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FY11 DEVELOPMENT OF FULLY COUPLED REPOSITORY THCM SIMULATION TOOLS REPORT-THERMODYNAMIC DATABASE DEVELOPMENT, WITH EMPHASIS ON COMPLEX CLAY MINERALS -

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FY11 DEVELOPMENT OF FULLY COUPLED REPOSITORY THCM SIMULATION TOOLS REPORT

- THERMODYNAMIC DATABASE DEVELOPMENT, WITH EMPHASIS ON COMPLEX CLAY MINERALS -

Lawrence Livermore National Laboratory

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Introduction

Thermodynamic data are essential for understanding and evaluating geochemical processes, as by speciation-solubility calculations, reaction -path modeling, or reactive transport simulation. These data are required to evaluate both equilibrium states and the kinetic approach to such states (via the affinity term in rate laws). The development of thermodynamic databases for these purposes has a long history in geochemistry (e.g., Garrels and Christ, 1965; Helgeson et al., 1969; Helgeson et al., 1978, Johnson et al., 1992; Robie and Hemingway, 1995), paralleled by related and applicable work in the larger scientific community (e.g., Wagman et al., 1982, 1989; Cox et al., 1989; Barin and Platzki, 1995; Binneweis and Milke, 1999). The Yucca Mountain Project developed two qualified thermodynamic databases for to model geochemical processes, including ones involving repository components such as spent fuel. The first of the two (BSC, 2007a) was for systems containing dilute aqueous solutions only, the other (BSC, 2007b) for systems involving concentrated aqueous solutions and incorporating a model for such based on Pitzer's (1991) equations . A 25°C-only database with similarities to the latter was also developed for WIPP (cf. Xiong, 2005).

The YMP dilute systems database is widely used in the geochemistry community for a variety of applications involving rock/water interactions. It builds on the work of Prof. Helgeson and his students (see BSC, 2007a for many applicable references), and covers a significant range of temperature (25-300°C). The last version covers 86 chemical elements, 1219 aqueous species, 1156 minerals and other solids species, and 128 gas species. Many data for actinide species have been adopted from the Nuclear Energy Agency (NEA) series of volumes on actinide thermodynamics (see references given in BSC, 2007a), and the appropriate temperature extrapolations have been applied. The YMP concentrated systems database covers a smaller chemical system (40 chemical elements, 237 aqueous species, 470 minerals and other solids, and 11 gas species). It includes temperature dependence, which for many species extends to 200°C, but for others extends to 250°C, to 110°C, or is restricted to 25°C. It is based on many sources (see BSC, 2007b), but draws in particular from the work of Pabalan and Pitzer (1987) and Greenberg and Møller (1989). In addition to their other characteristics, these databases have a regulatory cachet as qualified products of the Yucca Mountain Project.

The purpose of the present task is to improve these databases for work on the Used Fuel Disposition Project and maintain some semblance of order that will support qualification in support of the development of future underground high level nuclear waste disposal. The Yucca Mountain Project was based on disposal in volcanic stuff, in a thick vadose zone in which oxidizing conditions were expected to prevail. A 50 year period of tunnel ventilation was planned to limit maximum temperature. Concentrated solutions were not originally expected at Yucca Mountain. Later concerns about dust deliquescence and evaporative concentration led to the development of the YMP concentrated solutions thermodynamic database (see BSC, 2007b). The Yucca Mountain Project design scenario was very different from those for planned repositories in other countries, which envision disposal below the water table (generally under reducing conditions) in clay, salt, granite or other hard rock, usually incorporating relatively low maximum temperature in the designs. The Used Fuel Disposition program is investigating potential disposal in mined repositories in these three rock types, plus a deep borehole option (which appears to imply in granite or other hard rock). The UFD may consider higher maximum temperatures than are presently being considered in other countries, although at present it is focusing on similar design options.

