		1029.6	La Iglesia and Felix (1994)	Karpov et al. (1971)
		-1012.11		Parker et al. (1971)
estimated value		-66.02[(1)]		Mel'nik (1972)
estimated value		-48.41[(1)]		Mel'nik (1972)
estimated value		-1029.72		Mel'nik (1972)
estimated value		-1012.11		Mel'nik (1972)
recommended value		-66.02[(1)]		Mel'nik (1972)
recommended value		-1029.72		Mel'nik (1972)
		-1029.7	Woods and Garrels (1987)	Mel'nik (1972)
		-1029.7	La Iglesia and Felix (1994)	Mel'nik (1972)
		-1012.3	Woods and Garrels (1987)	Naumov et al. (1974)
		-1012.5	Saldi (2009)	Dandurand and Schott (1977)
			Saldi (2009)	Hemingway et al. (1977)
		-1027.83	BSC (2007)	Helgeson et al. (1978)
		-1027.8	Woods and Garrels (1987)	Helgeson et al. (1978)
		-1027.8	Saldi (2009)	Helgeson et al. (1978)
		-1027.8	La Iglesia and Felix (1994)	Helgeson et al. (1978)
		-1029.5	Woods and Garrels (1987)	Robie et al. (1978)
		-1029.48	Saldi (2009)	Robie et al. (1978)
		-1029.5	La Iglesia and Felix (1994)	Robie et al. (1979)
		-1026.6	Saldi (2009)	Sadiq and Lindsay (1979)
		-1012.1	Woods and Garrels (1987)	Wagman et al. (1982)

Table 2a. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Gibbs Free Energies of Formation (Continued)

Mineral Name	Formula	$\Delta G^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
		-1012.1	Meng et al. (1995)	Wagman et al. (1982)
		-1012.1	Saldi (2009)	Wagman et al. (1982)
		-1027.3	Woods and Garrels (1987)	Harvie et al. (1984)
		-1027.3	La Iglesia and Felix (1994)	Harvie et al. (1984)
		-1026.0 ± 2.1	Saldi (2009)	Kittrick and Peryea (1986)
		-1029.875	Saldi (2009)	Berman (1988)
		-1030.709	Saldi (2009)	Chernosky and Berman (1989)
				Holland and Powell (1990)
			Saldi (2009)	Holland and Powell (1990)
		-1027.436	Saldi (2009)	Trommsdorff and Connolly (1990)
		-1115.39	Stern (2000)	Knacke et al. (1991)
predicted		-1029.0 ± 1.0		La Iglesia and Felix (1994)
			Saldi (2009)	Koziol and Newton (1995)
		-1029.5		Robie and Hemingway (1995)
		-1029.5 ± 1.4	Saldi (2009)	Robie and Hemingway (1995)
		+1027.74		Holland and Powell (1998)
		-1030.5 ± 0.4	Saldi (2009)	Konigsberger et al. (1999)
		-1007.47		Rock et al. (2001)
		-1030.6		Hummel et al. (2002)
		-1027.1 ± 2.0		Saldi (2009)
Meionite	$Ca_4Al_6Si_6O_24CO_3$	-13142.7	Woods and Garrels (1987)	Robinson et al. (1982)
Al/Si ordered		-13131.8 ± 6.2	Robie and Hemingway (1995)	Moecher and Essene (1990)
Al/Si ordered		-13131.8		Robie and Hemingway (1995)
		-13131.8	Radha and Navrotsky (2013)	Robie and Hemingway (1995)
Monohydrocalcite	$CaCO_3$• (H_2O)	-1361.600 ± 1.130	Robie et al. (1979)	Hull and Turnbull (1973)
		-1361.6 ± 1.1	Robie and Hemingway (1995)	Hull and Turnbull (1973)

Table 2a. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Gibbs Free Energies of Formation (Continued)

Mineral Name	Formula	$\Delta G^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
		-1361.600 ± 1.13	Radha and Navrotsky (2013)	Hull and Turnbull (1973), Robie et al. (1978)
		-1361.6	Woods and Garrels (1987)	Robie et al. (1978)
		-1361.6	BSC (2007)	Robie et al. (1979)
Nahcolite	$NaHCO_3$	-848.89	Karapet'yants and Karapet'yants (1970)	Latimer (1952)
		-851.86	Latimer (1952)	Rossini et al. (1952)?
		-851.86	Karpov et al. (1968)	Rossini et al. (1952)
		-851.9	Woods and Garrels (1987)	Rossini et al. (1952)
		-815.88	Naumov et al. (1974)	Rupert et al. (1965)
		-815.9	Woods and Garrels (1987)	Naumov et al. (1974)
		-851.2 ± 0.6	Robie and Hemingway (1995)	Berg and Vanderzee (1978)
		-851.0	Woods and Garrels (1987)	Wagman et al. (1982)
		-851.0	Meng et al. (1995)	Wagman et al. (1982)
		-849.461	BSC (2007)	Barin and Platski (1995); Binnewies and Milke (1999)
Natrite	Na_2CO_3	-1045.830		Saegusa (1950a)
		-1045.83	Karapet'yants and Karapet'yants (1970)	Saegusa (1950a)
		-1050.64	Karpov et al. (1968)	Bauer and Dorland (1952)
		-1050.54	Karapet'yants and Karapet'yants (1970)	Bauer and Dorland (1952)
		-1051.86	Karapet'yants and Karapet'yants (1970)	Latimer (1952)
		-1047.67	Latimer (1952)	Rossini et al. (1952)?
		-1047.67	Karpov et al. (1968)	Rossini et al. (1952)
		-1047.7	Woods and Garrels (1987)	Rossini et al. (1952)
		-1045.83	Karpov et al. (1968)	Karapet'yants and Karapet'yants (1961)

Table 2a. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Gibbs Free Energies of Formation (Continued)

Mineral Name	Formula	$\Delta G^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
		-1047.76	Naumov et al. (1974)	Rupert et al. (1965)
		-1047.510	Karapet'yants and Karapet'yants (1970)	Stull and Prophet (1965)
		-1047.8	Woods and Garrels (1987)	Naumov et al. (1974)
		-1045.3 ± 0.4	Robie and Hemingway (1995)	Berg and Vanderzee (1978)
		-1044.4	Woods and Garrels (1987)	Wagman et al. (1982)
		-1044.44	Meng et al. (1995)	Wagman et al. (1982)
		-1172.15	Stern (2000)	Knacke et al. (1991)
		-1046.874	BSC (2007)	Barin and Platski (1995), Binnewies and Milke (1999)
		-1049.5 ± 0.4	Radha and Navrotsky (2013)	Kiseleva et al. (1996), Robie et al. (1978)
Natron	Na_2CO_3•10(H_2O)	-3428.60		Saegusa (1950a)
		-3428.604	Karapet'yants and Karapet'yants (1970)	Saegusa (1950a)
		-3429.0	Woods and Garrels (1987)	Saegusa (1950a)
		-3424.31	Karapet'yants and Karapet'yants (1970)	Bauer and Dorland (1952)
		-3425.02	Karapet'yants and Karapet'yants (1970)	Karapet'yants (1957)
		-3424.31	Karpov et al. (1971)	Bauer and Dorland (1952)
		-3428.60	Karpov et al. (1971)	Karapet'yants and Karapet'yants (1961)
		-3425.02	Karpov et al. (1971)	Karapet'yants (1955)
		-3431.51 ± 1.3	Naumov et al. (1974)	Waterfield et al. (1968)
		-3427.66	BSC (2007)	Wagman et al. (1982)
		-3431.5	Woods and Garrels (1987)	Naumov et al. (1974)
		-3427.7	Woods and Garrels (1987)	Wagman et al. (1982)
		-3427.66	Radha and Navrotsky (2013)	Johnson et al. (1992)

Table 2a. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Gibbs Free Energies of Formation (Continued)

Mineral Name	Formula	$\Delta G^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
Nesquehonite	$MgCO_3$•3(H_2O)	+15.98	Karapet'yants and Karapet'yants (1970)	Halla (1962)
		+14.64	Karapet'yants and Karapet'yants (1970)	Halla (1962a)
		-1726.57 ± 2.09		Langmuir (1965)
		-1726.57 ± 2.09	Karpov et al. (1968)	Langmuir (1965)
		-1726.61	Mel'nik (1972)	Langmuir (1965)?
		-1726.61	Naumov et al. (1974)	Langmuir (1965)
		-1726.32		Parker et al. (1971)
recommended		-1726.61		Mel'nik (1972)
		-1726.6	Woods and Garrels (1987)	Mel'nik (1972)
		-1723.98 ± 0.50		Robie and Hemingway (1973)
		-1723.746 ± 0.500	Robie et al. (1979)	Robie and Hemingway (1973)
		-1723.8 ± 0.3	Robie and Hemingway (1995)	Robie and Hemingway (1973)
		-1723.75 ± 0.50	Radha and Navrotsky (2013)	Robie and Hemingway (1973), Robie et al. (1978)
		-1726.6	Woods and Garrels (1987)	Naumov et al. (1974)
		-1726.6	La Iglesia and Felix (1994)	Naumov et al. (1974); Mel'nik (1972)
		-1723.95	BSC (2007)	Helgeson et al. (1978)
		-1724.0	Woods and Garrels (1987)	Helgeson et al. (1978)
		-1723.7	Woods and Garrels (1987)	Robie et al. (1978)
		-1723.7	La Iglesia and Felix (1994)	Robie et al. (1979)
		-1724.0	La Iglesia and Felix (1994)	Helgeson et al. (1978)
		-1726.1	Woods and Garrels (1987)	Wagman et al. (1982)
		-1726.1	La Iglesia and Felix (1994)	Wagman et al. (1982)
predicted		-1729.8 ± 3.1		La Iglesia and Felix (1994)
(Nyerereite)	$Na_2Ca(CO_3)_2$	-2180.16		Alekseev and Barinova (1981)

Table 2a. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Gibbs Free Energies of Formation (Continued)

Mineral Name	Formula	$\Delta G^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
Pirssonite	$Na_2Ca(CO_3)_2$•2(H_2O)	-2648.85		Alekseev and Barinova (1981)
		-635.794	BSC (2007)	Harvie et al. (1984)
		-635.794	Radha and Navrotsky (2013)	Johnson et al. (1992)
Spurrite	$Ca_5Si_2O_8CO_3$	-5568.8	Woods and Garrels (1987)	Karpov et al. (1971)
		-5525.6 ± 5.9		Robie and Hemingway (1995)
Strontianite	$SrCO_3$	-1137.63	Karpov et al. (1968)	Latimer (1952)
		-1137.63	Latimer (1952)	Rossini et al. (1952)?
		-1137.63	Zhuk (1954)	Rossini et al. (1952), Karapet'yants (1953)
		-1137.6	Woods and Garrels (1987)	Rossini et al. (1952)
calculated		-1138.13		Zhuk (1954)
		-1138.13	Karpov et al. (1968)	Zhuk (1954)
		-1138.13	Karapet'yants and Karapet'yants (1970)	Zhuk (1954)
		-1138.05 ± 0.84	Robie (1962, 1966)	Garrels et al. (1960), Lander (1951)
		-1138.05 ± 0.84	Karpov et al. (1968)	Robie (1962)
		-1152.32	Naumov et al. (1974)	Adami and Conway (1966)
		-1137.640 ± 1.460	Robie et al. (1979)	Adami and Conway (1966)
		-1153.04 ± 2.09	Radha and Navrotsky (2013)	Adami and Conway (1966)
		-1140.14		Parker et al. (1971)
		-1152.3	Woods and Garrels (1987)	Naumov et al. (1974)
		-1248.79	Stern (2000)	Barin et al. (1977)
		-1152.6	Woods and Garrels (1987)	Helgeson et al. (1978)
		-1137.6	Woods and Garrels (1987)	Robie et al. (1978)
		-1140.1	Woods and Garrels (1987)	Wagman et al. (1982)
		-1144.73 ± 1.0		Busenberg et al. (1984)
		-1137.6 ± 1.5	Robie and Hemingway (1995)	Busenberg et al. (1984)

Table 2a. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Gibbs Free Energies of Formation (Continued)

Mineral Name	Formula	$\Delta G^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
		-1137.6		Robie and Hemingway (1995)
Thaumasite	$CaSiO_3 \cdot CaSO_4 \cdot CaCO_3 \bullet 15(H_2O)$	-7559.67	-	Blanc et al. (2010)
Thermonatrite	$Na_2CO_3 \bullet (H_2O)$	-1286.55		Saegusa (1950a)
		-1286.551	Karapet'yants and Karapet'yants (1970)	Saegusa (1950a)
		-1286.6	Woods and Garrels (1987)	Saegusa (1950a)
		-1291.35	Karpov et al. (1968)	Bauer and Dorland (1952)
		-1291.35	Karapet'yants and Karapet'yants (1970)	Bauer and Dorland (1952)
		-1290.76	Karpov et al. (1968)	Karapet'yants (1955)
		-1290.76	Karapet'yants and Karapet'yants (1970)	Karapet'yants (1957)
		-1286.55	Karpov et al. (1968)	Karapet'yants and Karapet'yants (1961)
		-1288.71	Naumov et al. (1974)	Waterfield et al. (1968)
		-1288.7	Woods and Garrels (1987)	Naumov et al. (1974)
		-1288.7	La Iglesia and Felix (1994)	Naumov et al. (1974)
		-1286.1 ± 0.5	Robie and Hemingway (1995)	Berg and Vanderzee (1978)
		-1285.3	Woods and Garrels (1987)	Wagman et al. (1982)
		-1285.3	La Iglesia and Felix (1994)	Wagman et al. (1982)
		-1285.31	BSC (2007)	Wagman et al. (1982)
		-1286.0	Woods and Garrels (1987)	Harvie et al. (1984)
predicted		-1285.7 ± 1.5		La Iglesia and Felix (1994)
		-1286.1	Radha and Navrotsky (2013)	Robie and Hemingway (1995)
Tilleyite	$Ca_5Si_2O_7(CO_3)_2$	-6009.8	Woods and Garrels (1987)	Karpov et al. (1971)
		-6013.5 ± 6.0	Robie and Hemingway (1995)	Treiman and Essene (1983); Holland and Powell (1990)
		-6013.5		Robie and Hemingway (1995)

Table 2a. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Gibbs Free Energies of Formation (Continued)

Mineral Name	Formula	$\Delta G^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
Trona	$Na_3(CO_3)(HCO_3)•2(H_2O)$	-2380.7		Rupert et al. (1965)
		-2383.4	Woods and Garrels (1987)	Wagman et al. (1982)
		-2380.5	Woods and Garrels (1987)	Harvie et al. (1984)
		-2386.6	Woods and Garrels (1987)	Garrels and Christ (1985)
Vaterite	$CaCO_3$	-1125.540 ± 1.500	Robie et al. (1979)	Turnbull (1973)
		-1125.540 ± 1.50	Radha and Navrotsky (2013)	Turnbull (1973)
		-1125.5 ± 1.5	Robie and Hemingway (1995)	Plummer and Busenberg (1982); Turnbull (1973)
		-1125.5	Woods and Garrels (1987)	Robie et al. (1978)
Wegscheiderite	$Na_5(HCO_3)_3CO_3$		Robie and Hemingway (1995)	Vanderzee and Wigg (1981)
Synthetic Phases				
$Na_2CO_3•7(H_2O)$	$Na_2CO_3•7(H_2O)$	-2714.97		Saegusa (1950a)
		-2714.972	Karapet'yants and Karapet'yants (1970)	Saegusa (1950a)
		-2715.9	Woods and Garrels (1987)	Saegusa (1950a)
		-2710.77	Karpov et al. (1968)	Bauer and Dorland (1952)
		-2710.77	Karapet'yants and Karapet'yants (1970)	Bauer and Dorland (1952)
		-2716.67	Karpov et al. (1968)	Karapet'yants (1955)
		-2716.67	Karapet'yants and Karapet'yants (1970)	Karapet'yants (1957)
		-2714.97	Karpov et al. (1968)	Karapet'yants and Karapet'yants (1961)
		-2714.2	Woods and Garrels (1987)	Wagman et al. (1982)
		-2714.2	BSC (2007)	Wagman et al. (1982)
Trona-K	$K_2NaH(CO_3)_2•2(H_2O)$	-575.74	BSC (2007)	Harvie et al. (1984)

Table 2a. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Gibbs Free Energies of Formation (Continued)

Mineral Name	Formula	$\Delta G^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
K_2CO_3	K_2CO_3	-1052.09		Saegusa (1950b)
		-1069.01	Latimer (1952)	Rossini et al. (1952)?
		-1069.01	Karpov et al. (1968)	Latimer (1952)
		-1092.86	Karapet'yants and Karapet'yants (1970)	Latimer (1952)
		-1069.01	Karapet'yants and Karapet'yants (1970)	Latimer (1952)
		-1069.0	Woods and Garrels (1987)	Latimer (1952)
		-1062.74	Karpov et al. (1968)	Karapet'yants (1954b)
		-347.27[(1)]	Karpov et al. (1968)	Kireev (1964)
		-1042.619	Karapet'yants and Karapet'yants (1970)	Stull and Prophet (1965)
		-1060.021	Karapet'yants and Karapet'yants (1970)	Stull and Prophet (1965)
		-1063.99	Naumov et al. (1974)	Stull and Prophet (1965), *et seq.* (-1968)
		-1060.64	Karpov et al. (1968)	Matveev et al. (1966)
		-1060.6	Woods and Garrels (1987)	Karpov et al. (1968)
		-1064.0	Woods and Garrels (1987)	Naumov et al. (1974)
		-1063.5	Woods and Garrels (1987)	Wagman et al. (1982)
		-1063.5	Meng et al. (1995)	Wagman et al. (1982)
		-1060.6	Woods and Garrels (1987)	Babushkin et al. (1985)
		-1196.55	Stern (2000)	Knacke et al. (1991)
K_2CO_3•1.5(H_2O)	K_2CO_3•1.5(H_2O)	-1431.27	BSC (2007)	Harvie et al. (1984)
$K_8H_4(CO_3)_6$•3(H_2O)	$K_8H_4(CO_3)_6$•3(H_2O)	-1514.032	BSC (2007)	Harvie et al. (1984)
$KNaCO_3$•6(H_2O)	$KNaCO_3$•6(H_2O)	-596.513	BSC (2007)	Harvie et al. (1984)

Table 2a. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Gibbs Free Energies of Formation (Continued)

Mineral Name	Formula	$\Delta G^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
$MgCO_3$•2(H_2O)	$MgCO_3$•2(H_2O)	+0.29	Karapet'yants and Karapet'yants (1970)	Halla (1962)
Hemicarboaluminate	3CaO.Al_2O_3.0.5$CaCO_3$.0.5$Ca(OH)_2$•10 5(H_2O)	N/A	BSC (2007)	Damidot et al. (1994)
Hemicarboaluminate	$Ca_4Al_2(CO_3)_{0.5}(OH)_{13}$•5.5($H_2O$)	-7336.0	-	Matschei et al. (2007)
Hemicarboaluminate	6CaO·2Al_2O_3·$CaCO_3$·$Ca(OH)_2$•21(H_2O)	-14685.62	-	Blanc et al. (2010)
Monocarboaluminate	3CaO.Al_2O_3.$CaCO_3$•10(H_2O)	N/A	BSC (2007)	Damidot et al. (1994)
Monocarboaluminate	$Ca_4Al_2(CO_3)(OH)_{12}$•5(H_2O)	-7337.5	-	Matschei et al. (2007)
Monocarboaluminate	3CaO·Al_2O_3·$CaCO_3$•10.68(H_2O)	-7269.02	-	Blanc et al. (2010)
Tricarboaluminate	$Ca_6Al_2(CO_3)_3(OH)_{12}$•26($H_2O$)	-14565.6	-	Matschei et al. (2007)
$SrH(CO_3)_2$	$SrH(CO_3)_2$	-1764.18	Karpov et al. (1968)	Zhuk (1954)
		-1764.18	Karapet'yants and Karapet'yants (1970)	Zhuk (1954)

(1) Formation from the oxides

(2) Formation with respect to $CaCO_3$ plus $MgCO_3$

Table 2b. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Enthalpies of Formation

Mineral Name	Formula	$\Delta H^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
Minerals				
Ankerite		-1971.5 ± 1.48	Holland and Powell (1990)	
Aragonite	$CaCO_3$	-1207.04	Karpov et al. (1968)	Latimer (1952)
		-1207.04	Latimer (1952)	Rossini et al. (1952)?
		-1205.55 ± 1.05	Robie (1962, 1966)	Rossini et al. (1952), Garrels et al. (1960)
		-1207.0	Woods and Garrels (1987)	Rossini et al. (1952)
		-1207.0	La Iglesia and Felix (1994)	Rossini et al. (1952), Naumov et al. (1974)
		-1205.55 ± 1.05	Karpov et al. (1968)	Robie (1962)
		-179.49[(1)]	Karpov et al. (1968)	Kireev (1964)
		-1207.00 ± 0.5	Naumov et al. (1974)	Backstrom (1925); Kelley and Anderson (1935)
		-1207.13		Parker et al. (1971)
		-1207.430 ± 1.423	Robie et al. (1979)	Parker et al. (1971)
		-1207.43 ± 1.42	Radha and Navrotsky (2013)	Parker et al. (1971), Robie et al. (1978)
		-1207.0	Woods and Garrels (1987)	Naumov et al. (1974)
		-1208.0	Woods and Garrels (1987)	Helgeson et al. (1978)
		-1208.0	La Iglesia and Felix (1994)	Helgeson et al. (1978)
		-1207.4	Woods and Garrels (1987)	Robie et al. (1978)
		-1207.4	La Iglesia and Felix (1994)	Robie et al. (1979)
		-1207.4 ± 1.4	Robie and Hemingway (1995)	Plummer and Busenberg (1982)
		-1209.7	La Iglesia and Felix (1994)	Robinson et al. (1982)
		-1209.7	Woods and Garrels (1987)	Robinson et al. (1982),
		-1207.1	Woods and Garrels (1987)	Wagman et al. (1982)
		-1207.1	La Iglesia and Felix (1994)	Wagman et al. (1982)
		-1207.21		BSC (2007)
		-1208.16 ± 1.11		Holland and Powell (1990)
		-1207.0 ± 1.0		La Iglesia and Felix (1994)