Although the Yucca Mountain Project thermodynamic databases incorporated many data of value to generic geochemistry applications, in some areas development was limited owing to the expected generally oxidizing conditions and limited maximum temperatures associated with the Yucca Mountain design scenario. Consequently, these databases need some additional development to adequately address the different design scenarios being addressed by the Used Fuel Disposition program. There is a need to address a somewhat wider range of mineralogy because of the different rock types. There is a need to fill some gaps arising due to the expectation of reducing instead of oxidizing conditions. There is also a need to address some other things that were not addressed because they were not important to Yucca Mountain. Finally, in any effort using thermodynamic data, there is the ever present factor of flaws being discovered in existing data, and the potential impact of new data reported elsewhere. Errors (and the suspicion of errors) generally come to light in the application of the data.

The following three areas are now of particular concern for thermodynamic database development under UFD:

- Data (and mixing models) for complex clays, including illites and smectites, and certain related sheet silicates
- Data for certain zeolites, particularly ones for which the data do not trace to Helgeson et al. (1978)
- Data that continue to come out of the NEA program review program
- Other new data from other sources not previously incorporated into the database (e.g., the Fe^{2+} and Fe^{3+} data recommended by Parker and Khodakovskii, 1995, which are likely to be adopted by the NEA)
- Isolated errors discovered since the termination of the YMP (example: the Gibbs energy and related calorimetric data for $NaHCO_3$(c) in the YMP concentrated systems database were found to be inaccurate in the course of a CO_2 air capture project).
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For FY2011, we are mainly addressing the complex clays issue and the few known isolated errors. The remainder of this chapter will address the work on clays, which is expected to continue into FY2012.

Improved Thermodynamic Data and Models for Clay Minerals

Clay minerals play various roles in the geologic disposal of nuclear waste [for an overview of clays from the perspective of the UFD Natural Systems department, see Chapter 4 of *Natural System Evaluation and Tool Development – FY11 Progress Report*: Wang et al., 2011]. Clay minerals are nearly ubiquitous at some level in nearly all rock types, ranging from minor alteration components in igneous rocks to major components in sedimentary rocks, notably shales and claystones. Clays may be used as components (often with modification) in an engineered repository, usually in an attempt to limit the access of water to waste containers and/or waste forms. Clays may form (or transform , potentially to other minerals) in a repository, in response to water circulation and the thermal field that decaying waste may generate.

Clay are sheet silicates that have a very wide range of chemical compositions and which exhibit complex behavior. Some clay and clay-like minerals, such as kaolinite ($Al_2Si_2O_5(OH)_4$) and pyrophyllite ($Al_2Si_4O_{10}(OH)2$) have a narrow range of chemical composition and relatively simple crystallographic structure. The more complex clays, including the illites, smectites, and vermiculites, vary considerably in chemical composition and are somewhat more complex structurally (in part due to the variable chemical composition). Complex clays (and in most instances, simple clays as well) have crystal sizes that are < 2 μm. Imaging generally requires methods like Scanning Electron Microscopy (Figure 1 shows an SEM image of smectite showing a common "wet cornflakes" appearance). Complex clay mineral crystals of 10 μm size would be considered "large"). Such small crystals correlate with high specific surface area. The small size also makes it difficult to separate natural samples from mixtures containing small grains of other minerals. Furthermore, chemical interactions may take place in different parts of a clay crystal, and at different rates. The interpretation of experimental measurement of the thermodynamic properties of complex clays is difficult because the number of variables that can affect results is generally too high to permit full control.

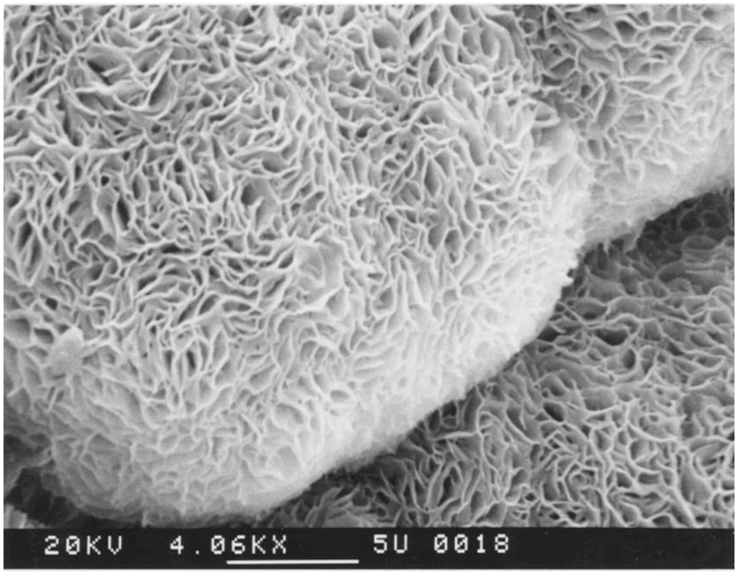

Figure 1. SEM image of smectite from Yucca Mountain Nevada (taken by Steve Chipera, Los Alamos National Laboratory).

Smectites are probably the most complex clays, as well as one of the most important types geologically. Smectites are a layered class of clay minerals that are comprised of repeating, parallel nanoscale sheets. Each framework sheet is composed of an octahedral layer of molecules that is sandwiched between two tetrahedral layers (forming a "t-o-t" structure; see Figure 2). Each tetrahedron is arranged so that a point joins the octahedral layer and a base is exposed on the outside of the t-o-t structure. The center of a tetrahedron in the t-layer is typically occupied by Si^{4+}, but Al^{3+} can substitute, leading to a net negative charge in the layer. Similar, the center of an octahedron in the o-layer is typically occupied by Al^{3+}, Mg^{2+}, Fe^{2+}, Fe^{3+}, and Li^{+}, and usually also by some vacancies. The o-layer can also develop electrical charge. Oxygen is located at the vertices of the tetrahedra and octahedra and some oxygens are shared by adjoining t- and o-layers. Minor hydrogen is tied to some oxygens. In smectites, t-o-t sheets are separated by a layer (the *interlayer*) that contains mono- and divalent cations (e.g., Na^+, Ca^{2+}) and water. In a fully hydrated smectite, the interlayer is thought to contain two layers of water molecules, or 4.5 moles H_2O per "$O_{10}(OH)_2$" in the common molar formula of smectite, where the "$(OH)_2$" is considered as containing *structural* water (cf. Ransom and Helgeson, 1993). Cations in the interlayer are easily exchanged with aqueous solution. Interlayer water can be removed by heating and other means, to the point that the interlayer becomes essentially dry.

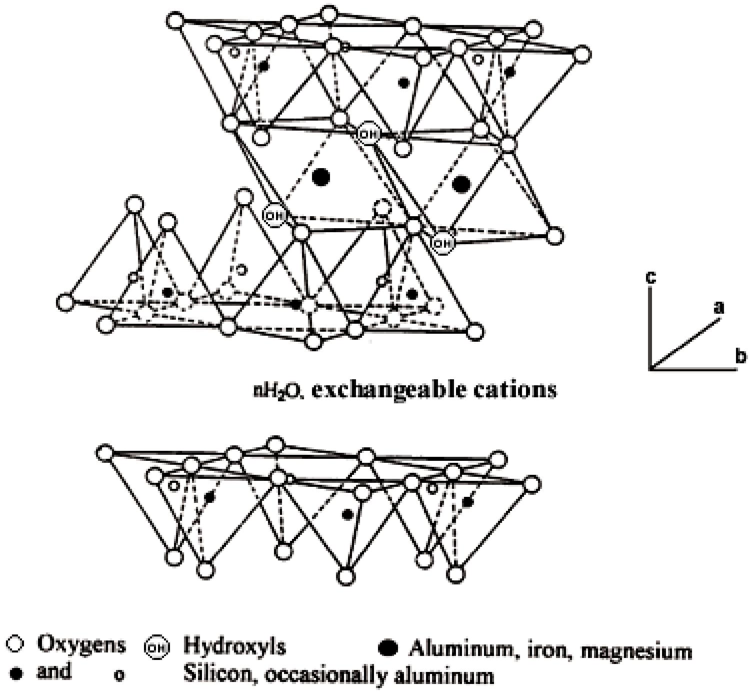

Figure 2. The crystal structure of smectite, showing a t-o-t framework layer at the top, with an interlayer shown below, with the t-layer of another t-o-t framework layer shown below that. Figure reproduced from Valenzuela Diaz and de Souza Santos (2001) under the terms of a Creative Commons Attribution License.