Table 2b. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Enthalpies of Formation (Continued)

Mineral Name	Formula	$\Delta H^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
		-1207.4		Robie and Hemingway (1995)
		-1207.65 ± 0.52		Holland and Powell (1998)
		-1208.200		Matas et al. (2000)
		-1207.48		Hummel et al. (2002)
Artinite	$Na_2(OH)_2CO_3$•3(H_2O)	-2920.61 ± 0.71		Hemingway and Robie (1973)
		-2920.610 ± 0.710	Robie et al. (1979)	Hemingway and Robie (1973)
		-2920.6 ± 0.7	Robie and Hemingway (1995)	Hemingway and Robie (1973)
		-2920.61 ± 0.71	Radha and Navrotsky (2013)	Hemingway and Robie (1973), Robie et al. (1978)
		-2920.6	Woods and Garrels (1987)	Helgeson et al. (1978)
		-2568.6	La Iglesia and Felix (1994)	Helgeson et al. (1978)
		-2920.6	Woods and Garrels (1987)	Robie et al. (1978)
		-2568.3	La Iglesia and Felix (1994)	Robie et al. (1979)
predicted		-2920.6 ± 2.3		La Iglesia and Felix (1994)
		-2920.61		BSC (2007)
Burkeite	$Na_6CO_3(SO_4)_2$	N/A		BSC (2007)
Butschliite	$K_2Ca(CO_3)_2$	-1824.0 ± 3.9	Radha and Navrotsky (2013)	Robie et al. (1978), Navrotsky et al. (1997)
Calcite	$CaCO_3$	-1206.83 ± 0.8	Naumov et al. (1974)	Kelley and Anderson (1935); Wells and Taylor (1937)
		-1206.87	Latimer (1952)	Rossini et al. (1952)?
		-1206.87	Zhuk (1954)	Rossini et al. (1952), Karapet'yants (1953)
		-177.82 ± 0.42	Weeks (1956)	Rossini et al. (1952)
		-1205.35 ± 1.05	Robie (1962, 1966)	Rossini et al. (1952), Garrels et al. (1960)

Table 2b. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Enthalpies of Formation (Continued)

Mineral Name	Formula	$\Delta H^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
		-1206.87	Karpov et al. (1968)	Rossini et al. (1952)
		-1206.9	Woods and Garrels (1987)	Rossini et al. (1952)
		-1206.9	La Iglesia and Felix (1994)	Rossini et al. (1952), Wagman et al. (1982)
		-177.82[(1)]	Karpov et al. (1968)	Weeks (1956)
		-1205.35 ± 5.23	Karpov et al. (1968)	Robie (1962)
		-178.32	Karapet'yants and Karapet'yants (1970)	Meadowcroft and Richardson (1963)
		-1207.7	Woods and Garrels (1987)	Karpov et al. (1971)
		-1207.7	La Iglesia and Felix (1994)	Karpov et al. (1971)
		-1206.92		Parker et al. (1971)
		-1207.370 ± 1.339	Robie et al. (1979)	Parker et al. (1971)
		-1207.37 ± 1.34	Radha and Navrotsky (2013)	Parker et al. (1971), Robie et al. (1978)
		-1206.8	Woods and Garrels (1987)	Naumov et al. (1974)
		-1208.8	La Iglesia and Felix (1994)	Naumov et al. (1974)
		-1208.2	Woods and Garrels (1987)	Helgeson et al. (1978)
		-1208.2	La Iglesia and Felix (1994)	Helgeson et al. (1978)
		-1207.4	Woods and Garrels (1987)	Robie et al. (1978)
		-1207.4	La Iglesia and Felix (1994)	Robie et al. (1979), Sangameshwar and Barnes (1983)
		-1206.87		Alekseev, and Barinova (1981)
		-1207.4 ± 1.3	Robie and Hemingway (1995)	Plummer and Busenberg (1982), Ko et al. (1982)
		-1209.0	Woods and Garrels (1987)	Robinson et al. (1982)
		-1209.0	La Iglesia and Felix (1994)	Robinson et al. (1982)
		-1206.9	Woods and Garrels (1987)	Wagman et al. (1982)
		-1206.92	Meng et al. (1995)	Wagman et al. (1982)
		-1207.4	Woods and Garrels (1987)	Sangameshwar and Barnes (1983)

Table 2b. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Enthalpies of Formation (Continued)

Mineral Name	Formula	$\Delta H^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
		-1207.77 ± 1.11		Holland and Powell (1990)
		-1206.92	Stern (2000)	Barin (1993)
		-1208.9 ± 0.8		La Iglesia and Felix (1994)
		-1207.4		Robie and Hemingway (1995)
		-1221.99 ± 1.13	Radha and Navrotsky (2013)	Kiseleva et al. (1996), Robie et al. (1978)
		-1207.54 ± 0.52		Holland and Powell (1998)
		-1208.200		Matas et al. (2000)
		-1208.705		Hummel et al. (2002)
		-1207.3		BSC (2007)
Cancrinite (NC2)	$Na_{7.770}[Al_{6.003}Si_{5.997}O_{24}](NO_3)_{1.474}(CO_3)_{0.146}$•2.175($H_2O$)	14258.27 ± 17.34	Radha and Navrotsky (2013)	Liu et al. (2007)
Cancrinite (NC85)	$Na_{7.282}[Al_{5.854}Si_{6\cdot146}O_{24}](NO3)_{1.336}(CO_3)_{0.046}$•3.365($H_2O$)	14258.27 ± 17.34	Radha and Navrotsky (2013)	Liu et al. (2007)
Cancrinite (CAN7)	$Na_{7.571}[Al_{6.103}Si_{5.897}O_{24}](NO3)_{1.242}(CO_3)_{0.113}$•3.533($H_2O$)	14384.09 ± 15.76	Radha and Navrotsky (2013)	Liu et al. (2007)
Cancrinite (CAN25)	$Na_{7.887}[Al_{5.982}Si_{6.018}O_{24}](NO_3)_{1.433}(CO_3)_{0.236}$•2.457($H_2O$)	14207.51 ± 11.62	Radha and Navrotsky (2013)	Liu et al. (2007)
Cancrinite (CAN50)	$Na_{7.725}[Al_{5.969}Si_{6.031}O_{24}](NO_3)_{1.234}(CO_3)_{0\cdot261}$•2.829($H_2O$)	14257.26 ± 11.32	Radha and Navrotsky (2013)	Liu et al. (2007)
Cancrinite CAN75)	$Na_{8.072}[Al_{6.055}Si_{5.945}O_{24}](NO_3)_{1.320}(CO_3)_{0.348}$•2.501($H_2O$)	14292.44 ± 12.13	Radha and Navrotsky (2013)	Liu et al. (2007)
Cancrinite (FB2-49)	$Na_{7.771}[Al_{5.956}Si_{6.004}O_{24}](CO_3)_{0.881}$•3.480($H_2O$)	14524.07 ± 14.09	Radha and Navrotsky (2013)	Liu et al. (2007)
Dawsonite	$NaAlCO_3(OH)_2$	-1963.970 ± 2.936	Robie et al. (1979)	Ferrante et al. (1976)
		-1964.0 ± 2.9	Robie and Hemingway (1995)	Ferrante et al. (1976)
		-1964 ± 4	Benezeth et al. (2007)	Ferrante et al. (1976)
		-1963.97 ± 2.93	Radha and Navrotsky (2013)	Ferrante et al. (1976), Robie et al. (1978)
		-1964.0	Woods and Garrels (1987)	Robie et al. (1978)

Table 2b. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Enthalpies of Formation (Continued)

Mineral Name	Formula	$\Delta H^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
		-1964.0		Robie and Hemingway (1995)
		-1960 ± 7		Benezeth et al. (2007)
		-1699		Łodziana et al. (2011)
		-1963.956		BSC (2007)
Dolomite	$CaMg(CO_3)_2$	-301.92 ± 1.46	Weeks (1956)	Rossini et al. (1952)
		-2331.7	Woods and Garrels (1987)	Rossini et al. (1952)
		-2331.7	La Iglesia and Felix (1994)	Rossini et al. (1952)
		-2332.86 ± 3.35	Robie (1962)	Robie (1957)
		-2332.86	Karpov et al. (1968)	Robie (1962)
		-8.20 ± 1.55[(2)]	Karpov et al. (1968)	Halla (1965)
		-2326.30	Karpov et al. (1968)	Karapet'yants and Karapet'yants (1961)
		-2332.86 ± 3.35	Robie (1966)	Stout and Robie (1963)
		-12.30[(2)]	Karpov et al. (1968)	Stout and Robie (1963)
		-2314.59	Naumov et al. (1974)	Stout and Robie (1963)
		-2324.480 ± 1.460	Robie et al. (1978)	Stout and Robie (1963)
		-301.92 ± 1.46[(1)]	Karpov et al. (1968)	Weeks (1956)
		-2332.7	Woods and Garrels (1987)	Karpov et al. (1971)
		-2314.6	Woods and Garrels (1987)	Naumov et al. (1974)
		-2314.6	La Iglesia and Felix (1994)	Naumov et al. (1974)
		-2329.9	Woods and Garrels (1987)	Helgeson et al. (1978)
		-2329.9	La Iglesia and Felix (1994)	Helgeson et al. (1978)
		-2324.5	Woods and Garrels (1987)	Robie et al. (1978)
		-2324.5	La Iglesia and Felix (1994)	Robie et al. (1978)
		-2326.3	Woods and Garrels (1987)	Wagman et al. (1982)
		-2326.3	La Iglesia and Felix (1994)	Wagman et al. (1982)
		-2325.72 ± 1.26		Holland and Powell (1990)
		-2325.7	Sherman and Barak (2000)	Holland and Powell (1990)

Table 2b. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Enthalpies of Formation (Continued)

Mineral Name	Formula	$\Delta H^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
		-2327.9	Sherman and Barak (2000)	Knacke et al. (1991)
		-2331.64 ± 2.07		Tareen et al. (1992)
		-2324.5 ± 1.5	Robie and Hemingway (1995)	Hemingway and Robie (1994)
		-2324.5 ± 1.1	Radha and Navrotsky (2013)	Hemingway and Robie (1994)
		-2319.9 ± 1.3		La Iglesia and Felix (1994)
		-2324.5		Robie and Hemingway (1995)
		-2324.56 ± 0.70		Holland and Powell (1998)
		-2329.400		Matas et al. (2000)
		-2321.148		Hummel et al. (2002)
		-2328.94		BSC (2007)
Fairchildite	$K_2Ca(CO_3)_2$	-1790.4 ± 4.0	Radha and Navrotsky (2013)	Robie et al. (1978), Navrotsky et al. (1997)
(Gaylussite)	$Na_2Ca(CO_3)_2$•5(H_2O)	-3424.65		Alekseev, and Barinova (1981)
Gaylussite		N/A		BSC (2007)
Huntite	$CaMg_3(CO_3)_4$	-4529.60 ± 1.57		Hemingway and Robie (1973)
		-4529.600 ± 1.570	Robie et al. (1979)	Hemingway and Robie (1973)
		-4529.6 ± 1.6	Robie and Hemingway (1995)	Hemingway and Robie (1973), Königsberger and Gamsjäger (1987)
		-4529.60 ± 1.57	Radha and Navrotsky (2013)	Hemingway and Robie (1973), Robie et al. (1978)
		-4529.6	Woods and Garrels (1987)	Robie et al. (1978)
		-4629.6	La Iglesia and Felix (1994)	Robie et al. (1979)
predicted		-4545.9 ± 2.7		La Iglesia and Felix (1994)
		-4529.6		BSC (2007)
Hydromagnesite (II)	$Mg_5(CO_3)_4(OH)_2$•4(H_2O)	-6514.86 ± 1.05		Robie and Hemingway (1973)
		-6514.860 ± 1.060	Robie et al. (1979)	Robie and Hemingway (1973)

Table 2b. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Enthalpies of Formation (Continued)

Mineral Name	Formula	$\Delta H^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
		-6514.9 ± 1.1	Robie and Hemingway (1995)	Robie and Hemingway (1973)
		-6514.86 ± 1.06	Radha and Navrotsky (2013)	Robie and Hemingway (1973), Robie et al. (1978)
		-6514.9	Woods and Garrels (1987)	Helgeson et al. (1978)
		-6514.9	Woods and Garrels (1987)	Robie et al. (1978)
		-6514.86		BSC (2007)
Hydrotalcite-CO_3	$Mg_{0.69}Al_{0.31}(OH)_2(CO_3)_{0.15}$•$0.30(H_2O)$	-1170.34 ± 1.81		Allada et al. (2005a)
	$Mg_{0.69}Al_{0.31}(OH)_2(CO_3)_{0.16}$•$0.30(H_2O)$	-1170.34 ± 1.81	Radha and Navrotsky (2013)	Allada et al. (2005a,b)
	$Mg_{0.74}Al_{0.26}(OH)_2(CO_3)_{0.13}$•$0.39(H_2O)$	-1165.98 ± 2.06		Allada et al. (2005a)
	$Mg_{0.74}Al_{0.26}(CO_3)_{0.13}(OH)_2$•$0.39(H_2O)$	-1165.98 ± 2.06		Allada et al. (2005b)
	$Mg_{0.74}Al_{0.26}(OH)_2(CO_3)_{0.13}$•$0.39(H_2O)$	-1165.98 ± 2.06	Radha and Navrotsky (2013)	Allada et al. (2005a,b)
	$Mg_{0.67}Al_{0.33}(OH)_2(CO_3)_{0.17}$•$0.69(H_2O)$	-1284.65 ± 1.97		Allada et al. (2005a)
	$Mg_{0.67}Al_{0.33}(OH)_2(CO_3)_{0.17}$•$0.69(H_2O)$	-1284.65 ± 1.97	Radha and Navrotsky (2013)	Allada et al. (2005a,b)
	$Mg_{0.66}Al_{0.34}(OH)_2(CO_3)_{0.17}$•$0.70(H_2O)$	-1292.07 ± 2.05		Allada et al. (2005a)
	$Mg_{0.66}Al_{0.34}(OH)_2(CO_3)_{0.17}$•$0.70(H_2O)$	-1292.08 ± 2.05	Radha and Navrotsky (2013)	Allada et al. (2005a,b)
	$Mg_{0.73}Al_{0.27}(CO_3)_{0.16}(OH)_{1.95}$•$0.83H_2O$	-1297.19 ± 1.97		Allada et al. (2005b)
	$Mg_{0.73}Al_{0.27}(CO_3)_{0.16}(OH)_{1.95}$•$0.83(H_2O)$	-1297.19 ± 1.97	Radha and Navrotsky (2013)	Allada et al. (2005a,b)
	$Mg_{0.74}Al_{0.26}[(NO_3)_{0.2}(OH)_{0.06}](OH)_2$•$0.39(H_2O)$	-1119.36 ± 2.50		Allada et al. (2005b)
	$Mg_{0.67}Al_{0.33}(OH)_2(CO_3)_{0.16}$•$0.70(H_2O)$	-1284.65 ± 1.75		Allada et al. (2006)
	$Mg_{0.66}Al_{0.34}(OH)_2(CO_3)_{0.17}$•$0.69(H_2O)$	-1292.07 ± 1.63		Allada et al. (2006)
	$Mg_{0.69}Al_{0.31}(OH)_2(CO_3)_{0.15}$•$0.30(H_2O)$	-1168.52 ± 1.81		Allada et al. (2006)
	$Mg_{0.74}Al_{0.26}(OH)_2(CO_3)_{0.13}$•$0.39(H_2O)$	-1165.98 ± 2.06		Allada et al. (2006)
	$Mg_{0.73}Al_{0.27}(OH)_2(CO_3)_{0.16}$•$0.83(H_2O)$	-1279.19 ± 1.97		Allada et al. (2006)
3R1 polytype *experimental*	$Mg_{2/3}Al_{1/3}(OH)_2(CO_3)_{1/6}$•$4/6(H_2O)$	-57.99 ± 1.67[(1)]	Costa et al. (2010)	Allada et al. (2006)
	$Mg_4Al_2(OH)_{12}(CO_3)$ •$2(H_2O)$	-7374	-	Lothenbach et al. (2008)
	$Mg_4Al_2(OH)_{12}(CO_3)$ •$2(H_2O)$	-7078.83	-	Blanc et al. (2010)

Table 2b. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Enthalpies of Formation (Continued)

Mineral Name	Formula	$\Delta H^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
calculated	$Mg_{2/3}Al_{1/3}(OH)_2(CO_3)_{1/6}$•4/6($H_2O$)	-65.23(1)		Costa et al. (2010)
Ikaite	$CaCO_3$•6(H_2O)	-2954.1 ± 5.0	Robie and Hemingway (1995)	Marland (1975)
		-2954.1	Radha and Navrotsky (2013)	Robie and Hemingway (1995)
Kalicinite	$KHCO_3$	-959.39	Latimer (1952)	Rossini et al. (1952)?
		-959.39	Karpov et al. (1968)	Rossini et al. (1952)
		-966.09 9 ± 4.2	Naumov et al. (1974)	Rossini et al. (1952)
		-963.2	Meng et al. (1995)	Wagman et al. (1982)
		N/A		BSC (2007)
Lansfordite	$MgCO_3$•5(H_2O)	N/A		BSC (2007)
Magnesite	$MgCO_3$	[blank]	Karpov et al. (1968)	Roth (1948)
		-1121.73	Karpov et al. (1968)	Britske et al. (1949)
		-1112.94	Latimer (1952)	Rossini et al. (1952)?
		-1112.94	Zhuk (1954)	Rossini et al. (1952), Karapet'yants (1953)
		-117.61 ± 1.26	Weeks (1956)	Rossini et al. (1952)
		-1112.94	Karpov et al. (1968)	Rossini et al. (1952)
		-1096.21	Karpov et al. (1968)	Rossini et al. (1952)
		-1096.21	Karapet'yants and Karapet'yants (1970)	Rossini et al. (1952), Roth (1948)
		-1113.0	Woods and Garrels (1987)	Rossini et al. (1952)
		-1113.0	La Iglesia and Felix (1994)	Rossini et al. (1952)
		-1112.9	Saldi (2009)	Rossini et al. (1952)
		-117.61 ± 1.26(1)	Mel'nik (1972)	Nikolaev and Dolivo-Dobrovolskii (1961), Rossini et al. (1952)
		-1089.51	Mel'nik (1972)	Kapustinskii and Stakhanova (1954)

Table 2b. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Enthalpies of Formation (Continued)

Mineral Name	Formula	$\Delta H^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
		-117.61 ± 1.26[(1)]	Karpov et al. (1968)	Weeks (1956)
		-1113.15 ± 1.67	Karpov et al. (1968)	Robie (1962)
		-1113.16 ± 1.67	Robie (1962)	Stout and Robie (1963)
		-1095.71 ± 2.51		Langmuir (1965)
		-1095.71 ± 2.51	Karpov et al. (1968)	Langmuir (1965)
		-100.53[(1)]	Mel'nik (1972)	Langmuir (1965)
		-1095.79	Naumov et al. (1974)	Langmuir (1965)
			Saldi (2009)	Langmuir (1965)
		-118.11 ± 0.84[(1)]		Robie (1965)
		-118.11[(1)]	Karpov et al. (1968)	Robie (1965)
		-1113.280 ± 1.339	Robie et al. (1979)	Robie (1965)
		-1113.28 ± 1.34	Radha and Navrotsky (2013)	Robie (1965)
		-1113.3 ± 1.3	Robie and Hemingway (1995)	Robie (1965)
		-118.11 ± 0.84[(1)]	Mel'nik (1972)	Robie (1965), Robie and Waldbaum (1968)
			Saldi (2009)	Robie (1965)
		-1112.94	Karapet'yants and Karapet'yants (1970)	Stull and Prophet (1965)
		-1089.51	Karpov et al. (1968)	Gerasimov et al. (1966)
		-1115.45	Karpov et al. (1968)	Gerasimov et al. (1966)
		-1095.71	Mel'nik (1972)	Karpov et al. (1968), Naumov et al. (1971), Langmuir (1965)
			Saldi (2009)	Robie and Waldbaum (1968)
		-1095.79		Parker et al. (1971)
recommended value		-118.11[(1)]		Mel'nik (1972)
recommended value		-1113.11		Mel'nik (1972)
		-1113.1	Woods and Garrels (1987)	Mel'nik (1972)
		-1113.1	La Iglesia and Felix (1994)	Mel'nik (1972)
		-1113.2	Woods and Garrels (1987)	Karpov et al. (1971)
		-1113.2	La Iglesia and Felix (1994)	Karpov et al. (1971)