Smectites are generally divided into the following types:

- Beidellites, which are aluminous. The o-layer is mainly filled with Al^{3+} and vacancies in nearly 2:1 ration (little or no net electrical charge, and electrical charge is developed in the t-layer by substitution of Al^{3+} or Si^{4+}. The composition of an idealized sodium beidellite is $Na_{0.33}Al_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$.
- Nontronites, which are ferric iron rich: Like beidellites, but with Fe^{3+} replacing Al^{3+} in the o-layer. The composition of an idealized sodium nontronite is $Na_{0.33}Fe_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$.
- Saponites, which are magnesium rich: Like beidellites, but with Mg^{2+} replacing Al^{3+} in the o-layer. The composition of an idealized sodium saponite is $Na_{0.33}Mg_3Al_{0.33}Si_{3.67}O_{10}(OH)_2$.

- Montmorillonites: Unlike the above types, electrical charge in the framework is developed in the o-layer, typically by the substitution of some Mg^{2+} for Al^{3+}, while the t-layer is remains largely uncharged. The composition of an idealized sodium montmorillonite is $Na_{0.33}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2$.
- Hectorites (rare), which are lithium rich: Like montmorillonites, but with Mg^{2+} and Li^+ in the o-layer.

Ion exchange in smectites (and vermiculites, which are like smectites but have higher framework charge and higher cation exchange capacity) is rapid. However, ion exchange (and other sorptive processes) may occur not only in the interlayer, but also on the crystal edges and on the basal planes at the top and bottom of the crystal. One would like to distinguish the effects at these different loci. However, it is difficult to do so, and often the gross effect is represented by a lumped exchange constant or a distribution coefficient (K_d). Furthermore, while interactions in the interlayer and the outer clay crystal surface are relatively rapid, other reactions such as exchange of cations in the framework layer and dissolution and growth of the framework layer itself are relatively slow.

Illites can be thought of as similar to the smectites as they also have t-o-t framework layers. However, the “interlayers” have little or no water, and somewhat characteristically contain potassium ions, which tend not to easily exchange with aqueous solution. The ion exchange capacity is therefore relatively low. In general, due to common geologic occurrence in deep sedimentary basins and in geothermal systems, illites are often thought of as clays that form at higher temperatures than the smectites. However, dehydrated smectites are stable to very high temperatures as shown by dehydration experiments and experimental synthesis (to 1500°C in one study reported by Tamura et al., 2000). Other clay-like minerals such as pyrophyllite ($Al_2Si_4O_{10}(OH)_2$) and talc ($Mg_3Si_4O_{10}(OH)_2$) contain t-o-t frameworks that are electrically neutral overall and in each type of sublayer (thus no additional cations are required). These may be considered structural analogs, to a point, of smectites and illites.

Thermodynamic data and models for the complex clays (including the all-important smectites and illites) have always been problematic to geochemists. Typical experimental approaches such as solubility and calorimetry have been of limited value owing to the reactive nature of these phases and the difficulty in adequately characterizing them. Thus, models are generally used to estimate the relevant thermodynamic data from corresponding data for related phases, generally including simple clays, clay-like minerals, and other sheet silicates including various micas and chlorites. One of the best known of these is the model of Tardy and Garrels (1974), which derives data for the Gibbs energies of “silicated” oxide components from the known Gibbs energies of the related sheet silicates (kaolinite, micas, chlorites). The Gibbs energies of these “silicated” oxides are generally different from those of the corresponding real oxides, and the difference is referred to as the free energy of silication. A correlation with cation electronegativities developed by Tardy and Garrels (1974) suggests that the free energies of silication of SiO_2 and Fe_2O_3 should be nearly zero and provides one means of extending the set of treatable oxides (whether the free energy of silication should be zero or not). Estimated values for other thermodynamic properties (entropies, heat capacities, and molar volumes) can be estimated by a variety of similar “additive” or quasi-additive schemes (cf. Helgeson et al., 1978; Ransom and Helgeson, 1994a), though these tend to use the properties of the real oxides. These additional properties are needed to extrapolate the Gibbs energy with respect to temperature (entropy, heat capacity) and pressure (volume).

Tardy and Garrels (1974) developed a similar set of data for oxide components s corresponding to exchangeable cations (e.g., $Na_2O_{(ex)}$). These data are derived from ion exchange constant data. The assumption is made (see Tardy and Garrels, 1974) that the free energy of $K_2O_{(ex)}$ is the same as that for silicated K_2O. Although Tardy and Garrels (1974) offer a justification for this, it is perhaps not entirely compelling. The development of data for these exchangeable oxide components allows the method to be applied to clays with exchangeable cations, which are likely to behave distinctly from the corresponding non-exchangeable cations (or so Tardy and Garrels thought). Tardy and Garrels would have argued that using a second set of oxide components was justified because a different set of values was obtained. Using the data for exchangeable components to calculate Gibbs energies for end-member components forces a simple mixing model to be consistent with the original ion exchange data. However, a catch is that when Tardy and Garrels developed their model, they did not explicitly account for the water in the interlayer. Therefore, results from there procedure for say an idealized Na-beidellite of formula $Na_{0.33}Al_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$ would imply the interlayer water through the usage of the exchangeable oxide Na_2O_{ex}.However, this sort of treatment is not suficient if the loss or gain of interlayer water is sufficient to affect the local mass balance. Ransom and Helgeson (1993) suggest that a fully hydrated smectite would have about 4.5 H_2O of interlayer water per $O_{10}(OH)_2$ in the chemical formula (corresponding to ½ unit cell), equivalent to about 2 water layers in the interlayer.

Another factor is that if one were to extrapolate the stabilities of the exchangeable oxide components to higher temperature and pressure, one should really corresponding entropy, heat capacity, and molar volume functions. In fact, such data are difficult to come by. There is not much data on ion exchange constants for clays at temperatures other than 25°C (although we are presently searching the literature for such data).

Using schemes like the Tardy and Garrels (1974) method, one can estimate the properties of a clay mineral or other sheet silicate by stoichiometrically summing the values for the relevant oxides. For greater accuracy, such estimations may be made by using component oxide substitutions starting with a closely related phase for which real data exist, such as pyrophyllite ($Al_2Si_4O_{10}(OH)_2$). [The late Robert M. Garrels used say, "Pyrophyllite is the mother of montmorillonite" to make this point.] Another twist is to account for mixing effects, using the basic estimation methods to define the properties of end-members, and assuming (usually) ideal mixing in the site-mixing sense to define the properties of phases of intermediate composition.

The last YMP dilute systems thermodynamic database (data0.ymp.R5) contains data derived by such means for some clay compositions shown below in Table 1. A detailed description of the methods and derivation of the corresponding thermodynamic data is given in the Analysis/Model Report ANL-WIS-GS-000003 Rev. 1 (BSC, 2007a). Basically, this development follows Wolery (1978), who applied the Tardy-Garrels method but using updated values for the Gibbs energy data used to regress the values for the silicate oxides and also, in the case of subsequent calculation of equilibrium constants, updated values for the Gibbs energies of the relevant aqueous species. The later YMP work applied another level of updating. Data were obtained for five idealized beidellites, five idealized montmorillonites, five idealized saponites, five idealized nontronites, three complex smectites, an illite, and three idealized celadonites. The beidellite, montmorillonite, saponite, and nontronite data were intended to be used in solid solution models in modeling software. Some data were also obtained by the same process for some chlorite and chlorite-related sheet silicates, though these will not be noted here.