Table 2b. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Enthalpies of Formation (Continued)

Mineral Name	Formula	$\Delta H^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
		-1095.8	Woods and Garrels (1987)	Naumov et al. (1974)
			Saldi (2009)	Dandurand and Schott (1977)
			Saldi (2009)	Hemingway et al. (1977)
		-1111.4	Woods and Garrels (1987)	Helgeson et al. (1978)
		-1111.4	La Iglesia and Felix (1994)	Helgeson et al. (1978)
		-1111.4	Saldi (2009)	Helgeson et al. (1978)
		-1113.3	Woods and Garrels (1987)	Robie et al. (1978)
		-1113.28	Saldi (2009)	Robie et al. (1978)
		-1113.3	La Iglesia and Felix (1994)	Robie et al. (1979)
			Saldi (2009)	Sadiq and Lindsay (1979)
		-1095.8	Woods and Garrels (1987)	Wagman et al. (1982)
		-1095.8	Meng et al. (1995)	Wagman et al. (1982)
		-1095.8	Saldi (2009)	Wagman et al. (1982)
			Saldi (2009)	Kittrick and Peryea (1986)
		-1113.636	Saldi (2009)	Berman (1988)
		-1114.505	Saldi (2009)	Chernosky and Berman (1989)
		-1112.48 ± 0.81		Holland and Powell (1990)
		-1112.48 ± 0.81	Saldi (2009)	Holland and Powell (1990)
			Saldi (2009)	Trommsdorff and Connolly (1990)
		-1095.80	Stern (2000)	Knacke et al. (1991)
predicted		-1113.0 ± 0.7		La Iglesia and Felix (1994)
		-1111.68	Saldi (2009)	Koziol and Newton (1995)
		-1113.3		Robie and Hemingway (1995)
		-1113.3 ± 1.3	Saldi (2009)	Robie and Hemingway (1995)
		-1111.59 ± 0.36		Holland and Powell (1999)
		-1117.94 ± 0.4	Saldi (2009)	Konigsberger et al. (1999)
		-1113.300		Matas et al. (2000)
				Hummel et al. (2002)
		-1111.7 ± 2.55		Allada et al. (2006)

Table 2b. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Enthalpies of Formation (Continued)

Mineral Name	Formula	$\Delta H^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
		-116.7 ± 2.55[(1)]		Allada et al. (2006)
		-1110.99 ± 2.0		Saldi (2009)
		-1111.4		BSC (2007)
Meionite	$Ca_4Al_6Si_6O_24CO_3$	-13897.5	Woods and Garrels (1987)	Robinson et al. (1982)
Al/Si ordered		-13881.4 ± 6.2	Robie and Hemingway (1995)	Moecher and Essene (1990)
Al/Si ordered		-13881.4		Robie and Hemingway (1995)
Al/Si ordered		-13881.4	Radha and Navrotsky (2013)	Robie and Hemingway (1995)
Monohydrocalcite	$CaCO_3$•(H_2O)	-1498.3 ± 1.2	Robie and Hemingway (1995)	Hull and Turnbull (1973)
		-1498.29 ± 1.17	Radha and Navrotsky (2013)	Hull and Turnbull (1973), Robie et al. (1978)
		-1498.3	Woods and Garrels (1987)	Robie et al. (1978)
		-1498.29		BSC (2007)
Nahcolite	$NaHCO_3$	-947.68	Latimer (1952)	Rossini et al. (1952)?
		-947.68	Karpov et al. (1968)	Rossini et al. (1952)
		-947.7	Woods and Garrels (1987)	Rossini et al. (1952)
		-913.45 ± 1.3	Naumov et al. (1974)	Rupert et al. (1965)
		-913.4	Woods and Garrels (1987)	Naumov et al. (1974)
		-949.0 ± 0.2	Robie and Hemingway (1995)	Berg and Vanderzee (1978)
		-950.8	Woods and Garrels (1987)	Wagman et al. (1982)
		-950.81	Meng et al. (1995)	Wagman et al. (1982)
		-947.257		BSC (2007)
Natrite	Na_2CO_3	-1129.05		Saegusa (1950a)
		-1129.05	Karapet'yants and Karapet'yants (1970)	Saegusa (1950a)
		-1133.95	Karpov et al. (1968)	Bauer and Dorland (1952)

Table 2b. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Enthalpies of Formation (Continued)

Mineral Name	Formula	$\Delta H^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
		-1133.95	Karapet'yants and Karapet'yants (1970)	Bauer and Dorland (1952)
		-1130.94	Latimer (1952)	Rossini et al. (1952)?
		-1130.94	Karpov et al. (1968)	Rossini et al. (1952)
		-1130.9	Woods and Garrels (1987)	Rossini et al. (1952)
		-1136.37	Karpov et al. (1968)	Kubachewski and Evans (1958)
		-1129.05	Karpov et al. (1968)	Karapet'yants and Karapet'yants (1961)
		-1136.37	Karapet'yants and Karapet'yants (1970)	Kubaschewski and Evans (1963)
		-321.96	Karapet'yants and Karapet'yants (1970)	Meadowcroft and Richardson (1963)
		-1131.44 ± 1.3	Naumov et al. (1974)	Rupert et al. (1965)
		-1130.94	Karapet'yants and Karapet'yants (1970)	Stull and Prophet (1965)
		-1131.4	Woods and Garrels (1987)	Naumov et al. (1974)
		-1129.2 ± 0.3	Robie and Hemingway (1995)	Berg and Vanderzee (1978)
		-1131.44		Alekseev and Barinova (1981)
		-1130.7	Woods and Garrels (1987)	Wagman et al. (1982)
		-1130.68	Meng et al. (1995)	Wagman et al. (1982)
		-1130.77	Stern (2000)	Knacke et al. (1991)
		-1130.68		EQ3/6
Natron	Na_2CO_3•10(H_2O)	-4075.76		Saegusa (1950a)
		-4075.756	Karapet'yants and Karapet'yants (1970)	Saegusa (1950a)
		-4083.50	Karpov et al. (1968)	Bauer and Dorland (1952)
		-4083.50	Karapet'yants and Karapet'yants (1970)	Bauer and Dorland (1952)
		-4075.76	Karpov et al. (1968)	Karapet'yants and Karapet'yants (1961)
		-4082.04 ± 1.3	Naumov et al. (1974)	Waterfield et al. (1968)
		-4082.0	Woods and Garrels (1987)	Naumov et al. (1974)

Table 2b. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Enthalpies of Formation (Continued)

Mineral Name	Formula	$\Delta H^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
		-4081.3	Woods and Garrels (1987)	Wagman et al. (1982)
		-4079.39	Radha and Navrotsky (2013)	Johnson et al. (1992)
		-4079.394		BSC (2007)
Nesquehonite	$MgCO_3$•3(H_2O)	+11.21	Karapet'yants and Karapet'yants (1970)	Halla (1962)
		-1985.73 ± 4.2	Naumov et al. (1974)	Langmuir (1965)
		-1977.26 ± 0.46		Robie and Hemingway (1973)
		-1977.260 ± 0.260	Robie et al. (1979)	Robie and Hemingway (1973)
		-1977.3 ± 0.3	Robie and Hemingway (1995)	Robie and Hemingway (1973)
		-1977.26 ± 0.26	Radha and Navrotsky (2013)	Robie and Hemingway (1973), Robie et al. (1978)
		-1985.7	Woods and Garrels (1987)	Naumov et al. (1974)
		-1726.6	La Iglesia and Felix (1994)	Naumov et al. (1974)
		-1977.2	Woods and Garrels (1987)	Helgeson et al. (1978)
		-1724.0	La Iglesia and Felix (1994)	Helgeson et al. (1978)
		-1977.3	Woods and Garrels (1987)	Robie et al. (1978)
		-1723.7	La Iglesia and Felix (1994)	Robie et al. (1979)
predicted		-1987.2 ± 3.1		La Iglesia and Felix (1994)
		-1977.26		BSC (2007)
(Nyerereite)	$Na_2Ca(CO_3)_2$	-2342.58		Alekseev, and Barinova (1981)
Pirssonite	$Na_2Ca(CO_3)_2$•2(H_2O)	-2941.31		Alekseev, and Barinova (1981)
		N/A		BSC (2007)
Spurrite	$Ca_5Si_2O_8CO_3$	-5899.3	Woods and Garrels (1987)	Karpov et al. (1971)
		5840.2 ± 5.7		Robie and Hemingway (1995)

Table 2b. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Enthalpies of Formation (Continued)

Mineral Name	Formula	$\Delta H^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
Strontianite	$SrCO_3$	-1217.07		Kapustinsky and Dezideryeva (1946)
		-1221.31	Karpov et al. (1968)	Latimer (1952)
		-1221.31	Latimer (1952)	Rossini et al. (1952)?
		-1218.38	Zhuk (1954)	Rossini et al. (1952), Karapet'yants (1953)
		-1218.4	Woods and Garrels (1987)	Rossini et al. (1952)
		-1216.41 ± 2.09	Robie (1962)	Garrels et al. (1960), Lander (1951)
		-1216.41 ± 2.09	Karpov et al. (1968)	Robie (1962)
		-1232.61 ± 2.1	Naumov et al. (1974)	Adami and Conway (1966)
		-1218.680 ± 1.450	Robie et al. (1978)	Adami and Conway (1966)
		-1233.43 ± 2.09	Radha and Navrotsky (2013)	Adami and Conway (1966)
		-1220.05		Parker et al. (1971)
		-1232.6	Woods and Garrels (1987)	Naumov et al. (1974)
		-1219.85	Stern (2000)	Barin et al. (1977)
		-1232.6	Woods and Garrels (1987)	Helgeson et al. (1978)
		-1218.7	Woods and Garrels (1987)	Robie et al. (1978)
		-1220.1	Woods and Garrels (1987)	Wagman et al. (1982)
		-1225.77 ± 1.1		Busenberg et al. (1984)
		-1218.7 ± 1.5	Robie and Hemingway (1995)	Busenberg et al. (1984)
		-1231.4 ± 3.2	Radha and Navrotsky (2013)	Kiseleva et al. (1994), Robie et al. (1978)
		-1218.7		Robie and Hemingway (1995)
Thaumasite	$CaSiO_3 \cdot CaSO_4 \cdot CaCO_3 \bullet 15(H_2O)$	-8682.04	-	Blanc et al. (2010)
Thermonatrite	$Na_2CO_3 \bullet (H_2O)$	-1428.71		Saegusa (1950\a)
		-1428.706	Karapet'yants and Karapet'yants (1970)	Saegusa (1950\a)
		-1433.94	Karpov et al. (1968)	Bauer and Dorland (1952)

Table 2b. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Enthalpies of Formation (Continued)

Mineral Name	Formula	$\Delta H^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
		-1433.94	Karapet'yants and Karapet'yants (1970)	Bauer and Dorland (1952)
		-1428.71	Karpov et al. (1968)	Karapet'yants and Karapet'yants (1961)
		-1432.02 ± 1.3	Naumov et al. (1974)	Waterfield et al. (1968)
		-1432.0	Woods and Garrels (1987)	Naumov et al. (1974)
		-1432.0	La Iglesia and Felix (1994)	Naumov et al. (1974)
		-1429.7 ± 0.4	Robie and Hemingway (1995)	Berg and Vanderzee (1978)
		-1431.3	Woods and Garrels (1987)	Wagman et al. (1982)
		-1431.3	La Iglesia and Felix (1994)	Wagman et al. (1982)
predicted		-1426.3 ± 1.5		La Iglesia and Felix (1994)
		-1429.7	Radha and Navrotsky (2013)	Robie and Hemingway (1995)
		-1428.784		BSC (2007)
Tilleyite	$Ca_5Si_2O_7(CO_3)_2$	-6371.6	Woods and Garrels (1987)	Karpov et al. (1971)
		-6372.2 ± 5.7	Robie and Hemingway (1995)	Treiman and Essene (1983); Holland and Powell (1990)
		-6372.2		Robie and Hemingway (1995)
Tricarboaluminate	$Ca_6Al_2(CO_3)_3(OH)_{12}$•$26(H_2O)$	-16792	-	Matschei et al. (2007)
Trona	$Na_3(CO_3)(HCO_3)$•$2(H_2O)$	-2681.9		Rupert et al. (1965)
		-2684.9	Woods and Garrels (1987)	Wagman et al. (1982)
		-2682.1 ± 0.4	Robie and Hemingway (1995)	Vanderzee and Wigg (1981)
Wegscheiderite	$Na_5(HCO_3)_3CO_3$	-3984.0 ± 0.8		Robie and Hemingway (1995)
Synthetic Phases				
Na_2CO_3•$7(H_2O)$	Na_2CO_3•$7(H_2O)$	-3192.74		Saegusa (1950a)
		-3192.743	Karapet'yants and Karapet'yants (1970)	Saegusa (1950a)

Table 2b. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Enthalpies of Formation (Continued)

Mineral Name	Formula	$\Delta H^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
		-3203.35	Karpov et al. (1968)	Bauer and Dorland (1952)
		-3203.35	Karapet'yants and Karapet'yants (1970)	Bauer and Dorland (1952)
		-3192.74	Karpov et al. (1968)	Karapet'yants and Karapet'yants (1961)
		-3200.0	Woods and Garrels (1987)	Wagman et al. (1982)
		N/A		BSC (2007)
$NaHCO_3.Na_2CO_3•2(H_2O)$	$NaHCO_3.Na_2CO_3•2(H_2O)$	-2675.25	Karapet'yants and Karapet'yants (1970)	Gancy (1963)
$3NaHCO_3.Na_2CO_3$	$3NaHCO_3.Na_2CO_3$	-3986.93	Karapet'yants and Karapet'yants (1970)	Gancy (1963)
Dawsonite-K	$KAlCO_3(OH)_2$	-1714		Łodziana et al. (2011)
Trona-K	$K_2NaH(CO_3)_2•2(H_2O)$	N/A		BSC (2007)
K_2CO_3	K_2CO_3	-1138.41		Saegusa (1950b)
		-1146.1	Woods and Garrels (1987)	Latimer (1952)
		-1146.12	Latimer (1952)	Rossini et al. (1952)?
		-1146.12	Karpov et al. (1968)	Rossini et al. (1952)
		-390.91[(1)]	Karpov et al. (1968)	Karapet'yants and Karapet'yants (1961)
		-1129.30	Karapet'yants and Karapet'yants (1970)	Stull and Prophet (1965)
		-1146.12	Karapet'yants and Karapet'yants (1970)	Stull and Prophet (1965)
		-1149.76 ± 2.1	Naumov et al. (1974)	Stull and Prophet (1965), *et seq.* (-1968)
		-1149.8	Woods and Garrels (1987)	Naumov et al. (1974)
		-1151.0	Woods and Garrels (1987)	Wagman et al. (1982)

Table 2b. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Enthalpies of Formation (Continued)

Mineral Name	Formula	$\Delta H^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
		-1151.02	Meng et al. (1995)	Wagman et al. (1982)
		-1146.1	Woods and Garrels (1987)	Babushkin et al. (1985)
		−991.1 ± 2.4	Radha and Navrotsky (2013)	Kiseleva et al. (1996), Robie et al. (1978)
		-1150.18	Stern (2000)	Knacke et al. (1991)
K_2CO_3•0.5(H2O)	K_2CO_3•0.5(H_2O)	-1298.84	Karapet'yants and Karapet'yants (1970)	Karapet'yants (1959-1966)
K_2CO_3•1.5(H_2O)	K_2CO_3•1.5(H_2O)	-1604.15	Karapet'yants and Karapet'yants (1970)	Karapet'yants (1959-1966)
		N/A		BSC (2007)
$K_8H_4(CO_3)_6$•3(H_2O)	$K_8H_4(CO_3)_6$•3(H_2O)	N/A		BSC (2007)
$KNaCO_3$•6(H_2O)	$KNaCO_3$•6(H_2O)	N/A		BSC (2007)
$K_2Ca_2(CO_3)_3$	$K_2Ca_2(CO_3)_3$	- 2821.1 ± 6.4	Radha and Navrotsky (2013)	Robie et al. (1978), Navrotsky et al. (1997)
$Mg(HCO_3)_2$	$Mg(HCO_3)_2$	-1824.22 ± 62.76	Estimated value of fictive compound	Wilcox and Bromley (1963)
		-1824.22	Karapet'yants and Karapet'yants (1970)	Wilcox and Bromley (1963)
$Ca(HCO_3)_2$	$Ca(HCO_3)_2$	-1940.12	Karapet'yants and Karapet'yants (1970)	Yatsimirskii (1956)
		-1494.74 ± 62.76	Estimated value of fictive compound	Wilcox and Bromley (1963)
		-1949.74	Karapet'yants and Karapet'yants (1970)	Wilcox and Bromley (1963)

Table 2b. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Enthalpies of Formation (Continued)

Mineral Name	Formula	$\Delta H^0_{f,P_r,T_r}$ kJ	Secondary Reference	Primary Reference
Hemicarboaluminate	$3CaO.Al_2O_3.0.5CaCO_3.0.5Ca(OH)_2•10.5(H_2O)$	N/A		BSC (2007)
Hemicarboaluminate	$Ca_4Al_2(CO_3)_{0.5}(OH)_{13}•5.5(H_2O)$	-8270	-	Matschei et al. (2007)
Hemicarboaluminate	$6CaO·2Al_2O_3·CaCO_3·Ca(OH)_2•21(H_2O)$	-16600.31	-	Blanc et al. (2010)
	$3CaO·Al_2O_3·3CaCO_3•30(H_2O)$	-16217.18		Parker et al. (1971)
Monocarboaluminate	$Ca_4Al_2(CO_3)(OH)_{12}•5(H_2O)$	-8250	-	Matschei et al. (2007)
Monocarboaluminate	$3CaO·Al_2O_3·CaCO_3•10.68(H_2O)$	-8175.75	Blanc et al. (2010)	Berman and Newman (1963)
		-8175.54		Parker et al. (1971)
Monocarboaluminate	$3CaO.Al_2O_3.CaCO_3•10(H_2O)$	N/A		BSC (2007)
$Sr(HCO_3)_2$	$Sr(HCO_3)_2$	-1941.38	Karpov et al. (1968)	Yatsirmirskii (1956)
		-1941.38	Karapet'yants and Karapet'yants (1970)	Yatsimirskii (1956)
		-1953.93	Karpov et al. (1968)	Karapet'yants (1957)
		-1953.93	Karapet'yants and Karapet'yants (1970)	Karapet'yants (1957), Wilcox and Bromley (1963)
		-1953.93 ± 62.76	Estimated value of fictive compound	Wilcox and Bromley (1963)

(1) Formation from the oxides

(2) Formation with respect to $CaCO_3$ plus $MgCO_3$

Table 2c. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Entropies

Mineral Name	Formula	$S^0_{P_r,T_r}$ J K^{-1} gfw^{-1}	Secondary Reference	Primary Reference
Minerals				
Aragonite	$CaCO_3$	88.62 ± 1.26		Anderson (1934a)
		88.70 ± 1.26	Kelley and King (1961)	Anderson (1934a)
		88.70	Latimer (1952)	Rossini et al. (1952)?
		88.7	Woods and Garrels (1987)	Rossini et al. (1952)
		88.70 ± 1.26	Robie (1962, 1966)	Kelley and King (1961)
		88.70 ± 1.26	Karpov et al. (1968)	Kelley and King (1961)
		87.99 ± 0.21	Naumov et al. (1974)	Stavely and Linford (1969)
		87.99 ± 0.20	Robie et al. (1979)	Stavely and Linford (1969)
		88.0 ± 0.2	Robie and Hemingway (1995)	Stavely and Linford (1969)
		88.7	Woods and Garrels (1987)	Karpov et al. (1971)
		88.70		Parker et al. (1971)
		88.0	Woods and Garrels (1987)	Naumov et al. (1974)
		90.2	Woods and Garrels (1987)	Helgeson et al. (1978)
		88.0	Woods and Garrels (1987)	Robie et al. (1978)
		88.7	Woods and Garrels (1987)	Wagman et al. (1982)
		87.9	Woods and Garrels (1987)	Robinson et al. (1982)
		88.00		Holland and Powell (1990)
		87.99		Robie and Hemingway (1995)
		89.50		Holland and Powell (1998)
		87.93		Matas et al. (2000)
				Hummel et al. (2002)
		90.207		BSC (2007)
Artinite	$Mg_2CO_3(OH)_2$•$3(H_2O)$	259.41 ± 8.79		Langmuir (1965)
		259.41 ± 8.79	Karpov et al. (1968)	Langmuir (1965)
		232.92 ± 0.67	Robie et al. (1979)	Hemingway and Robie (1972)
		232.9 ± 0.7	Robie and Hemingway (1995)	Hemingway and Robie (1972)
		232.9	Woods and Garrels (1987)	Helgeson et al. (1978)
		232.9	Woods and Garrels (1987)	Robie et al. (1978)

Table 2c. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Entropies (Continued)

Mineral Name	Formula	$S^0_{P_r,T_r}$ J K^{-1} gfw^{-1}	Secondary Reference	Primary Reference
		232.92		BSC (2007)
Burkeite	$Na_6CO_3(SO_4)_2$	N/A		BSC (2007)
Calcite	$CaCO_3$	93.05 ± 1.67		Anderson (1934a)
		92.88 ± 0.84	Kelley and King (1961)	Anderson (1934a), Nernst and Schwers (1914), Simon and Swain (1935)
		92.88 ± 0.84	Weeks (1956)	Kelley (1950)
		92.88	Latimer (1952)	Rossini et al. (1952)?
		92.88	Zhuk (1954)	Rossini et al. (1952), Karapet'yants (1953)
		92.88	Karpov et al. (1968)	Rossini et al. (1952)
		92.9	Woods and Garrels (1987)	Rossini et al. (1952)
calculated		92.47		Zhuk (1954)
		92.47	Karpov et al. (1968)	Zhuk (1954)
		92.47	Karapet'yants and Karapet'yants (1970)	Zhuk (1954)
		84.52	Karpov et al. (1968)	Yatsimirskii and Krestov (1960)
		84.52	Karapet'yants and Karapet'yants (1970)	Yatsimirskii and Krestov (1960)
		92.88 ± 0.84	Robie (1962, 1966)	Kelley and King (1961)
		92.88 ± 0.84	Karpov et al. (1968)	Kelley and King (1961)
		91.84 ± 0.21	Naumov et al. (1974)	Stavely and Linford (1969)
		91.71 ± 0.20	Robie et al. (1979)	Stavely and Linford (1969)
		91.7 ± 0.2	Robie and Hemingway (1995)	Stavely and Linford (1969)
		92.9	Woods and Garrels (1987)	Karpov et al. (1971)
		92.88		Parker et al. (1971)
		91.7	Woods and Garrels (1987)	Naumov et al. (1974)
		92.7	Woods and Garrels (1987)	Helgeson et al. (1978)
		91.7	Woods and Garrels (1987)	Robie et al. (1978)
		92.9	Woods and Garrels (1987)	Wagman et al. (1982)
		91.8	Woods and Garrels (1987)	Robinson et al. (1982)

Table 2c. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Entropies (Continued)

Mineral Name	Formula	$S^0_{P_r,T_r}$ J K^{-1} gfw^{-1}	Secondary Reference	Primary Reference
		92.90	Stern (2000)	Barin (1993)
		91.70		Holland and Powell (1990)
		91.71		Robie and Hemingway (1995)
		92.50		Holland and Powell (1998)
		91.07		Matas et al. (2000)
				Hummel et al. (2002)
		92.676		BSC (2007)
Dawsonite	$NaAlCO_3(OH)_2$	132.00 ± 0.50	Robie et al. (1979)	Ferrante et al. (1976)
		132.0 ± 0.5	Robie and Hemingway (1995)	Ferrante et al. (1976)
		132 ± 2	Bénézeth et al. (2007)	Ferrante et al. (1976)
		132.0	Woods and Garrels (1987)	Robie et al. (1978)
		132.00		Robie and Hemingway (1995)
		131 ± 1		Bénézeth et al. (2007)
		132		BSC (2007)
Dolomite	$CaMg(CO_3)_2$	158.57		Weeks (1956)
		155.18 ± 0.29	Robie (1962)	Robie (1957)
		155.18 ± 0.29	Robie (1966)	Stout and Robie (1963)
		155.18 ± 0.42	Karpov et al. (1968)	Stout and Robie (1963)
		155.18	Karapet'yants and Karapet'yants (1970)	Stout and Robie (1963)
		155.18 ± 0.4	Naumov et al. (1974)	Stout and Robie (1963)
		155.18 ± 0.29	Robie et al. (1979)	Stout and Robie (1963)
		155.2 ± 0.3	Robie and Hemingway (1995)	Stout and Robie (1963)
		155.2	Woods and Garrels (1987)	Karpov et al. (1971)
		155.2	Woods and Garrels (1987)	Naumov et al. (1974)
		155.2 ± 0.3		Robie and Hemingway (1995)
		155.2	Woods and Garrels (1987)	Helgeson et al. (1978)
		155.2	Woods and Garrels (1987)	Robie et al. (1978)
		155.2	Woods and Garrels (1987)	Wagman et al. (1982)

Table 2c. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Entropies (Continued)

Mineral Name	Formula	$S^0_{P_r,T_r}$ J K^{-1} gfw^{-1}	Secondary Reference	Primary Reference
		155.20		Holland and Powell (1990)
		155.18		Robie and Hemingway (1995)
		156.00		Holland and Powell (1998)
		155.48		Matas et al. (2000)
				Hummel et al. (2002)
		155.18		BSC (2007)
(Gaylussite)	$CaNa_2(CO_3)_2$•5(H_2O)	363.6		Alekseev, and Barinova (1981)
Gaylussite		N/A		BSC (2007)
Huntite	$CaMg_3(CO_3)_4$	299.53 ± 0.88	Robie et al. (1979)	Hemingway and Robie (1972)
		299.5 ± 0.9	Robie and Hemingway (1995)	Hemingway and Robie (1972)
		299.5	Woods and Garrels (1987)	Robie et al. (1978)
		299.53		BSC (2007)
Hydromagnesite (I)	$3Mg(CO_3)Mg(OH)_2$•3(H_2O)	391.20 ± 9.20		Langmuir (1965)
		391.20 ± 9.20	Karpov et al. (1968)	Langmuir (1965), (reference 521a not listed)
Hydromagnesite (II)	$Mg_5(CO_3)4(OH)_2$•4(H_2O)	503.67 ± 1.55	Robie et al. (1979)	Robie and Hemingway (1972)
		503.7 ± 1.6	Robie and Hemingway (1995)	Robie and Hemingway (1972)
		541.3	Woods and Garrels (1987)	Helgeson et al. (1978)
		503.7	Woods and Garrels (1987)	Robie et al. (1978)
		541.33		BSC (2007)
Hydrotalcite-CO_3	$Mg_{0.74}Al_{0.26}(OH)_2(CO_3)_{0.13}$•0.39($H_2O$)	85.58 ± 0.17		Allada et al. (2005a)
	$Mg_4Al_2(OH)_{12}(CO_3)$•2(H_2O)	551		Lothenbach et al. (2008)
	$Mg_4Al_2(OH)_{12}(CO_3)$•2(H_2O)	552.07		Blanc et al. (2010)

Table 2c. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Entropies (Continued)

Mineral Name	Formula	$S^0_{P_r,T_r}$ J K^{-1} gfw^{-1}	Secondary Reference	Primary Reference
Ikaite	$CaCO_3$•6(H_2O)	370.0 ± 5.0	Robie and Hemingway (1995)	Marland (1975)
Kalicinite	$KHCO_3$	111.29	Karpov et al. (1968)	Saegusa (1950b)
		111.29		Latimer (1952)
estimate		111.29	Karapet'yants and Karapet'yants (1970)	Latimer (1952)
		114.22	Karapet'yants and Karapet'yants (1970)	Drozin (1961)
		109.20 ± 12.		Naumov et al. (1974)
		N/A		BSC (2007)
Lansfordite	$MgCO_3$•5(H_2O)	-117.15	Karapet'yants and Karapet'yants (1970)	Halla (1962)
		283.26 ± 14.64		Langmuir (1965)
		283.26 ± 14.64	Karpov et al. (1968)	Langmuir (1965), (reference 521a not listed)
		N/A		BSC (2007)
Magnesite *graphical*	$MgCO_3$	65.7 ± 0.8		Anderson (1934b)
c*alculated*		66.1		Anderson (1934b)
		65.69 ± 0.84	Kelley and King (1961)	Anderson (1934b)
		65.69 ± 0.84	Weeks (1956)	Kelley (1950)
		65.69	Latimer (1952)	Rossini et al. (1952)?
		65.69	Zhuk (1954)	Rossini et al. (1952), Karapet'yants (1953)
		65.69	Karpov et al. (1968)	Rossini et al. (1952)
		65.7	Woods and Garrels (1987)	Rossini et al. (1952)
		65.7	Saldi (2009)	Rossini et al. (1952)
c*alculated*		9.20		Zhuk (1954)
		70.29	Karapet'yants and Karapet'yants (1970)	Yatsimirskii and Krestov (1960)
		65.69 ± 0.84	Robie (1962, 1966)	Kelley and King (1961)
		65.69 ± 0.84	Karpov et al. (1968)	Kelley and King (1961)
		65.81 ± 1.00		Langmuir (1965)

Table 2c. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Entropies (Continued)

Mineral Name	Formula	$S^0_{P_r,T_r}$ J K^{-1} gfw^{-1}	Secondary Reference	Primary Reference
		65.81 ± 1.00	Karpov et al. (1968)	Langmuir (1965), (reference 521a not listed)
			Saldi (2009)	Langmuir (1965)
			Saldi (2009)	Robie (1965)
		65.69	Karapet'yants and Karapet'yants (1970)	Stull and Prophet (1965)
		65.69 ± 0.84	Mel'nik (1972)	Robie and Waldbaum (1968), Naumov et al. (1971)
		65.7	Saldi (2009)	Robie and Waldbaum (1968)
		65.8	Woods and Garrels (1987)	Karpov et al. (1971)
		65.69		Parker et al. (1971)
recommended value		65.69		Mel'nik (1972)
		65.7	Woods and Garrels (1987)	Mel'nik (1972)
		65.69 ± 0.8		Naumov et al. (1974)
		65.7	Woods and Garrels (1987)	Naumov et al. (1974)
			Saldi (2009)	Dandurand and Schott (1977)
		65.09 ± 0.14	Robie et al. (1979)	Hemingway et al. (1977)
		65.1 ± 0.1	Robie and Hemingway (1995)	Hemingway et al. (1977)
			Saldi (2009)	Hemingway et al. (1977)
		65.7	Woods and Garrels (1987)	Helgeson et al. (1978)
			Saldi (2009)	Helgeson et al. (1978)
		65.1	Woods and Garrels (1987)	Robie et al. (1978)
		65.09	Saldi (2009)	Robie et al. (1978)
			Saldi (2009)	Sadiq and Lindsay (1979)
		65.7	Woods and Garrels (1987)	Wagman et al. (1982)
		65.7	Saldi (2009)	Wagman et al. (1982)
			Saldi (2009)	Kittrick and Peryea (1986)
		65.210	Saldi (2009)	Berman (1988)
		65.09	Saldi (2009)	Chernosky and Berman (1989)
		65.21	Saldi (2009)	Trommsdorff and Connolly (1990)
		65.10		Holland and Powell (1990)

Table 2c. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Entropies (Continued)

Mineral Name	Formula	$S^0_{P_r,T_r}$ J K^{-1} gfw^{-1}	Secondary Reference	Primary Reference
		65.10	Saldi (2009)	Holland and Powell (1990)
		65.70	Stern (2000)	Knacke et al. (1991)
		65.09	Saldi (2009)	Koziol and Newton (1995)
		65.09		Robie and Hemingway (1995)
		65.1 ± 0.1	Saldi (2009)	Robie and Hemingway (1995)
		65.10		Holland and Powell (1998)
			Saldi (2009)	Konigsberger et al. (1999)
		64.95		Matas et al. (2000)
				Hummel et al. (2002)
		64.8 ± 2.0		Saldi (2009)
		65.689		BSC (2007)
Meionite	$Ca_4Al_6Si_6O_24CO_3$	691.4	Woods and Garrels (1987)	Robinson et al. (1982)
Al/Si ordered		715.2 ± 1.0	Robie and Hemingway (1995)	Moecher and Essene (1990)
Al/Si ordered		715.2		Robie and Hemingway (1995)
Monohydrocalcite	$CaCO_3$•(H_2O)	131.1 ± 3.0	Robie and Hemingway (1995)	Hull and Turnbull (1973)
		129.853		BSC (2007)
Nahcolite	$NaHCO_3$	102.09 ± 1.67	Kelley and King (1961)	Anderson (1933)
		155.23	Karapet'yants and Karapet'yants (1970)	Latimer (1952)
		102.09	Latimer (1952)	Rossini et al. (1952)?
		102.09	Karpov et al. (1968)	Rossini et al. (1952)
		102.1	Woods and Garrels (1987)	Rossini et al. (1952)
		102.09 ± 1.7	Naumov et al. (1974)	Kelley and King (1961)
		102.1	Woods and Garrels (1987)	Naumov et al. (1974)
		102.1 ± 1.7	Robie and Hemingway (1995)	Berg and Vanderzee (1978)
		101.7	Woods and Garrels (1987)	Wagman et al. (1982)
		102.09		BSC (2007)

Table 2c. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Entropies (Continued)

Mineral Name	Formula	$S^0_{P_r,T_r}$ J K^{-1} gfw^{-1}	Secondary Reference	Primary Reference
Natrite	Na_2CO_3	135.98 ± 2.51	Kelley and King (1961)	Anderson (1933)
		136.82		Saegusa (1950a)
		136.82	Karapet'yants and Karapet'yants (1970)	Saegusa (1950a)
		135.98	Karpov et al. (1968)	Bauer and Dorland (1952)
		135.98	Karapet'yants and Karapet'yants (1970)	Bauer and Dorland (1952), Kelley and King (1961)
estimate		135.98		Latimer (1952)
		135.98	Karpov et al. (1968)	Latimer (1952)
		135.98	Karapet'yants and Karapet'yants (1970)	Latimer (1952)
		136.0	Woods and Garrels (1987)	Rossini et al. (1952)
		123.85	Karpov et al. (1968)	Yatsimirskii (1960)
		123.85	Karapet'yants and Karapet'yants (1970)	Yatsimirskii and Krestov (1960)
		136.82	Karpov et al. (1968)	Karapet'yants and Karapet'yants (1961)
		135.98 ± 2.51	Karpov et al. (1968)	Kelley and King (1961)
		134.98 ± 0.4	Naumov et al. (1974)	Thompson et al. (1962)
		136.40	Karapet'yants and Karapet'yants (1970)	Stull and Prophet (1965)
		135.0 ± 0.6	Robie and Hemingway (1995)	Waterfield et al. (1968), Berg and Vanderzee (1978)
		135.0	Woods and Garrels (1987)	Naumov et al. (1974)
		135.0	Woods and Garrels (1987)	Wagman et al. (1982)
		138.78	Stern (2000)	Knacke et al. (1991)
		134.98		BSC (2007)
Natron	Na_2CO_3•10(H_2O)	2171.08	Karapet'yants and Karapet'yants (1970)	Saegusa (1950a)
		2171.08	Karpov et al. (1968)	Karapet'yants and Karapet'yants (1961)
		564.71 ± 0.8		Naumov et al. (1974)
		564.7	Woods and Garrels (1987)	Naumov et al. (1974)
		562.7	Woods and Garrels (1987)	Wagman et al. (1982)
		562.7		BSC (2007)

Table 2c. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Entropies (Continued)

Mineral Name	Formula	$S^0_{P_r,T_r}$ J K^{-1} gfw^{-1}	Secondary Reference	Primary Reference
Nesquehonite	$MgCO_3$•3(H_2O)	196.23 ± 8.79		Langmuir (1965)
		196.23 ± 8.79	Karpov et al. (1968)	Langmuir (1965), (reference 521a not listed)
		-4.18	Karapet'yants and Karapet'yants (1970)	Halla (1962)
		195.62 ± 0.59	Robie et al. (1979)	Robie and Hemingway (1972)
		195.6 ± 0.6	Robie and Hemingway (1995)	Robie and Hemingway (1972)
		158.99 ± 33.		Naumov et al. (1974)
		159	Woods and Garrels (1987)	Naumov et al. (1974)
		195.6	Woods and Garrels (1987)	Helgeson et al. (1978)
		195.6	Woods and Garrels (1987)	Robie et al. (1978)
		195.64		BSC (2007)
(Nyerereite)	$Na_2Ca(CO_3)_2$	231.38		Alekseev, and Barinova (1981)
Pirssonite	$Na_2Ca(CO_3)_2$•2(H_2O)	268.49		Alekseev, and Barinova (1981)
		N/A		BSC (2007)
Spurrite	$Ca_5Si_2O_8CO_3$	270.8	Woods and Garrels (1987)	Karpov et al. (1971)
		331.0 ± 2.0		Robie and Hemingway (1995)
Strontianite	$SrCO_3$	97.11 ± 1.67		Anderson (1934a)
		97.07 ± 1.67	Kelley and King (1961)	Anderson (1934b)
		97.07 ± 1.7	Naumov et al. (1974)	Anderson (1934b)
		97.07 ± 1.67	Karpov et al. (1968)	Britske et al. (1949)
		97.07	Latimer (1952)	Rossini et al. (1952)?
		97.07	Zhuk (1954)	Rossini et al. (1952), Karapet'yants (1953)
		97.07	Karpov et al. (1968)	Latimer (1952)
		97.1	Woods and Garrels (1987)	Rossini et al. (1952)
		94.98	Karpov et al. (1968)	Karapet'yants (1954a)
		94.98	Karapet'yants and Karapet'yants (1970)	Karapet'yants (1954b)

Table 2c. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Entropies (Continued)

Mineral Name	Formula	$S^0_{P_r,T_r}$ J K^{-1} gfw^{-1}	Secondary Reference	Primary Reference
calculated		98.32		Zhuk (1954)
		98.32	Karpov et al. (1968)	Zhuk (1954)
		98.32	Karapet'yants and Karapet'yants (1970)	Zhuk (1954)
		99.58	Karpov et al. (1968)	Yatsimirskii (1960)
		99.58	Karapet'yants and Karapet'yants (1970)	Yatsimirskii and Krestov (1960)
		97.07 ± 1.67	Robie (1962, 1966)	Kelley and King (1961)
		97.07 ± 1.67	Robie et al. (1979)	Kelley and King (1961)
		97.07		Parker et al. (1971)
		97.1	Woods and Garrels (1987)	Naumov et al. (1974)
		97.07	Stern (2000)	Barin et al. (1977)
		97.1	Woods and Garrels (1987)	Helgeson et al. (1978)
		97.1	Woods and Garrels (1987)	Robie et al. (1978)
		97.1	Woods and Garrels (1987)	Wagman et al. (1982)
		97.2 ± 1.7	Busenberg et al. (1984)	
		97.1 ± 1.7	Robie and Hemingway (1995)	Busenberg et al. (1984)
		97.07		Robie and Hemingway (1995)
Thaumasite	$CaSiO_3 \cdot CaSO_4 \cdot CaCO_3 \bullet 15(H_2O)$		Blanc et al. (2010)	Schmidt et al. (2008)
Thermonatrite	$Na_2CO_3 \bullet (H_2O)$	476.98	Karapet'yants and Karapet'yants (1970)	Saegusa (1950a)
		393.51	Karpov et al. (1968)	Bauer and Dorland (1952)
		395.39	Karapet'yants and Karapet'yants (1970)	Bauer and Dorland (1952)
		476.98	Karpov et al. (1968)	Karapet'yants and Karapet'yants (1961)
		168.15 ± 0.4	Naumov et al. (1974)	Waterfield et al. (1968)
		168.1 ± 0.8	Robie and Hemingway (1995)	Waterfield et al. (1968), Berg and Vanderzee (1978)
		168.2	Woods and Garrels (1987)	Naumov et al. (1974)
		168.1	Woods and Garrels (1987)	Wagman et al. (1982)
		168.11		BSC (2007)

Table 2c. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Entropies (Continued)

Mineral Name	Formula	$S^0_{P_r,T_r}$ J K^{-1} gfw^{-1}	Secondary Reference	Primary Reference
Tilleyite, Calculated	$Ca_5Si_2O_7(CO_3)_2$	376.7	Woods and Garrels (1987)	Karpov et al. (1971)
		394.0 ± 4.0	Robie and Hemingway (1995)	Robie and Hemingway (1995, ref. 450)
		394.00		Robie and Hemingway (1995)
Trona	$Na_3(CO_3)(HCO_3)•2(H_2O)$	301.7 ± 4.2		Rupert et al. (1965)
		301.2	Woods and Garrels (1987)	Wagman et al. (1982)
Vaterite	$CaCO_3$			Robie and Hemingway (1995)
		93.6 ± 0.5		Wolf et al. (2000)
Wegscheiderite	$Na_5(HCO_3)_3CO_3$			Robie and Hemingway (1995)
Synthetic Phases				
$Na_2CO_3•7(H_2O)$	$Na_2CO_3•7(H_2O)$	1602.89	Karapet'yants and Karapet'yants (1970)	Saegusa (1950a)
		1602.89	Karpov et al. (1968)	Karapet'yants and Karapet'yants (1961)
		422.2	Woods and Garrels (1987)	Wagman et al. (1982)
		N/A		BSC (2007)
Trona-K	$K_2NaH(CO_3)_2•2(H_2O)$	N/A		BSC (2007)
K_2CO_3	K_2CO_3	151.04		Saegusa (1950b)
Estimate		140.58		Latimer (1952)
		140.58	Karpov et al. (1968)	Latimer (1952)
		140.6	Woods and Garrels (1987)	Latimer (1952)
		149.37	Karapet'yants and Karapet'yants (1970)	Yatsimirskii and Krestov (1960)
		151.84	Karapet'yants and Karapet'yants (1970)	Stull and Prophet (1965)
		156.32	Karapet'yants and Karapet'yants (1970)	Stull and Prophet (1965)
		155.52 ± 0.4	Naumov et al. (1974)	Stull and Prophet (1965), *et seq.* (-1968)

Table 2c. Thermodynamic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O: Entropies (Continued)

Mineral Name	Formula	$S^0_{P_r,T_r}$ J K^{-1} gfw^{-1}	Secondary Reference	Primary Reference
		149.37	Karpov et al. (1968)	Matveev et al. (1966)
		155.5	Woods and Garrels (1987)	Naumov et al. (1974)
		155.5	Woods and Garrels (1987)	Wagman et al. (1982)
		155.52	Stern (2000)	Knacke et al. (1991)
K_2CO_3•1.5(H_2O)	K_2CO_3•1.5(H_2O)	N/A		BSC (2007)
$K_8H_4(CO_3)_6$•3(H_2O)	$K_8H_4(CO_3)_6$•3(H_2O)	N/A		BSC (2007)
$KNaCO_3$•6(H_2O)	$KNaCO_3$•6(H_2O)	N/A		BSC (2007)
$MgCO_3$•2(H_2O)	$MgCO_3$•2(H_2O)	-29.29	Karapet'yants and Karapet'yants (1970)	Halla (1962)
Hemicarboaluminate	$Ca_4Al_2(CO_3)_{0.5}(OH)_{13}$•5.5 ($H_2O$)	713	-	Matschei et al. (2007)
Hemicarboaluminate	6CaO·2Al_2O_3·$CaCO_3$·Ca(OH) $_2$•21(H_2O)	1269.09	-	Blanc et al. (2010)
Hemicarboaluminate	3CaO.Al_2O_3.0.5$CaCO_3$•0.5Ca ($OH)_2$•10 5(H_2O)	N/A		BSC (2007)
Monocarboaluminate	$Ca_4Al_2(CO_3)(OH)_{12}$•5(H_2O)	657	-	Matschei et al. (2007)
Monocarboaluminate	3CaO·Al_2O_3·$CaCO_3$•10.68(H_2 O)	601.89	-	Blanc et al. (2010)
Monocarboaluminate	3CaO.Al_2O_3.$CaCO_3$•10(H_2O)	N/A		BSC (2007)
Tricarboaluminate	$Ca_6Al_2(CO_3)_3(OH)_{12}$•26($H_2O$)	1858	-	Matschei et al. (2007)

Table 3. Crystallographic Properties of Solid Carbonates in the System Na_2O-K_2O-MgO-CaO-SrO-CO_2-H_2O

	Name	Formula	Reference
	Minerals		
1	Ankerite	$CaFe^{II}_{0.6}Mg_{0.3}Mn^{2+}_{0.1}(CO_3)_2$	Gaines et al. (1997)
2	Aragonite	$CaCO_3$	Gaines et al. (1997)
3	Aragonite	$CaCO_3$	Antao and Hassan (2009)
4	Artinite	$Mg2(\mathbf{C}O_3)(OH)_2•3(H_2O)$	Gaines et al. (1997)
5	Artinite	$Mg_2(CO_3)(OH)_2•3(H_2O)$	Akao and Iwai (1977b)
6	Barringtonite	$MgCO_3•2(H_2O)$	Nashar (1965)
7	Barringtonite	$MgCO_3•2(H_2O)$	Gaines et al. (1997)
8	Baylissite	$K_2Mg(CO_3)_2•4((H_2O))$	Gaines et al. (1997)
9	Burkeite	$Na_6CO_3(SO_4)_2$	Gaines et al. (1997)
10	Burkeite	$Na_6CO_3(SO_4)_2$	Mineralogy Database (http://webmineral.com/)
11	Burkeite	$Na_6CO_3(SO_4)_2$	Guiseppetti et al. (1988). See also Shi and Rousseau (2003)

	Name	Cell Constants							Space Group	$V^{o\#}$ cm^3 gfw^{-1}
		a_o (Å)	b_o (Å)	c_o (Å)	α	β	γ	Z		
	Minerals									
1	Ankerite	4.830		16.167				3	R-3	65.626
2	Aragonite	4.959	7.968	5.741				4	Pmcn	34.152
3	Aragonite	4.96062	7.97006	5.74181				4	Pmcn	32.317
4	Artinite	16.56	3.15	6.22		99		2	C2 or C2/m	96.495
5	Artinite	16.560(5)	3.153(1)	6.231(3)		90.10(4)		2	C2/m	97.963
6	Barringtonite	9.155	6.202	6.092	94.00	95.53	108.20(?)	4	tricl	48.867
7	Barringtonite	9.156	6.206	6.092	94.0	95.5	108.7	4	P1 or P-1	48.859
8	Baylissite	12.37	6.24	6.86		114.5		2	P 2_1/a	145.09
9	Burkeite	5.167	9.215	7.055				4/3	P1 or P-1	151.76
10	Burkeite	21.15	27.63	5.16				12	Pmmm	151.32
11	Burkeite	5.170	9.217	7.058				4/3	Pmnm	151.94

[#]Calculated from cell constants, this work

	Name	Formula	Reference
12	Chlorartinite	$[Mg_2CO_3(H_2O)(OH)]Cl•(H_2O)$	Sugimoto et al. (2007)
13	Dehydrated chlorartinite	$[Mg_2CO_3(H_2O)(OH)]Cl$	Sugimoto et al. (2007)
14	Calcite	$CaCO_3$	Gaines et al. (1997)
15	Calcite	$CaCO_3$	Mineralogy Database (http://webmineral.com/)
16	Calcite	$CaCO_3$	Graf (1961)
17	Dawsonite	$NaAlCO_3(OH)_2$	Gaines et al. (1997)
18	Dawsonite	$NaAlCO_3(OH)_2$	Mineralogy Database (http://webmineral.com/)
19	Dawsonite	$NaAlCO_3(OH)_2$	Chinh et al. (1987)
20	Dawsonite	$NaAlCO_3(OH)_2$	Łodziana et al. (2011)
21	Dolomite (ord)	$CaMg(CO_3)_2$	Gaines et al. (1997)
22	Dolomite (ord)	$CaMg(CO_3)_2$	Mineralogy Database (http://webmineral.com/)
23	Dolomite (ord)	$CaMg(CO_3)_2$	Graf (1961)

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o (Å)	b_o (Å)	c_o (Å)	α	β	γ	Z		
12	Chlorartinite	23.14422 (16)		7.22333(5)				18	R3c	112.11
13	Dehydrated chlorartinite	22.6791**(5)**		7.22336(14)				18	R3c	107.65
14	Calcite	4.9896		17.061				6	R3c	36.920
15	Calcite	4.989		17.062				6	R3c	36.914
16	Calcite	4.9900		17.0615				6	R3c	36.927
17	Dawsonite	6.71	10.411	5.58				4	Imam	58.687
18	Dawsonite	6.73	10.36	5.575				4	Imam	58.512
19	Dawsonite	6.762	10.428	5.593				4	I2cm	59.376
20	Dawsonite	6.709	5.599	10.494				4	Imma	59.347
21	Dolomite (ord)	4.8069		16.0034				3	R-3	64.284
22	Dolomite (ord)	4.842		15.95				3	R-3	65.009
23	Dolomite (ord)	4.8079		16.010				3	R-3	64.337

[#]Calculated from cell constants, this work

	Name	Formula	Reference
24	Dypingite	$Mg_5(CO_3)_4(OH)_2•5(H_2O)$	Gaines et al. (1997)
25	Dypingite	$Mg_5(CO_3)_4(OH)_2•5(H_2O)$	Raade (1970), Canterford et al. (1984)
26	Dypingite	$Mg_5(CO_3)_4(OH)_2•5(H_2O)$	Ballirano et al. (2013)
27	Dypingite	$Mg_5(CO_3)_4(OH)_2•5(H_2O)$	Ballirano et al. (2013)
28	Dypingite	$Mg_5(CO_3)_4(OH)_2•5(H_2O)$	Ballirano et al. (2013)
29	Gaylussite	$CaNa_2(CO_3)_2•5(H_2O)$	Gaines et al. (1997)
30	Gaylussite	$CaNa_2(CO_3)_2•5(H_2O)$	Dickens and Brown (1969)
31	Giorgiosite	$Mg_5(CO_3)_4(OH)_2•6(H_2O)$	Friedel (1975), Canterford et al. (1984)
32	Huntite	$CaMg_3(CO_3)_4$	Gaines et al. (1997)
33	Huntite	$CaMg_3(CO_3)_4$	Mineralogy Database (http://webmineral.com/)
34	Huntite	$CaMg_3(CO_3)_4$	Dollase and Reeder (1986)
35	Hydromagnesite (II)	$Mg_5(CO_3)_4(OH)_2•4(H_2O)$	Gaines et al. (1997)
36	Hydromagnesite (II)	$Mg_5(CO_3)_4(OH)_2•4(H_2O)$	Akao and Iwaj (1977a)

	Name	Cell Constants							Space Group	$V^{o\#}$
		a_o (Å)	b_o (Å)	c_o (Å)	α	β	γ	Z		$cm^3\ gfw^{-1}$
24	Dypingite	32.6	23.8	9.45		?		8	monocl	?
25	Dypingite									
26	Dypingite	10.3816(7)	33.7446(16)	35.6806(14)		114.567(5)		32	monocl	213.94
27	Dypingite	10.3824(11)	33.6541(31)	35.6468(32)		114.573(9)		32	monocl	213.18
28	Dypingite	10.3369(7)	33.7934(25)	35.7059(20)		114.548(5)		32	monocl	213.52
29	Gaylussite	11.589	7.779	11.207		102.0		4	I2/a	148.78
30	Gaylussite	14.361	7.781	4.209		127.84		4	C2/c or Cc	148.93
31	Giorgiosite									
32	Huntite	9.505		7.821				3	R32	122.84
33	Huntite	9.5027		7.8212				3	R32	122.78
34	Huntite	9.5027		7.8212				3	R32	122.78
35	Hydromagnesite (II)	10.11	8.94	8.38		114.5		2	$P2_1/c$	207.53
36	Hydromagnesite (II)	10.105(5)	8.954(2)	8.378(4)		114.44(5)		2	$P2_1/c$	207.80

[#]Calculated from cell constants, this work

	Name	Formula	Reference
37	Ikaite	$CaCO_3$•6(H_2O)	Gaines et al. (1997)
38	Ikaite	$CaCO_3$•6(H_2O)	Hesse et al. (1983)
39	Kalicinite	$KHCO_3$	Mineralogy Database (http://webmineral.com/)
40	Kalicinite	$KHCO_3$	Gaines et al. (1997)
41	Kalicinite	$KHCO_3$	Kaji et al. (2003)
42	Kalicinite	$KHCO_3$	Duan (2012a)
43	Lansfordite	$MgCO_3$•5(H_2O)	Gaines et al. (1997)
44	Lansfordite	$MgCO_3$•5(H_2O)	Liu et al. (1990)
45	Magnesite	$MgCO_3$	Gaines et al. (1997)
46	Magnesite	$MgCO_3$	Mineralogy Database (http://webmineral.com/)
47	Magnesite	$MgCO_3$	Graf (1961)

	Name	Cell Constants							Space Group	$V^{o\#}$ cm^3 gfw^{-1}
		a_o (Å)	b_o (Å)	c_o (Å)	α	β	γ	Z		
37	Ikaite	8.87	8.23	11.02		110.2		4	C2/c or Cc	113.67
38	Ikaite	8.792	8.310	11.021		110.53		4	C2/c	113.53
39	Kalicinite	15.11	5.67	3.71		103.8		4	$P2_1/c$	46.473
40	Kalicinite	15.173	5.628	3.711		104.63		4	P2-1/c	46.163
41	Kalicinite	15.192	5.6290	3.7067		104.538		4	P2-1/c	46.195
42	Kalicinite	15.1725	5.6283	3.7110		104.631		4	$P12_1/a1$	46.164
43	Lansfordite	12.48	7.55	7.34		101.7		4	$P2_1/c$	101.96
44	Lansfordite	7.364	7.632	12.488		101.75		4	P2-1/c	103.45
45	Magnesite	4.633		15.013				6	R3c	28.011
46	Magnesite	4.633		15.15				6	R3c	28.266
47	Magnesite	4.6330		15.016				6	R3c	28.016

[#]Calculated from cell constants, this work

	Name	Formula	Reference
48	Meionite	$Ca_4Al_6Si_6O_{24}CO_3$	Gaines et al. (1997)
49	Meionite (Al/Si ordered)	$Ca_4Al_6Si_6O_{24}CO_3$	Antao and Hassan (2008)
50	Monohydrocalcite	$CaCO_3•(H_2O)$	Gaines et al. (1997)
51	Monohydrocalcite	$CaCO_3•(H_2O)$	Swainson (2008)
52	Nahcolite	$NaHCO_3$	Gaines et al. (1997)
53	Nahcolite	$NaHCO_3$	Sass and Scheuerman (1962)
54	Natrite	Na_2CO_3	Gaines et al. (1997)
55	Natrite	Na_2CO_3	Arakcheeva et al. (2010)
56	Natron	$Na_2CO_3•10(H_2O)$	Gaines et al. (1997)
57	Natron	$Na_2CO_3•10(H_2O)$	Taga (1969)

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o (Å)	b_o (Å)	c_o (Å)	α	β	γ	Z		
48	Meionite	12.26	12.26	7.61				2	P4/m	344.42
49	Meionite (Al/Si ordered)	12.16711	12.16711	7.575466				2	!4/m	337.67
50	Monohydrocalcite	10.566		7.573				9	$P3_112$	48.992
51	Monohydrocalcite	10.5547		7.5644				9	P3-1	48.832
52	Nahcolite	7.475	9.686	3.481		93.38		4	$P2_1/n$	37.879
53	Nahcolite	3.51(1)	9.71(1)	8.05(1)		111.85		4	P2-1/c	38.339
54	Natrite	8.906	5.238	6.045		101		4	C2 or Cm	41.676
55	Natrite	8.8818	5.235	6.0455		101.464			C2/m	41.476
56	Natron	12.83	9.026	13.44		123.0		4	Cc	196.52
57	Natron	12.83	9.026	13.44		123.0		4	Cc	196.52

[#]Calculated from cell constants, this work

	Name	Formula	Reference
58	Nesquehonite	$MgCO_3•3(H_2O)$	Gaines et al. (1997)
59	Nesquehonite	$MgCO_3•3(H_2O)$	Mineralogy Database (http://webmineral.com/)
60	Nesquehonite	$MgCO_3•3(H_2O)$	Stephan and MacGillavry (1972)
61	Nesquehonite	$MgCO_3•3(H_2O)$	Giester et al. (2000)
62	Not characterized	$(Mg_{0.92}Ca_{0.08})CO_3•3(H_2O)$	Queralt et al. (1997)
63	Pirssonite	$Na_2Ca(CO_3)_2•2(H_2O)$	Gaines et al. (1997)
64	Pirssonite	$Na_2Ca(CO_3)_2•2(H_2O)$	Dickens and Brown (1969)
65	Pokrovskite	$Mg_2(CO_3)(OH)_2•0.5(H_2O)$	Gaines et al. (1997)
66	Pokrovskite	$Mg_2(CO_3)(OH)_2$	Perchiazzi and Merlino (2006)
67	$Mg_2(CO_3)(OH)_2$	$Mg_2(CO_3)(OH)_2$	Günter and Ostwald (1977)
68	Shortite	$Ca_2Na_2(CO_3)_3$	Gaines et al. (1997)
69	Shortite	$Ca_2Na_2(CO_3)_3$	Dickens et al. (1970)

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o (Å)	b_o (Å)	c_o (Å)	α	β	γ	Z		
58	Nesquehonite	7.705	5.367	12.121		90.6		4	$P2_1/n$	75.459
59	Nesquehonite	12	5.39	7.68		90.45		4	$P2_1/n$	74.784
60	Nesquehonite	7.7053(11)	5.3673(6)	12.1212(11)		90.451(13)		4	P2-1/n	75.469
61	Nesquehonite	7.701(1)	5.365(1)	12.126(2)		90.41(1)		4	$P2_1/n$	75.425
62	Not characterized	6.063(6)	10.668(5)	6.014(4)		107.28		4?	$P2_1/n$	55.921
63	Pirssonite	11.32	20.06	6				8	Fdd2	102.56
64	Pirssonite	11.340	20.096	6.034				8	Fdd2	103.51
65	Pokrovskite	9.43	12.27	3.395		96.6		4	$P2_1/a$	58.749
66	Pokrovskite	12.2396(4)	9.3506(4)	3.1578(1)		96.445(5)		4	$P2_1/a$	54.067
67	$Mg_2(CO_3)(OH)_2$	9.34	3.15	12.18		90.		4	monocl	53.951
68	Shortite	4.961	11.03	7.12				2	Amm2	117.31
69	Shortite	4.947(1)	11.032(1)	7.108(1)				2	Amm2	116.81

[#]Calculated from cell constants, this work

	Name	Formula	Reference
70	Paraspurrite	$Ca_5Si_2O_8CO_3$	Gaines et al. (1997)
71	Spurrite	$Ca_5Si_2O_8CO_3$	Gaines et al. (1997)
72	Spurrite	$Ca_5Si_2O_8CO_3$	Grice (2005)
73	Strontianite	$SrCO_3$	Gaines et al. (1997)
74	Strontianite	$SrCO_3$	Mineralogy Database (http://webmineral.com/)
75	Strontianite	$SrCO_3$	Antao and Hassan (2009)
76	Thaumasite	$[Ca_3Si)(OH)_6•12(H_2O)](SO_4)\ (CO_3)$	Edge and Taylor (1971)
77	Thaumasite	$Ca_3Si(CO_3)(SO_4)(OH)_6•12(H_2O)$	Gaines et al. (1997)
78	Thaumasite	$CaSiO_3·CaSO_4·CaCO_3•15(H_2O)$	Blanc et al. (2010)
79	Thermonatrite	$Na_2CO_3•(H_2O)$	Gaines et al. (1997)
80	Thermonatrite	$Na_2CO_3•(H_2O)$	Wu and Brown (1975)

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o (Å)	b_o (Å)	c_o (Å)	α	β	γ	Z		
70	Paraspurrite	10.473	6.706	27.78		90.58		8	P2-1/a	146.86
71	Spurrite	10.49	6.705	14.15		101.3		4	P2-1/a	145.90
72	Spurrite	10.484	6.712	14.156		101.27		4	P2-1/a	147.08
73	Strontianite	5.090	8.358	5.997				4	Pmcn	38.410
74	Strontianite	5.107	8.414	6.029				4	Pmcn	39.004
75	Strontianite	5.107499	8.413820	6.026924				4	Pmcn	38.993
76	Thaumasite	11.030		10.396				2	$P6_3$	329.81
77	Thaumasite	11.04		10.39				2	$P6_3/m$	330.22
78	Thaumasite							2		329.40
79	Thermonatrite	10.72	5.249	6.469				4	$Pca2_1$	54.802
80	Thermonatrite	6.472	10.724	5.259				4	P2-1/ab	54.953

[#]Calculated from cell constants, this work

	Name	Formula	Reference
81	Tilleyite	$Ca_5Si_2O_7(CO_3)_2$	Gaines et al. (1997)
82	Tilleyite	$Ca_5Si_2O_7(CO_3)_2$	Mineralogy Database (http://webmineral.com/)
83	Tilleyite	$Ca_5Si_2O_7(CO_3)_2$	Grice (2005)
84	Trona	$Na_3(CO_3)(HCO_3)•2(H_2O)$	Gaines et al. (1997)
85	Trona	$Na_3(CO_3)(HCO_3)•2(H_2O)$	Mineralogy Database (http://webmineral.com/)
86	Trona	$Na_3(CO_3)(HCO_3)•2(H_2O)$	Choi and Mighell (1982)
87	Vaterite	$CaCO_3$	Gaines et al. (1997)
88	Vaterite	$CaCO_3$	Kamhi (1963)
89	Vaterite	$CaCO_3$	Wang and Becker (2009)
90	Vaterite	$CaCO_3$	Wang and Becker (2009)
91	Vaterite	$CaCO_3$	Wang and Becker (2009)
92	Wegscheiderite	$Na_5(HCO_3)_3CO_3$	Gaines et al. (1997)
93	Wegscheiderite	$Na_5(HCO_3)_3CO_3$	Fernandes et al. (1990)

	Name	Cell Constants							Space Group	$V^{o\#}$
		a_o (Å)	b_o (Å)	c_o (Å)	α	β	γ	Z		$cm^3\ gfw^{-1}$
81	Tilleyite	15.108-15.111	10.241-10.242	7.577-7.579		105.15-105.47		4	$P2_1/a$	170.36-170.20
82	Tilleyite	15.025	10.269	7.628		105.833		4	$P2_1/a$	170.47
83	Tilleyite	15.082	10.236	7.572		105.17		4	P2-1/a	169.86
84	Trona	20.362	3.481	10.291		106.48		4	I2/a	105.31
85	Trona	20.106	3.492	10.303		103.05		4	I2/a	106.10
86	Trona	20.36	3.48	10.29		106.48		4	C2/c	105.26
87	Vaterite	7.135		16.98				12	P6-3/mmc	37.569
88	Vaterite	4.13		8.49				2	P6-3/mmc	37.762
89	Vaterite	7.103		25.271				18	P1	36.942
90	Vaterite	7.103		25.249				18	P_3321	36.909
91	Vaterite	7.103		25.249				18	$P6_522$	36.909
92	Wegscheiderite	10.04	15.56	3.466	91.92	95.82	108.67	2	P-1	153.30
93	Wegscheiderite	3.4762	10.0393	15.5969	107.770	95.589	95.028	2	P-1	154.14

[#]Calculated from cell constants, this work

	Name	Formula	Reference
	Synthetic Phases		
94	$Na_2CO_3•7(H_2O)$	$Na_2CO_3•7(H_2O)$	Wagman et al. (1982)
95	Dawsonite-K	$KAlCO_3(OH)_2$	Łodziana et al. (2011)
96	Trona-K	$K_2NaH(CO_3)_2•2(H_2O)$	Harvie et al. (1984)
97	K_2CO_3	K_2CO_3	Gatehouse and Lloyd (1973)
98	K_2CO_3	K_2CO_3	Duan et al. (2011), Duan et al. (2012b)
99	$K_2CO_3•1.5(H_2O)$	$K_2CO_3•1.5(H_2O)$	Skakle et al. (2001), Duan et al. (2012c)
100	$K_8H_4(CO_3)_6•3(H_2O)$	$K_8H_4(CO_3)_6•3(H_2O)$	Harvie et al. (1984)
101	$KNaCO_3•6(H_2O)$	$KNaCO_3•6(H_2O)$	Bois et al. (1984)
102	$Mg_2(HCO_3)_3Cl•6(H_2O)$	$Mg_2(HCO_3)_3Cl•6(H_2O)$	Dinnebier and Jansen (2008)
103	$Mg_4(CO_3)_3(OH)_2•3(H_2O)$	$Mg_4(CO_3)_3(OH)_2•3(H_2O)$	
104	$Mg_5(CO_3)_4(OH)_2•8(H_2O)$	$Mg_5(CO_3)_4(OH)_2•8(H_2O)$	Suzuki and Ito (1973), Canterford et al. (1984)

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o (Å)	b_o (Å)	c_o (Å)	α	β	γ	Z		
	Synthetic Phases									
94	$Na_2CO_3•7(H_2O)$									
95	Dawsonite-K	6.619	11.631	5.722				4	Cmcm	66.321
96	Trona-K									
97	K_2CO_3	5.64(3)	9.80(4)	6.88(3)		98.8(5)		4	$P2_1/\mathbf{c}$	56.578
98	K_2CO_3	5.63961	9.8312	6.83407		98.703		4	$P12_1/\mathbf{c}1$	56.390
99	$K_2CO_3•1.5(H_2O)$	11.8175	13.7466	7.1093		120.769		8	C12/c1	74.702
100	$K_8H_4(CO_3)_6•3(H_2O)$									
101	$KNaCO_3•6(H_2O)$								$P2_1/c$	
102	$Mg_2(HCO_3)_3Cl•6(H_2O)$	8.22215(2)		39.5044(2)				6	R3c	232.14
103	$Mg_4(CO_3)_3(OH)_2•3(H_2O)$									
104	$Mg_5(CO_3)_4(OH)_2•8(H_2O)$									

[#]Calculated from cell constants, this work

	Name	Formula	Reference
105	Hemi-carboaluminate	$3CaO.Al_2O_3.0.5CaCO_3.0.5Ca(OH)_2•10(H_2O)$	Damidot et al. (1994)
106	$C_4A.1/2CO_2•12(H_2O)$	$4CaO·Al_2O_3·0.5CO_2•12(H_2O)$	Fischer and Kuzel (1982)
107	$C_4A.CO_2•11(H_2O)$	$4CaO·Al_2O_3·CO_2•11(H_2O)$	Fischer and Kuzel (1982)
108	Hydrated tetracalcium Mono-carboaluminate	$4CaO·Al_2O_3·CO_2•11(H_2O)$	Renaudin et al. (1999)
109	Hemi-carboaluminate	$Ca_4Al_2(CO_3)_{0.5}(OH)_{13}•5.5(H_2O)$	Lothenbach et al. (2008), Taylor (1992)
110	Hemi-carboaluminate	$6CaO·2Al_2O_3·CaCO_3·Ca(OH)_2•21(H_2O)$	Blanc et al. (2010), Taylor (1992)
111	Mono-carboaluminate	$3CaO.Al_2O_3.CaCO_3•10(H_2O)$	Damidot et al. (1994)
112	Mono-carboaluminate	$Ca_4Al_2(CO_3)(OH)_{12}•5(H_2O)$	Lothenbach et al. (2008), Taylor (1992)
113	Mono-carboaluminate	$3CaO·Al_2O_3·CaCO_3•10.68(H_2O)$	Blanc et al. (2010), Taylor (1992)
114	Tricarboaluminate	$Ca_6Al_2(CO_3)_3(OH)_{12}•26(H_2O)$	Lothenbach et al. (2008), Taylor (1992)
115	tetracalcium dialuminium hydroxide carbonate pentahydrate	$Ca_4Al_2(OH)_{12}CO_3•5(H_2O)$	Francois et al. (1998)

	Name	Cell Constants							Space Group	$V^{o\#}$ $cm^3\ gfw^{-1}$
		a_o (Å)	b_o (Å)	c_o (Å)	α	β	γ	Z		
105	Hemi-carboaluminate									
106	$C_4A.1/2CO_2•12(H_2O)$	5.770(1)		49.159(5)				3	R3c	284.52
107	$C_4A.CO_2•11(H_2O)$	5.781(1)	5.744(1)	7.855(1)	92.61(2)	101.96(2)	120.09(2)	1/2	triclinic	261.76
108	Hydrated tetracalcium Mono-carboaluminate	5.7422(4)	5.7444(4)	15.091(3)	92.29(1)	87.45(1)	119.47(1)	1	P-1	260.58
109	Hemi-carboaluminate									285
110	Hemi-carboaluminate									569.02
111	Mono-carboaluminate									
112	Mono-carboaluminate									262
113	Mono-carboaluminate									261.96
114	Tricarboaluminate									650
115	Tetracalcium dialuminium hydroxide carbonate pentahydrate	5.7747(14)	8.4689(11)	9.923(3)	64.77(2)	82.75(2)	81.43(2)	1	triclinic	260.77

[#]Calculated from cell constants, this work

References

Adami, L.H. and Conway, K.C. (1966). Heats and free energies of formation of anhydrous carbonates of barium, strontium, and lead (No. N-66-32390; BM-RI-6822). Bureau of Mines, Berkeley, California.

Akao, M., and Iwai, S. (1977a). The hydrogen bonding of hydromagnesite. Acta Crystallographica, B33, 1273-1275.

Akao, M., and Iwai, S. (1977b). The hydrogen bonding of artinite. Acta Crystallographica, B33, 3951-3953.

Alekseev, A.I. and Barinova, L.D. (1981). Thermodynamic parameters of double carbonate salts of the Na_2CO_3•$CaCO_3$•nH_2O type. Zhurnal Prikladnoi Khimii. 54, 1925-1928. [In Russian]

Allada, R.K., Navrotsky, A. and Boerio-Goates, J. (2005a). Thermochemistry of hydrotalcite-like phases in the MgO-Al_2O_3-CO_2-H_2O system: A determination of enthalpy, entropy, and free energy. American Mineralogist, 90, 329-335.

Allada, R.K., Pless, J.D., Nenoff, T.M and Navrotsky, A. (2005b). Thermochemistry of hydrotalcite-like phases intercalated with CO_3^{2-}, NO_3^-, Cl^-, I^-, and ReO_4^-. Chemistry of Materials, 17, 2455-2459.

Allada, R.K., Peltier, E., Navrotsky, A., Casey, W.H. Johnson, C.A., Berbeco, H.T. and Sparks, D.L. (2006). Subscribed Content Calorimetric determination of the enthalpies of formation of hydrotalcite-like solids and their use in the geochemical modeling of metals in natural waters. Clays and Clay Minerals, 54(4), 409-417.

Anderson, C.T. (1933). The Heat Capacities of Sodium Carbonate and Bicarbonate and Silver Carbonate at Low Temperatures1. Journal of the American Chemical Society, 55(9), 3621-3623.

Anderson, C.T. (1934a). The heat capacities at low temperatures of the alkaline earth carbonates. Journal of the American Chemical Society, 56(2), 340-342.

Anderson, C.T. (1934b). The heat capacities of magnesium, zinc, lead, manganese and iron carbonates at low temperatures. Journal of the American Chemical Society, 56(4), 849-851.

Antao, S.M. and Hassan I. (2008). Unusual Al-Si ordering in calcic scapolite, Me79.6, with increasing temperature. American Mineralogist, 93, 1470-1477.

Antao, S,M. and Hassan, I. (2009). The orthorhombic structure of $CaCO_3$, $SrCO_3$, $PbCO_3$ and $BaCO_3$: Linear structural trends. Canadian Mineralogist, 47, 1245-1255.

Arakcheeva, A., Bindi, L., Pattison, P., Meisser, N., Chapuis, G. and Pekov, I. (2010). The incommensurately modulated structures of natural natrite at 120 and 293 K from synchrotron X-ray data. American Mineralogist, 95, 574-581.

Babushkin, V.I., Matveyev, G.M., and Mchedlov-Petrossyan, O.P. (1985). Thermodynamics of Silicates. Springer-Verlag, Berlin, 459 p.

Backstrom, H.L.J. (1925). The heat of dissociation of calcium carbonate and the entropy of carbon dioxide. Journal of the American Chemical Society, 57, 2443-2449.

Ballirano, P., De Vito, C., Mignardi, S. and Ferrini, V. (2013). Phase transitions in the Mg-CO_2-H_2O system and the thermal decomposition of dypingite, $Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$: Implications for geosequestration of carbon dioxide. Chemical Geology, 340, 59-67.

Bär, O. (1932). Beitrag zur Thema Dolomitentstehung. Centralbl. Mineralog. Paliontologie, Abt. A, 46-62.

Barin, I., Knacke, O. and Kubaschewski, O. (1977). Thermochemical properties of inorganic substances: supplement. (vol. 380). Springer-Verlag, Berlin.

Barin, I. (1993). Thermochemical Data of Pure Substances. VCH Velagsgesellschaft, Weinheim, Germany.

Barin, I. and Platzki, G. (1995). Thermochemical Data of Pure Substances. (3rd Edition). Weinheim, Germany; New York, N.Y.

Barnes, I., and W. Back (1964). Dolomite solubility in ground water. p. D179–D180. In Art. 160, U.S. Geological Survey Professional Paper 475-D. U.S. Geological Survey, Reston, VA.

Bauer, T.W. and Dorland, R.M. (1952). Thermodynamic properties of the hydrates of sodium carbonate. A note. Canadian Journal of Chemistry, 30, 76-77.

Bellotto, M., Rebours, B., Clause, O., Lynch, J., Bazin, D. and Elkaim, E. (1996). A reexamination of hydrotalcite crystal chemistry. Journal of Physical Chemistry, 100(20), 8527-8534.

Bénézeth, P., Palmer, D.A., Anovitz, L.M. and Horita, J. (2007). Dawsonite synthesis and reevaluation of its thermodynamic properties from solubility measurements: Implications for mineral trapping of CO_2. Geochimica et Cosmochimica Acta, 71(18), 4438-4455.

Berg, R.L. and Vanderzee, C.E. (1978). Thermodynamics of carbon dioxide and carbonic acid: (a) the standard enthalpies of solution of Na_2CO_3(s), $NaHCO_3$(s), and CO_2(g) In water at 298.15 K; (b) the standard enthalpies of formation, standard Gibbs energies of formation, and standard entropies of CO_2(aq), HCO_3-(aq), $CO_3$2-(aq), $NaHCO_3$(s), Na_2CO_3(S), Na_2CO_3-H_2O(s), and Na_2CO_3.10H_2O(S). Journal of Chemical Thermodynamics, 10, 1113-1136.

Berman, R.G. (1988). Internally consistent thermodynamic data for minerals in the system Na_2O-K_2O-CaO-MgO-FeO-Fe_2O_3-Al_2O_3-SiO_2-TiO_2-H_2O-CO_2. Journal of Petrology, 29, 445-522.

Berner, R.A. (1967). Comparative dissolution characteristics of carbonate minerals in the presence and absence of aqueous magnesium ion. American Journal of Science, 265, 45-70.

Bialik, M.A., Theliander, H., Sedin, P., Verrill, C.L. and DeMartini, N. (2008). Solubility and solid-phase composition in Na_2CO_3-Na_2SO_4 solutions at boiling temperature: A modeling approach. Industrial and Engineering Chemistry Research, 47(9), 3233-3238.

Binnewies, M. and Milke, E. (1999). Thermochemical Data of Elements and Compounds. Wiley, New York, New York.

Blanc, P. Bourbon, X., Lassin, A. and Gaucher, E.C. (2010). Chemical model for cement-based materials: Thermodynamic data assessment for phases other than C-S-H. Cement and Concrete Research, 40, 1360-1374.

Bois, C., Papin, G. and Philoche-Levisalles, M. (1984). Structure cristalline de $KNaCO_3$,6H_2O. Revue de Chimie Minérale, 21(2), 152-158.

Britske, E.V., Kapustinskii, A.F., Veselovskii, B.K., Shamovskii, L.M., Chentsova, L.G. and Anvaer, B.I. (1949). Termicheskie konstanty neorganicheskikh veshchestv (Thermal Constants of Inorganic Substances). Ied-vo AN SSSR, 1010 p. [in Russian].

BSC (Bechtel SAIC Company) (2007). Qualification of Thermodynamic Data for Geochemical Modeling of Mineral–Water Interactions in Dilute Systems. ANL-WIS-GS-000003 REV 01. Las Vegas, Nevada: Bechtel SAIC Company.DOC.20070619.0007. [EQ3/6 Data0.YMP.R5 database]

Busenberg, E., Plummer, L.N., and Parker, V.B. (1984). The solubility of strontianite ($SrCO_3$,) in CO_2-H_2O solutions between 2 and 91ºC, the association constants of $SrHCO_3^+(aq)$ and $SrCO_3(aq)^0$ between 5 and 80°C, and an evaluation of the thermodynamic properties of $Sr^{2+}(aq)$ and $SrCO_3(cr)$ at 25ºC and 1 atm total pressure. Geochimica et Cosmochimica Acta, 48, 2021-2035.

Canterford, J.H., Tsambourakis, G. and Lambert, B. (1984). Some observations on the properties of dypingite, $Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$, and related minerals. Mineralogical Magazine, 48, 437-442.

Chai, L. and Navrotsky, A. (1993). Thermochemistry of carbonate-pyroxene equilibria. Contributions to Mineralogy and Petrology, 114(2), 139-147.

Chernosky, J.V. and Berman, R.G. (1989). Experimental reversal of the equilibrium: Clinochlore + 2 magnesite = 3 forsterite + spinel + 2 CO_2 + 4 H_2O and revised thermodynamic properties for magnesite. American Journal of Science, 289, 249-266.

Chinh, L.T., Pobedimskaya, E A. and Khomyakov, A P. (1987). Crystal structure of dawsonite, $NaAl(CO_3)(OH)_2$ and its first discovery in the Khibiny alkaline massiv. Vestnik Moskovskogo Universiteta Geologiya, 42, 74-77.

Choi, C.S. and Mighell, A.D. (1982). Neutron diffraction study of sodium sesquicarbonate dehydrate. Acta Crystallographica, B38, 2874-2876.

Christ, C.L. and Hostetler, P.B. (1970). Studies in the system MgO-SiO_2-CO_2-H_2O (II); the activity-product constant of magnesite. American Journal of Science, 268(5), 439-453.

Christ, C.L., Hostetler, P.B. and Siebert, R.M. (1974). Stabilities of calcite and aragonite. U.S. Geological Survey Journal of Research, 2, 175-184.

Costa, D.G., Rocha, A.B., Diniz, R., Souza, W.F., Chiaro, S.S.X. and Leitão, A.A. (2010). Structural model proposition and thermodynamic and vibrational analysis of hydrotalcite-like compounds by DFT calculations. Journal of Physical Chemistry C, 114(33), 14133-14140.

Damidot, D., Stronach, S., Kindness, A., Atkins, M. and Glasser, F.P. (1994). Thermodynamic investigation of the CaO-Al_2O_3-$CaCO_3$-H_2O closed system at 25 deg.C and influence of Na_2O. Cement and Concrete Research, 24(3), 563-572.

Dandurand J.-L. and Schott, J. (1977). Stabilite de la magnesite et de la dolomite; interpretation des resultants de mise en solution et de synthese par thermodiffusion. Bulletin de la Société française Mineral. Cristallogr., 100, 94-99.

Dickens, B. and Brown, W E. (1969). The crystal structures of $CaNa_2(CO_3)_2.5(H_2O)$, synthetic gaylussite, and $CaNa_2(CO_3)_2.2(H_2O)$, synthetic pirssonite. Inorganic Chemistry, 8, 2093-2103.

Dickens, B., Hyman, A. and Brown, W.E. (1971). Crystal structure of $Ca_2Na_2(CO_3)_3$ (shortite). Journal of Research of the National Bureau of Standards, A, 75, 129-135.

Dinnebier, R.E. and Jansen, M. (2008). The crystal structure of $[Mg_2(H_2O)_6(HCO_3)_3]^+ Cl^-$, containing a magnesium-based hetero-polycation. Zeitschrift für Naturforschung, 63b, 1347-1351

Dollase, W.A. and Reeder, R.J. (1986). Crystal structure refinement of huntite, $CaMg_3(CO_3)_4$, with X-ray powder data. American Mineralogist, 71, 163-166.

Drozin, N. (1961). Application of Berthelot's principle in calculating standard entropies of inorganic solids. Zhurnal Fizicheskoi Khimii, 35(8), 1789-1793. [In Russian].

Duan, Y., Zhang, K., Li, X. S., King, D. L., Li, B., Zhao, L., & Xiao, Y. (2014). Ab initio thermodynamic study of the CO_2 capture properties of M_2CO_3 (M= Na, K)-and $CaCO_3$-promoted MgO sorbents towards forming double salts. Aerosol and Air Quality Research, 14(2), 470-479.

Duan, Y., Zhang, B., Sorescu, D.C. and Johnson, J.K. (2011). CO_2 capture properties of *M*-C-O-H (*M* = Li, Na, K) systems: A combined density functional theory and lattice phonon dynamics study. Journal of Solid State Chemistry, 184(2), 304-311.

Duan, Y. (2012a). A first-principles density functional theory study of the electronic structural and thermodynamic properties of M_2ZrO_3 and M_2CO_3 (M= Na, K) and their capabilities for CO_2 capture. Journal of Renewable and Sustainable Energy, 4(1), 013109.

Duan, Y., Zhang, B., Sorescu, D.C., Johnson, J.K., Majzoub, E.H. and Luebke, D.R. (2012b). Density functional theory studies on the electronic, structural, phonon dynamical and thermo-stability properties of bicarbonates $MHCO_3$, M= Li, Na, K. Journal of Physics: Condensed Matter, 24(32), 325501.

Duan, Y., Luebke, D.R., Pennline, H.W., Li, B., Janik, M.J. and Halley, J.W. (2012c). Ab initio thermodynamic study of the CO_2 capture properties of potassium carbonate sesquihydrate, $K_2CO_3 \cdot 1.5H_2O$. Journal of Physical Chemistry C, 116(27), 14461-14470.

Edge, R.A. and Taylor, H.F.W. (1971). Crystal structure of thaumasite, $[Ca_3Si(OH)_6.12\ H_2O](SO_4)(CO_3)$. Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry, 27(3), 594-601.

Fernandes, N.G., Tellgren, R. and Olovsson, I. (1990). Structure and electron density of pentasodium trihydrogentetracarbonate. Acta Crystallographica, B46, 466-474.

Ferrante, M.J., Stuve, J.M. and Richardson, D.W. (1976). Thermodynamic data for synthetic dawsonite. U.S. Bureau of Mines Report of Investigations 8129, 13 p.

Fischer, R. and Kuzel, H.J. (1982). Reinvestigation of the system $C_4A.nH_2O$–$C_4A.CO_2.nH_2O$. Cement and Concrete Research, 12(4). 517-526.

François, O., Renaudin, G. and Evrard, O. (1998). A cementitious compound with composition $3CaO.Al_2O_3.CaCO_3.11H_2O$. Acta Crystallographica. Section C: Crystal Structure Communications, 54(9), 1214-1217.

Frear, G.L. and Johnston, J. (1929). The solubility of calcium carbonate (calcite) in certain aqueous solutions at 25° C. Journal of the American Chemical Society, 51(7), 2082-2093.

Frederick Jr, W.J., Shi, B., Euhus, D.D. and Rousseau, R.W. (2004). Control of soluble scale in black liquor evaporators and concentrators: Part 2. Interpretation of crystallization results. TAPPI Journal, 3(7).

Friedel, B. (1975). Synthetischer Giorgiosit. Neues Jahrbuch für Mineralogie, Monatshefte, 26, 196-208.

Gamsjäger, H., Riesen, W.F. and Schindler, F.W. (1973). Third International Conference on Thermodynamics, September 3-7, Baden bei Wien, IV, 116.

Gamsjäger, H. (1974). Wechselwirkung von Metalloxiden, -hydroxiden, -carbonaten und -sulfiden mit Wasser. Radex-Rundschau, 4, 274-285.

Gamsjäger, H. (1989). Thermodynamic aspects of dissolution reactions in the system Mg^{2+}-Ca^{2+}-CO_2-H_2O. Monograph Series on Mineral Deposits, 28, 269-285.

Gancy, A.B. (1963). Thermal decomposition of sodium sesquicarbonate. Journal of Chemical and Engineering Data, 8, 301-306.

Garrels, R.M. and Christ, C.L. (1965). Solutions, Minerals, and Equilibria. Harper and Row, New York.

Garrels, R.M., Thompson, M.E. and Siever, R. (1960). Stability of some carbonates at 25°C and 1 atmosphere total pressure. American Journal of Science, 258(6), 402-418.

Gatehouse, B.M. and Lloyd, D.J. (1973). Crystal structure of anhydrous potassium carbonate. Journal of Chemical Society, Dalton Transactions, 1, 70-72.

Gautelier, M., Schott, J. and Oelkers, E.H. (2007). An experimental study of dolomite dissolution rates at 80°C as a function of chemical affinity and solution composition. Chemical Geology, 242, 509-517.

Gerasimov, Ya.I., Krestovnikov, A.N. and Shakhov, A.S. (1966). Khimicheskaya Termodinamika v Tsvetnoi Metallurgii, Tom IV (Chemical Thermodynamics in Nonferrous Metallurgy, 4, 427 p. [In Russian].

Giester, G., Lengauer, C.L. and Rieck, B. (2000). The crystal structure of nesquehonite, $MgCO_3 \cdot 3H_2O$, from Lavrion, Greece. Mineralogy and Petrology, 70(3-4), 153-163.

Giuseppetti, G., Mazzi, F. and Tadini, C. (1988). The crystal structure of synthetic burkeite $Na_4SO_4(CO_3)_t(SO_4)_{1-t}$. Neues Jahrbuch für Mineralogie, Monatshefte, 203-221.

Glushko, V.P. et al. (1981). Thermodynamic Properties of Individual Substances, 3(1 and 2). Izdatelstvo "Nauka" Moscow. [in Russian].

Goskhimizdat. (1952). Chemical Reference, vol. 3. [In Russian]. (As cited in Zhuk, 1954).

Graf, D.L. (1961). Crystallographic tables for the rhombohedral carbonates. American Mineralogist. 46, 1283-1316.

Grice, J.D. (2005). The structure of spurrite, tilleyite and scawtite, and relationships to other silicate-carbonate minerals. Canadian Mineralogist, 43, 1489-1500.

Günter, J.R. and Oswald, H.R. (1977). Crystal structure of $Mg_2(OH)_2CO_3$, deduced from the topotactic thermal decomposition of artinite. Journal of Solid State Chemistry, 21(3), 211-215.

Haehnel, O. (1924a). Über die Löslichkeit des Calciumcarbonats in kohlensäurehaltigem Wasser unter hohen Drucken und die Eigenschaften solcher Lösungen. Journal für Praktische Chemie (Leipzig), 107, 165-176.

Haehnel, O. (1924b). Über die Löslichkeit des Magnesiumcarbonats in kohlensäurehaltigem Wasser unter höheren Kohlendioxyddrucken und über die Eigenschaften solcher Magnesiumbicarbonatlösungen. Journal für Praktische Chemie (Leipzig), 108(2), 61-74.

Haehnel, O. (1924c). Über die Löslichkeit der Carbonate des Strontiums, des Bariums und der Schwermetalle in Wasser unter hohen Kohlendioxyddrucken sowie über die Eigenschaften solcher Lösungen. Journal für Praktische Chemie (Leipzig), 108, 187-193

Halla, F. (1962). Free energy of hydration of magnesium carbonate. Zeitschrift für Physikalische Chemie (München, Germany), 32, 267-268.

Halla, F. (1962a). Zur Thermodynamik der Hydrate des Magnesiumcarbonats. Monatshefte für Chemie, 93(4), 948-951.

Halla, V.F. (1962c). The free energy of the formation of dolomite from its carbonate components. Sedimentology, 1, 191-199.

Halla, F. (1965). Thermodynamics of formation of dolomite. Journal of Physical Chemistry (1965), 69(3), 1065.

Halla, F. and Ritter, F. (1935). Eine Method zur Bestimmung der freien Energie bei Reacktionen des Typus A(s) + B(s) = AB(s) und ihre Anwendung auf das Dolomitproblem. Zeitschrift für Physikalische Chemie, A157, 63-82.

Halla, V.F. and R. Van Tassel (1965). Auflosungserscheinungen bei erdalkalikarbonaten I. (Dissolution phenomena of alkaline earth carbonates.) Radex-Rundschau, 4, 595-599.

Harvie, C.E., Moller, N. and Weare, J.H. (1984). The prediction of mineral solubilities in natural waters: The Na-K-Mg-Ca-H-CI-SO_4-OH-HCO_3-CO_3-CO_2-H_2O system to high ionic strengths at 25°C. Geochimica et Cosmochimica Acta, 48(4), 723-75.

Helgeson, H.C., Delany, J.M., Nesbitt, H.W. and Bird, D.K. (1978). Summary and critique of the thermodynamic properties of rock-forming minerals. American Journal of Science, 278A.

Helz, G.R. and Holland, H.D. (1965). The solubility and geologic occurrence of strontianite. Geochimica et Cosmochimica Acta, 29(12), 1303-1315.

Hemingway, B.S. and Robie, R.A., (1972). The heat capacities at low temperatures and entropies at 298.15 K of huntite, $CaMg_3(CO_3)_4$, and artinite, $Mg_2(OH)_2CO_3 \cdot 3H_2O$. American Mineralogist, 57, 1754-1767.

Hemingway, B.S. and Robie, R.A. (1973). A calorimetric determination of the standard enthalpies of formation of huntite, $CaMg_3(CO_3)_4$, and artinite, $Mg_2(OH)_2CO_3.3H_2O$ and their standard Gibbs free energies of formation. U.S. Geological Survey Journal of Research, 1, 535-541.

Hemingway, B.S. and Robie, R.A. (1994). Enthalpy and Gibbs energy of formation of dolomite, $CaMg(CO_3)_2$, at 298.15 K from HCI solution calorimetry. U.S. Geological Survey Open-File Report 94-575, 12 p.

Hemingway, B.S., Robie, R.A., Fisher, J.R. and Wilson, W.H. (1977). The heat capacities of gibbsite, $AI(OH)_3$, between 13 and 480 K and magnesite, $MgCO_3$, between 13 and 380 K and their standard entropies at 298.15 K, and the heat capacities of Calorimetry Conference benzoic acid between 1 2 and 316 K. U.S. Geological Survey Journal of Research, 5, 797-806.

Hemingway, B.S. and R.A. Robie (1994). Enthalpy and Gibbs energy of formation of dolomite, CaMg(CO3)2, at 298.15 K from HCl solution calorimetry. U.S. Geological Survey Open-file report 94-575. U.S. Geological Survey, Reston, VA.

Hesse, K.F., Kuppers, H., and Suess, E. (1983). Refinement of the structure of ikaite, $CaCO_3$*6(H_2O). Zeitschrift für Kristallographie, 163, 227-231.

Holland, T.J.B. and Powell, R. (1990). An enlarged and updated internally consistent thermodynamic dataset with uncertainties and correlation: the system K_2O-Na_2O-CaO-Mg0-MnO-FeO-Fe_2O_3-Al_2O_3-TiO_2-SiO_2-C-H_2-O_2. Journal of Metamorphic Geology, 8, 89-124.

Holland, T.J.B. and Powell, R. (1998). An internally consistent thermodynamic data set for phases of petrological interest. Journal of of Metamorphic Geology, 16, 309-343.

Horn, G. (1969). Löslichkeitskonstanten und freie Bildungsenthalpien von Magnesit, Brucit und Dolomit, ein Beitrag zur Bestimmung thermodynamischer Konstanten. Radex Rundschau, 1, 439-459.

Hostetler, P.B. (1970). Oral communication, April 15, 1970. As cited by Robie and Hemingway (1973).

Hsu, K.J. (1963). Solubility of dolomite and composition of Florida groundwaters. Journal of Hydrology, 1, 288-310.

Hull, H. and Turnbull, A.G. (1973). A thermochemical study of monohydrocalcite. Geochimica et Cosmochimica Acta, 37, 685-694.

Hummel, W., Berner, U., Curti, E., Pearson, F.J. and Thoenen, T. (2002). Nagra/PSI Chemical Thermodynamic Data Base 01/01. Universal Publishers/uPublish.com, Parkland, Florida. 565 p.

Jacobson, R.L. and Langmuir, D. (1974). Dissociation constants of calcite and $CaHCO_3^+$ from 0 to 50°C. Geochimica et Cosmochimica Acta, 38, 301-318.

Jantsch, G. and Zemek, F. (1949). Über die Darstellung von synthetischem, kristallisiertem Magnesiumcarbonat. Radex-Rundschau, Heft 3, 110-111.

Jensen, D.L., Boddum, J.K., Tjell, J.C. and Christensen, T.H. (2002). The solubility of rhodochrosite ($MnCO_3$) and siderite ($FeCO_3$) in anaerobic aquatic environments. Applied Geochemistry, 17(4), 503-511.

Johnson, C.A., and Glasser, F.P. (2003). Hydrotalcite-like minerals ($M_2Al(OH)_6(CO_3)_{0.5}.XH_2O$, where M = Mg, Zn, Co, Ni) in the environment: synthesis, characterization and thermodynamic stability. Clays and Clay Minerals, 51(1), 1-8.

Johnson, J.W., Oelkers, E.H. and Helgeson, H.C. (1992). SUPCRT92: A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bar and 0 to 1000°C. Computers and Geosciences,18, 899-947.

Kagi, H., Nagai, T., Loveday, J.S., Wada, C. and Parise, J.B. (2003). Pressure-induced phase transformation of kalicinite ($KHCO_3$) at 2.8 GPa and local structural changes around hydrogen atoms. American Mineralogist, 88, 1446-1451.

Kamhi, S R. (1963). On the structure of vaterite, $CaCO_3$. Acta Crystallographica, 16, 770-772.

Karapet'yants, M. Kh. (1953). Khimicheskaya Termodinamika (Chemical Thermodynamics). 2nd Edition. Goshkhimizdat. 611 p. [In Russian].

Karapet'yants, M. Kh. (1954a). Approximate method of calculation of the free energies and heats of formation of various substances. Zhurnal Fizicheskoi Khimii, 28, 353-358. [In Russian].

Karapet'yants, M.Kh. (1954b). Approximate method of calculation of entropy. Trudy Instituta - Moskovskii Khimiko-Tekhnologicheskii Institut imeni D. I. Mendeleeva, (No. 18), 27-34. [In Russian].

Karapet'yants, M. Kh. (1955). Approximate method for the calculation of the isobaric potential and heat of formation of different substances. Trudy Instituta - Moskovskii Khimiko-Tekhnologicheskii Institut imeni D. I. Mendeleeva, No. 20, p. 10-28. [In Russian].

Karapet'yants, M. Kh. (1957). Investigation of specific methods for the comparative calculation of physico-chmical properties of different substances. Author's dissertation for a degree in chemical sciences, MKhTI im D.I. Mendeleeva. [In Russian].

Karapet'yants, M. Kh. (1959-1966). Calculations carried out for inclusion in Karapet'yants and Karapet'yants (1970).

Karapet'yants, M.Kh. and Karapet'yants, M.L. (1961). Tablitsy nekotorykh termodinamicheskikh svoistv razlichnykh veshestv (Tables of certain thermodynamic Parameters of different Substances). Trudy MKhTI im D.I. Mendeleeva, vol. 34. [In Russian].

Karapet'yants, M.Kh. and Karapet'yants, M.L. (1970). Thermodynamic constants of Inorganic and Organic Compounds (trans. By J. Schmorak). Humphrey Science Publishers, Ann Arbor, Michigan. 461 p.

Kapustinsky, A.F. and Dezideryeva, I.P. (1946). The thermodynamics of strontium. Transactions of the Faraday Society, 42, 69-77.

Kapustinskii, A.F.and Stakhanova, M.S. (1954). Thermochemistry and atomic structure. VII. The study of the Group II (alkaline earth) carbonates. Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya (1954), 587-589. [In Russian]. See also Bulletin of the Academy of Sciences of the USSR, Division of Chemical Science (English Translation) (1954), 501-510.

Karpov, I.K., Kashik, S.A. and Pampura, V.D. (1968). Thermodynamic Constants for Calculations in Geochemistry and Petrology. Izdva, Nauka, 143 p. [In Russian].

Karpov, I.K., Kiseleva, I. and Letnikov, F.A. (1971). Chemical Thermodynamics in Petrology and Geochemistry. Akademii Nauka, Irkutsk, 385 p.

Kazakov, A.V., Tikhomirova, M.M and Plotnikova, V.I. (1959). The system of carbonate equilibria. International Geology Review, 1(10), 1-39.

Kelley, K.K. (1950). Contributions to the data on theoretical metallurgy, XI. The entropies of inorganic substances. U.S. Bureau of Mines Bulletin No. 477, 147 p.

Kelley, K.K. (1960). Contributions to the data on theoretical metallurgy, XIII. High-temperature, heat capacity and entropy data for the elements and inorganic compounds. U.S. Bureau of Mines Bulletin No. 584, 232 p.

Kelley, K.K. and Anderson, C.T. (1935). Theoretical metallurgy. IV. Metal carbonates-correlations and applications of thermodynamic properties. U.S. Bureau of Mines Bulletin No. 384, 73 p.

Kelley, K.K. and King. E.G. (1961). Contribution to the Data on Theoretical Metallurgy. XIV. Entropies of the Elements and Inorganic Compounds. U.S Bureau of Mines Bulletin No. 592, 149 p.

Kireev, V.A. (1964). Acid-base properties of oxides. Zhurnal Fizicheskoi Khimii, 38(8), 1881-1894. [In Russian].

Kiseleva, I.A., Navrotsky, A., Belitsky, I.A. and Fursenko, B.A. (1996). Thermochemistry of natural potassium sodium calcium leonhardite and its cation-exchanged forms. American Mineralogist, 81, 668-675.

Kiseleva, I.A., Kotelnikov, A.R., Martynov, K.V., Ogorodova, L.P. and Kabalov, J.K. (1994). Thermodynamic properties of strontianite-witherite solid solution (Sr,Ba)CO_3. Physics and Chemistry of Minerals, 21, 392-400.

Kittrick, J.A. and Peryea, F.J. (1986). Determination of the Gibbs free energy of formation of magnesite by solubility methods. Soil Science Society of America Journal, 50, 243-247.

Kline, W.D. (1929). The solubility of magnesium carbonate (nesquehonite) in water at 25° and pressures of carbon dioxide up to one atmosphere. Journal of the American Chemical Society, 51(7), 2093-2097.

Knacke, O., Kubaschewski, O. and Hesselman, K. (1991). Thermochemical Properties of Inorganic Substances. Springer Verlag, Berlin.

Ko, H.C., Ahmad, N. and Chang, Y.A. (1982). Thermodynamics of calcination of calcite. U.S. Bureau of Mines Report of Investigations 8647, 9 p.

Königsberger, E. and Gamsjäger, H. (1987). Solid-solute phase equilibrium in aqueous solution: I Solubility constant and free enthalpy of formation of huntite. Berichte der Bunsengesellschaft für Physikalische Chemie, 91, 785-790.

Königsberger, E., Schmidt, P. and Gamsjäger, H. (1992). Solid-solute phase equilibria in aqueous solution. VI. Solubilities, complex formation, and ion-interaction parameters for the system Na^+ - Mg^{2+} - ClO_4^- - CO_2 - H_2O at 25° C. Journal of Solution Chemistry, 21(12), 1195-1216.

Königsberger E., Königsberger L.-C. and Gamsjäger H. (1999). Low temperature thermodynamic model for the system Na_2CO_3-$MgCO_3$-$CaCO_3$-H_2O. Geochimica et Cosmochimica Acta, 63, 3105-3119.

Koziol, A.M. and Newton, R.C. (1995). Experimental determination of the reactions magnesite + quartz = enstatite + CO_2 and magnesite = periclase + CO_2, and enthalpies of formation of enstatite and magnesite. American Mineralogist, 80, 1252-1260.

Kramer, J.R. (1959). Correction of some earlier data on calcite and dolomite in sea water. Journal of Sedimentary Petrology, 29, 465-467.

Kubaschewski, O. and Evans, E.L. (1958). Metallurgical Thermochemistry, 3rd Edition, Pergamon Press, New York.

La Iglesia, A. and Félix, J.F. (1994). Estimation of thermodynamic properties of mineral carbonates at high and low temperatures from the sum of polyhedral contributions. Geochimica et Cosmochimica Acta, 58(19), 3983-3991.

Lander, J.J. (1951). Experimental Heat Contents of SrO, BaO, CaO, $BaCO_3$ and $SrCO_3$ at High Temperatures. Dissociation Pressures of $BaCO_3$ and $SrCO_3$. Journal of the American Chemical Society, 73(12), 5794-5797

Langmuir D. (1965). Stability of carbonates in the system MgO-CO_2-H_2O. Journal of Geology, 73(5), 730-750.

Langmuir, D. (1968). Stability of calcite based on aqueous solubility measurements. Geochimica et Cosmochimica Acta, 32, 835-851.

Langmuir, D. (1971). The geochemistry of some carbonate ground waters in central Pennsylvania. Geochimica et Cosmochimica Acta, 35, 1023-1045.

Latimer, W.M. (1952). The Oxidation States of the Elements and their Potentials in Aqueous Solutions. Second edition. Prentice Hall, New York, 392 p.

Leick, J. (1932). Über die Löslichkeit von Calciumcarbonat und Magnesiumcarbonat in kohlensäurefreien Wasser. Zeitschrift für Analytische Chemie, 87, 415-422.

Leitmeier, H. (1915). Zur Kenntnis der Carbonate: II. Neues Jahrbuch fur Mineralogie, Abteilung B., 655-700.

Lippmann, F. (1973). Sedimentary Carbonate Minerals: New York, Springer-Verlag, 228 p.

Liu, B.N., Zhou, X.T, Cui, X.S. and Tang, J.G. (1990). Synthesis of lansfordite $MgCO_3 \square 5H_2O$ and its crystal structure investigation. Science in China, Series B - Chemistry, B33(11), 1350–1356.

Liu, Q., Navrotsky, A., Jove-Colon, C.F. and Bonhomme, F. (2007). Energetics of cancrinite: Effect of salt inclusion. Microporous and Mesoporous Materials, 98, 227-233.

Łodziana, Z., Stoica, G. and Pérez-Ramírez, J. (2011). Reevaluation of the Structure and Fundamental Physical Properties of Dawsonites by DFT Studies. Inorganic Chemistry, 50(6), 2590-2598.

Lothenbach, B., Matschei, T., Möschner, G. and Glasser, F.P. (2008). Thermodynamic modelling of the effect of temperature on the hydration and porosity of Portland cement. Cement and Concrete Research, 38(1), 1-18.

Malinin S.D. (1963). An experimental investigation of the solubility of calcite and witherite under hydrothermal conditions. Geokhimiya, (7), 631-46. [In Russian]. Also in Geochemistry (English trans.), 650-667.

Malinin S.D. (1970). Application of the strong electrolyte theory to the solubility of carbonates (calcite and witherite) at high temperatures. Geokhimiya, 5, 540-551. [In Russian].

Marc, R. and Simek, A. (1913). Uber die thermische Dissoziation des Magnesiumkarbonats: Zeitschrift für anorganische Chemie, 82, 17-49.

Marland, G. (1975). The stability of $CaCO_3.6H_2O$ (ikaite). Geochimica et Cosmochimica Acta, 39, 83-91.

Matas, J., Gillet, P., Ricard, Y. and Martinez, I. (2000). Thermodynamic properties of carbonates at high pressures from vibrational modelling. European Journal of Mineralogy, 12(4), 703-720.

Matschei, T., Lothenbach, B. and Glasser, F.P. (2007). Thermodynamic properties of Portland cement hydrates in the system $CaO–Al_2O_3–SiO_2–CaSO_4–CaCO_3–H_2O$. Cement and Concrete Research, 37(10), 1379-1410

Matveev, M.A., Frenkel, B.N. and Matveev, G.M. (1966) [In Russian]. [**get trans from Karpov]**

Macphee, D.E. and Barnett, S.J. (2004). Solution properties of solids in the ettringite–thaumasite solid solution series. Cement and Concrete Research, 34, 1591-1598.

McCoy, H.N. and Smith, H.J. (1911). Equilibrium between alkali-earth carbonates, carbon dioxide and water. Journal of the American Chemical Society, 33(4), 468-473.

Meadowcroft, T.R. and Richardson, F.D. (1963). Heats of formation of some crystalline and glassy phosphates. Transactions of the Faraday Society, 59, 1564-1571.

Mel'nik, Y.P. (1972). Thermodynamic Constants for the Analysis of Conditions of Formation of Iron Ores. Naukova Dumka, Kiev, 196 p. [In Russian].

Meng, Z., Seinfeld, J.H., Saxena, P. and Kim, Y.P. (1995). Atmospheric gas-aerosol equilibrium: IV. Thermodynamics of carbonates. Aerosol Science and Technology, 23(2), 131-154.

Millero, F.J., Milne, P.J. and Thurmond, V.L. (1984). The solubility of calcite, strontianite and witherite in NaCl solutions at 25 C. Geochimica et Cosmochimica Acta, 48(5), 1141-1143.

Moecher, D.P. and Essene, E.J. (1990). Phase equilibria for calcic scapolite and implications of variable AI-Si disorder for P-T, T-X_{CO2} and a-X relations. Journal of Petrology, 31, 997-1024.

Morey, G. W. (1962). The action of water on calcite, magnesite and dolomite. American Mineralogist, 47, 1456-1460.

Morrow, D.W., B.L. Gorham, and J.N.Y. Wong (1994). Dolomite calcite equilibrium at 220 to 240°C at saturation vapor pressure: Experimental data. Geochimica et Cosmochimica Acta, 58, 169-177.

Nakayama, F.S. (1968). Calcium activity, complex and ion-pair in saturated CaCO3 solutions. Soil Science, 106, 429-434.

Nashar, B. (1965). Barringtonite–a new hydrous magnesium carbonate from Barrington Tops, New South Wales, Australia. Mineralogical Magazine and Journal of The Mineralogical Society, 34(268), 370-372.

Naumov, G.B., Ryzhenko, B.N. and Khodakovsky, I.L. (1974). Handbook of Thermodynamic Data. National Technical Information Service, 722176A, U.S. Dept. Commerce. 328 p.

Naumov, G.B., Ryzhenko, B.N., and Khodakovskii, I.L. (1971). Handbook of Thermodynamic Values. Atomizdat, Moscow. [In Russian].

Navrotsky, A. and C. Capobianco. 1987. Enthalpies of formation of dolomite and of magnesian calcites. American Mineralogist,72, 782-787.

Navrotsky, A., Putnam, R.L., Winbo, C. and Rosen, E. (1997). Thermochemistry of double carbonates in the K_2CO_3-$CaCO_3$ system. American Mineralogist. 82, 546-548.

Nernst, W. and Schwers, F. (1914). Untersuchungen über die spezifischen Warme bei tiefen Temperaturen. Sitzb. König preuss. Akad, Wiss., 355-. (Cited in Kelley and King, 1961.)

Nikolaev, V.A. and Dolivo-Dobrovolskii, V.V. (1961). *Osnovy teorii protsessov magmatizma i metamorfizma* (Fundamentals of the Theory of Processes of Magmatism and Metamorphism). Moscow. [In Russian].

Palmer, D.A. and van Eldik, R. (1983). The chemistry of metal carbonate and carbon dioxide complexes. Chemical Reviews, vol. 83, p. 651-731.

Parker V.B., Wagman D.D. and Evans W.H. (1971). Selected Values of Chemical Thermodynamic Properties. Tables for alkaline earth elements (elements 92 through 97 in the standard order of arrangement. Tech. Note 270-6, U.S. Department of Commerce, National Bureau of Standards, 106 p.

Perchiazzi, N. and Merlino, S. (2006). The malachite-rosasite group: crystal structures of glaukosphaerite and pokrovskite. European Journal of Mineralogy, 18, 787-792.

Picot, J.B., Mortha, G., Rueff, M. and Nortier, P. (2012). A thermodynamically consistent model for burkeite solubility. Chemical Engineering Science, 68(1), 383-391.

Plummer, L.N. and Busenberg, E. (1982). The solubilities of calcite, aragonite and vaterite In CO_2-H_2O solutions between 0 and 90°C, and an evaluation of the aqueous model for the system $CaCO_3$-CO_2-H_2O. Geochimica et Cosmochimica Acta, 46, 1011-1040.

Pokrovsky, O.S., and Schott, J. (2001). Kinetics and mechanism of dolomite dissolution in neutral to alkaline solutions revisited. American Journal of Science, 301, 597-626.

Queralt, I., Julia, R., Plana, F. and Bischoff, J.L. (1997). A hydrous Ca-bearing magnesium carbonate from playa lake sediments, Salines Lake, Spain. American Mineralogist, 82(7), 812-819.

Raade, G. (1970). Dypingite, a new hydrous basic carbonate of magnesium, from Norway. American Mineralogist, 55(9-10), 1457-1465.

Radha, A.V. and Navrotsky, A. (2013). Thermodynamics of carbonates. Reviews in Mineralogy and Geochemistry, 77(1), 73-121.

Renaudin, G., Francois, M. and Evrard, O. (1999). Order and disorder in the lamellar hydrated tetracalcium monocarboaluminate compound. Cement and Concrete Research, 29(1), 63–69.

Riesen, W. F. (1969). Thermodynamische Untersuchungen am Quaternären System Ca^{2+} - Mg^{2+} - CO_2 - H_2O. PhD Thesis, Universität Bern.

Robie, R.A. (1957). Unpublished Thesis, Univ. Chicago.

Robie, R.A. (1962). Thermodynamic properties of minerals. U.S. Geological Survey Open File Report TEI-816. 31 p.

Robie, R.A. (1965). Heats and free energies of formation of troilite, herzenbergite, rnagnesite, and rhodochrosite calculated from equilibrium data: U.S. Geological Survey Professional Paper 525-D, p. 65-72.

Robie, R.A. (1966). Section 20: Thermodynamic properties of minerals. Handbook of Physical Constants, Geological Society of America Memoirs, 97, 437-458.

Robie, R.A. and Hemingway, B.S. (1972). The heat capacities at low-temperatures and entropies at 298.15 K of nesquehonite, $MgCO_3.H_2O$, and hydromagnesite. American Mineralogist, 57, 1768-1781.

Robie, R.A. and Hemingway, B.S. (1973). The enthalpies of formation of nesquehonite, $MgCO_3.3H_2O$, and hydromagnesite, $5MgO.4CO_2.5H_2O$. U.S. Geological Survey Journal of Research, 1, 543-547.

Robie, R.A. and Hemingway, B.S. (1977). [Measurements on the enthalpy of formation of dolomite]. Unpublished data, cited in Robie et al. (1979)

Robie, R.A. and Hemingway, B.S. (1995). Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 Pascals) pressure and at higher temperatures. U.S. Geological Survey Bulletin No. 2131, 461 p.

Robie, R.A., and Waldbaum, D.R. (1968) Thermodynamic properties of minerals and related substances at 298.15 K (25.0ºC) and one atmosphere (1.013 bars) pressure and at higher temperatures. U.S. Geological Survey Bulletin No. 1259, 256 p.

Robie, R.A., Hemingway B.S., and Fisher J.R. (1978). Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 Pa) pressure and at higher temperatures. U.S. Geological Survey Bulletin No. 1452. U.S. Government Printing Office, Washington, DC. 456 p.

Robie, R.A., Hemingway, B.S. and Fisher, J.R. (1979). Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 Pa) pressure and at higher temperatures. U.S. Geological Survey Bulletin No. 1452. (Reprinted with corrections). U.S. Government Printing Office, Washington, DC. 456 p.

Robinson, G.R., Jr., Haas, J.L., Jr., Schafer, C.M. and Haselton, H.T., Jr. (1982).Thermodynamic and thermophysical properties of selected phases in the MgO-SiO_2-H_2O-CO_2, CaO-$A1_2O_3$-SiO_2-H_2O-CO_2, and Fe-FeO-Fe_2O_3-SiO_2 chemical systems, with special emphasis on the properties of basalts and their mineral components. U.S. Geological Survey Open File Report 83-79, 429 p.

Rock, P.A., Mandell, G.K., Casey, W.H. and Walling, E.M. (2001). Gibbs energy of formation of dolomite from electrochemical cell measurements and theoretical calculations. American Journal of Science, 301, 103-111.

Rossini, F.D., Wagman, D.D., Evans, W.H., Levine, S. and Jaffe, I. (1952). Selected values of chemical tbermodynamical properties. NBS Circular No. 500. 1268 p., Washington, D.C.

Roth, W.A. (1948). FIAT Reports of German Science 1939-1946. Inorganic Chemistry, 4, 214, (Cited by Krapet'yants ansd Karapet'yants, 1970)

Rozov, K., Berner, U., Taviot-Gueho, C., Leroux, F., Renaudin, G., Kulika, D., and Diamond, L.W. (2010). Synthesis and characterization of the LDH hydrotalcite–pyroaurite solid-solution series. Cement and Concrete Research, 40(8), 1248-1254.

Rupert, J.R., Hopkins, Jr., H.P. and Wulff, C.A. (1965). The Solution Thermochemistry of Polyvalent Electrolytes IV. Sodium Carbonate, Sodium Bicarbonate, and Trona. Journal of Physical Chemistry, 69(9), 3059-3062

Sadiq M. and Lindsay W. L. (1979). Selection of standard free energy of formation for use in soil chemistry. Colorado State Universiy Experimental Station Technical Bulletin No. 134.

Saegusa, F. (1950a). Thermodynamic studies of carbonates. II. Sodium carbonate. Science Reports, Tohoko University, 1st series, vol. 34, p. 104-111.

Saegusa, F. (1950b). Thermodynamic studies of carbonates. III. Potassium carbonate. Science Reports, Tohoko University, 1st series, vol. 34, p. 140-146.

Saldi, G. (2009). Les cinétiques de dissolution et précipitation de la magnésite aux conditions hydrothermales. Ph.D. Thesis, Université de Toulouse, 225 p.

Sangameshwar, S.R. and Barnes, H.L. (1983). Supergene processes in zinc-lead-silver sulfide ores in carbonates. Economic Geology, 78, 1379-1397.

Sass, R.L. and Scheuerman, R.F. (1962). The crystal structure of sodium bicarbonate. Acta Crystallographica, 15, 77-81.

Schindler, P., Gamsjäger, H. and Riesen, W. (1970). Chimia, 24, 32 (Cited in Gamsjäger et al., 1973.)

Schmidt, T., Lothenbach, B., Romer, M., Scrivener, K., Rentsch, D. and Figi, R. (2008). A thermodynamic and experimental study of the conditions of thaumasite formation. Cement and Concrete Research, 38, 337-349.

Schott, J. and Dandurand, J.-L. (1975). Sur la stabilite des carbonates naturels. Valeurs nouvelles des enthalpies libre de formation des phases des systemes MgO-CO_2-H_2O et CaO-MgO-CO_2. Comptes Rendus de l'Academie des Sciences de Paris, 281, Serie C, 1247-1250.

Sherman, L.A. and Barak, P. (2000). Solubility and Dissolution Kinetics of Dolomite in Ca-Mg-HCO_3/CO_3 Solutions at 25°C and 0.1 MPa Carbon Dioxide. Soil Science Society of America Journal, 64, 1959-1968.

Shi, B. and Rousseau, R.W. (2003). Structure of burkeite and a new crystalline species obtained from solutions of sodium carbonate and sodium sulfate. The Journal of Physical Chemistry B, 107(29), 6932-6937.

Simon, F. and Swain, R.C. (1935). Untersuchungen über die spezifischen Warme bei tiefen Temperaturen. Zeitschrift für Physikalische Chemie, B28, 189-198.

Skakle, J.M., Wilson, M. and Feldmann, J. (2001). Dipotassium carbonate sesquihydrate: rerefinement against new intensity data. Acta Crystallographica Section E: Structure Reports Online, 57(11), i94-i97.

Smith, R.M. and Martell, A.E. (1976). Critical Stability Constants, Volume 4, Inorganic Complexes. Plenum Press, New York.

Staveley, L.A.K. and Linford, R.G. (1969). The heat capacity and entropy of calcite and aragonite and their interpretation. Journal of Chemical Thermodynamics, 1, 1-11.

Stephan, G W, and MacGillavry, C H. (1972). The crystal structure of nesquehonite, $MgCO_3.3H_2O$. Acta Crystallographica, B28(4), 1031-1033.

Stern, K.H. (2000). High Temperature Properties and Thermal Decomposition of Inorganic Salts with Oxyanions. 256 p. CRC Press LLC, 2000 N.W. Corporate Blvd., Boca Raton Florida 33431.

Stieglitz, J. (1909). The relations of equilibrium between the carbon dioxide of the atmosphere and calcium sulphate, calcium carbonate and calcium bicarbonate in water solutions in contact with it. Carnegie Institute Publication, 107, 235-264.

Stout, J.W. and Robie, R.A. (1963). Heat capacity from 11 to 300°K. Entropy and heat of formation of dolomite. Journal Physical Chemistry, 67(11), 2248-2252.

Stull, D.R. and Prophet, H. (1965). JANAF Thermochemical Tablestull (Dow Chemical Co. Midland, MI, Thermal Research Lab.). U.S. Department of Commerce, National Bureau of Standards. Institute for Applied Technology, NSRDS-NBS 37, 1141 p.

Stull and Prophet (1965), *et seq*. (-1968). See above.

Sugimoto, K., Dinnebier, R.E. and Schlecht, T. (2006). Chlorartinite, a volcanic exhalation product also found in industrial magnesia screed. Journal of Applied Crystallography, 39, 739-744.

Sugimoto, K., Dinnebier, R.E. and Schlecht, T. (2007). Crystal structure of dehydrated chlorartinite by X-ray powder diffraction. Powder Diffraction, 22(1), 64-67.

Suzuki J. and Ito M. (1973) A new magnesium carbonate hydrate mineral, $Mg_5(CO_3)_4(OH)_2.8H_2O$, from Yoshikawa, Aichi Prefecture, Japan. Journal of Japan. Assoc. Mineral. Petrol. Econ. Geol. 68, 353-361.

Swainson, I.P. (2008). The structure of monohydrocalcite and the phase composition of the beachrock deposits of Lake Butler and Lake Fellmongery, South Australia. American Mineralogist, 93, 1014-1018.

Taga, T. (1969). Crystal structure of $Na_2CO_3.10H_2O$. Acta Crystallographica, B25, 2656-2657

Tareen, J.A.K., Fazeli, A.R., Basavalingu, B. and Bhandage, G.T. (1992). Thermodynamic data for dolomite and kutnahorite from the experimental decarbonation curves. Journal of the Geological Society of India, 40(6), 545-656.

Taylor, H.F.W. (1992). Cement Chemistry, 2nd edition, Thomas Telford, London, 459 p.

Thompson, C.J., Sinke, G.C. and Stull, D.R. (1962). Heat of formation of beryllium chloride. Journal of Chemical and Engineering Data, 7, 380-381.

Townley, R.W., Whitney, W.B. and Felsing, W.A. (1937). The solubilities of barium and strontium carbonates in aqueous solutions of some alkali chlorides. Journal of the American Chemical Society, 59, 631-633.

Treiman, A.H. and Essene, E.J. (1983). Phase equilibria in the system CaO-SiO_2-H_2O. American Journal of Science, 283-A, 97-120.

Trommsdorff, V. and Connolly, J.A.D. (1990). Constraints on phase diagram topology for the system CaO-MgO-SiO_2-CO_2-H_2O. Contributions to Mineralogy and Petrology, 104, 1-7.

Turnbull, A.G. (1973). A thermochemical study of vaterite. Geochimica et Cosmochimica Acta, 37, 1593-1601.

Vanderzee, C.E. and Wigg, D.A. (1981). The standard enthalpies of solution and formation of Wegscheider's salt: $Na_2CO_3.3NaHCO_3$(s) and of trona: $Na_2CO_3.NaHCO_3.2H_2O$(s) at 298.15 K. Journal of Chemical Thermodynamics, 13, 573-583.

Von der Borch, C.C. (1962). Sedimentary carbonate deposits of the Coorong Area-S. Australia. Unpublished Ph.D. dissertation, Adelaide University, South Australia.

Von der Borch, C.C. (1965). Wriiten communication to D. Langmuir.

Wagman, D.D., Evans, W.H., Parker, V.B., Schumm, R.H., Halow, I., Bailey, S.M., Churney, K.L. and Nuttall, R.L. (1982). The NBS Tables of Chemical Thermodynamic Properties: Selected Values for Inorganic and C1 and C2 Organic Substances in SI Units: American Chemical Society and the American Institute of Physics for the National Bureau of Standards (Journal of Physical and Chemical Reference Data, V. 11, supp. 2, 392 p.).

Walling, E.M., Rock, P.A. and Casey, W.H. (1995). The Gibbs energy of formation of huntite, $CaMg_3(CO_3)_4$, at 298 K and 1 bar from electrochemical cell measurements. American Mineralogist, 80(3), 355-360.

Wang, J. and Becker, U. (2009). Structure and carbonate orientation of vaterite ($CaCO_3$). American Mineralogist, 94, 380-386.

Waterfield, C.G., Linford, R.G., Goalby, B.B., Bates, T.R., Elyard, C.A. and Staveley, L.A.K. (1968). Thermodynamic investigation of disorder in the hydrates of sodium carbonate. Faraday Soc. Trans., 69, 868-874.

Wells, R.C. (1915). The solubility of magnesium carbonate in natural waters. Journal of the American Chemical Society, 37, 1704-1707.

Wells, L.S. and Taylor, K. (1937). Hydration of magnesia in dolomitic hydrated limes and putties. Journal of Research of the National Bureau of Standards, 19, 215-236.

Weeks, W.F. (1956). A thermochemical study of equilibrium relations during metamorphism of siliceous carbonate rocks. Journal of Geology, 64 (3), 245-270.

Wilcox. D.E. and Bromley, L.A. (1963). Computer Estimation of heat and free energy for simple inorganic compounds. Industrial and Engineering Chemistry, 55(7), 32-39.

Wolf, G., Königsberger, E., Schmidt, H.G., Königsberger, L.C. and Gamsjäger, H. (2000). Thermodynamic aspects of the vaterite-calcite phase transition. Journal of Thermal Analysis and Calorimetry, 60(2), 463-472.

Woods, T.L. and Garrels, R.M. (1987). Thermodynamic Values at Low Temperature for Natural Inorganic Materials. An Uncritical Summary. Oxford University Press. 242 p. plus references.

Wu, K K. and Brown I. D. (1975). A neutron diffraction study of Na_2CO3 $\square O\square H$Acta Crystallographica, B31, 890-892.

Yanat'eva, O.K. (1952). Solubility of dolomite in water salt solutions. Izvestiya Sektora FkhA Akademii Nauk SSSR, 20, 252-268. [In Russian].

Yanat'eva, O.K. (1954). Solubility in the system $CaCO_3$-$MgCO_3$-H_2O at different temperatures and pressures of CO_2. Doklady Akademii Nauk, SSSR, 96, 777-779. [In Russian].

Yanat'eva, O.K. and Rassonskaya, I.S. (1961). Metastable equilibriums and solid phases in the system $CaCO_3$-$MgCO_3$-H_2O. Zhurnal Neorganicheskoi Khimii, 6, 1424-1430. [In Russian].

Yatsimirskii, K.B. and Krestov, G.A. (1960). Entropy of the lattice of compounds with multiatomic ions. Zhurnal Fizicheskoi Khimii, 34, 2448-2453. [In Russian].

Yatsimirskii, K.B. (1956). The lattice energy of salts with polyatomic ions. Zhurnal Obshchei Khimii, 26, 2376-2380. [In Russian].

Yoder, C.H. and Rowand, J.P. (2006). Application of the simple salt lattice energy approximation to the solubility of minerals. American Mineralogist, 91(5-6), 747-752.

Yoder, C.H., Gotlieb, N.R. and Rowand, A.L. (2010). The relative stability of stoichiometrically related natural and synthetic double salts. American Mineralogist, 95(1), 47-51.

Zen, E. (1960). Carbonate equilibria in the open ocean and their bearing on the interpretation of ancient carbonate rocks. Geochimica et Cosmochimica Acta, 18, 57-71.

Zhuk, N.P. (1954). Thermodynamic constants of sulfates, carbonates, chromates, bromates, iodates, oxalates, and other salts slightly soluble in water. Zhurnal Fizicheskoi Khimii, 28, 1690-1697. [In Russian].

TRANSLATION EQUATION AND REACTION CONSTANT USED FOR STANDARDIZATION OF CARBONATE/BICARBONATE SPECIES

Table 1. Translation equations and reaction constants used for conversion of equations using HCO_3^- as a basis species to CO_3^{2-}.

Species or reaction data for standard state conditions, 298.15 K and 1 atm	Log K	$\Delta H^0_{R,P_r,T_r}$ kJ	Database	Source
$CO_3^{2-} + H^+ = HCO_3^-$	10.3288	-	Data0.YMP.R5	Shock and Helgeson (1988)
	10.329	-14.901	NAGRA/PSI (2001)	
	10.329	-14.899	Phreeqc (2009); Wateq4f (2005)	
	10.3268	-	Thermoddem (2009)	[not cited]

Table 2. Database References

Database	Reference
Data0.YMP.R5	BSC (Bechtel SAIC Company) (2007). Qualification of Thermodynamic Data for Geochemical Modeling of Mineral–Water Interactions in Dilute Systems. ANL-WIS-GS-000003 REV 01. Las Vegas, Nevada: Bechtel SAIC Company.DOC.20070619.0007.
NAGRA/PSI (2001)	Hummel, W., Berner, U., Curti, E., Pearson, F.J. and Thoenen, T. (2002). Nagra/PSI Chemical Thermodynamic Data Base 01/01. Universal Publishers/uPublish.com, Parkland, Florida. 565 p.
Phreeqc (2009)	USGS (2014). PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), phreeqc-2.18.3/Database/PHREEQC.DAT
Thermoddem (2009)	Blanc P., Lassin A. and Piantone P. (2007) THERMODDEM a database devoted to waste minerals. BRGM (Orléans, France). For updates: http://thermoddem.brgm.fr

Reference

Shock, E.L. and Helgeson, H.C. (1988). Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Correlation algorithms for ionic species and equation of state predictions to 5 kb and 1000 C. Geochimica et Cosmochimica Acta, 52(8), 2009-2036.