In the above derivations, the actual amount of water in the exchange layer of a smectite (beidellite, montmorillonite, saponite, nontronite, or “smectite”) was not explicitly taken into account (this water does not include the water that is structurally bound in the $(OH)_2$ part of the formula). . In deriving the data for the Na-beidellite, for example, the exchangeable sodium was represented by the $Na_2O_{(ex)}$ component. The associated water can be thought of as being dealt with implicitly, as noted previously. Interestingly, using the silicated Na_2O component instead would yield data for the dehydrated equivalent of this hydrated clay, which is something that we intend to do in future development. We note that data for exchangeable oxide components was based only on 25°C data, and that the temperature dependence of the properties of the exchangeable components was assumed to be the same as those of the corresponding non-exchangeable components. This reduces the reliability of the estimated data at elevated temperature (in particular, the stabilities of affected clays with respect to other minerals becomes more uncertain).. Also, because the water in the exchange layer is treated implicitly, dehydration cannot be properly accounted for.

Table 1. Gibbs Energy Data for 20 Idealized, Implicitly Fully Hydrated Smectite End-Members. The data shown here were derived in the YMP work described in BSC (2007a), except that the results for montmorillonites and nontronites that were originally obtained by oxide summation are here updated to correspond to the reference reactions shown here.

Name	Formula	$\Delta G_f°$, cal/mol	Reference Reaction
H-Beidellite	$H_{0.33}Al_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1260419.6	H-Beidellite = Pyrophyllite + 0.165 H_2O_{ex} + 0.165 Al_2O_3 - 0.33 SiO_2
Na-Beidellite	$Na_{0.33}Al_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1279691.6	Na-Beidellite = Pyrophyllite + 0.165 Na_2O_{ex} + 0.165 Al_2O_3 - 0.33 SiO_2
K-Beidellite	$K_{0.33}Al_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1281777.2	K-Beidellite = Pyrophyllite + 0.165 K_2O_{ex} + 0.165 Al_2O_3 - 0.33 SiO_2
Ca-Beidellite	$Ca_{0.165}Al_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1280912.6	Ca-Beidellite = Pyrophyllite + 0.165 CaO_{ex} + 0.165 Al_2O_3 - 0.33 SiO_2
Mg-Beidellite	$Mg_{0.165}Al_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1277068.1	Mg-Beidellite = Pyrophyllite + 0.165 MgO_{ex} + 0.165 Al_2O_3 - 0.33 SiO_2
H-Saponite	$H_{0.33}Mg_3Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1324610.6	H-Saponite = Talc + 0.165 H_2O_{ex} + 0.165 Al_2O_3 - 0.33 SiO_2
Na-Saponite	$Na_{0.33}Mg_3Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1343882.6	Na-Saponite = Talc + 0.165 Na_2O_{ex} + 0.165 Al_2O_3 - 0.33 SiO_2
K-Saponite	$K_{0.33}Mg_3Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1345968.2	K-Saponite = Talc + 0.165 K_2O_{ex} + 0.165 Al_2O_3 - 0.33 SiO_2
Ca-Saponite	$Ca_{0.165}Mg_3Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1345103.6	Ca-Saponite = Talc + 0.165 CaO_{ex} + 0.165 Al_2O_3 - 0.33 SiO_2
Mg-Saponite	$Mg_{0.165}Mg_3Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1341259.1	Mg-Saponite = Talc + 0.165 MgO_{ex} + 0.165 Al_2O_3 - 0.33 SiO_2
H-Montmorillonite	$H_{0.33}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2$	-1251321.9	H-Montmorillonite = Pyrophyllite + 0.165 H_2O_{ex} + 0.33 MgO - 0.165 Al_2O_3
Na-Montmorillonite	$Na_{0.33}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2$	-1270593.9	Na-Montmorillonite = Pyrophyllite + 0.165 Na_2O_{ex} + 0.33 MgO - 0.165 Al_2O_3
K-Montmorillonite	$K_{0.33}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2$	-1272679.5	K-Montmorillonite = Pyrophyllite

			+ 0.165 K_2O_{ex} + 0.33 MgO - 0.165 Al_2O_3
Ca-Montmorillonite	$Ca_{0.165}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2$	-1271814.9	Ca-Montmorillonite = Pyrophyllite + 0.165 CaO_{ex} + 0.33 MgO - 0.165 Al_2O_3
Mg-Montmorillonite	$Mg_{0.165}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2$	-1267970.4	Mg-Montmorillonite = Pyrophyllite + 0.165 MgO_{ex} + 0.33 MgO - 0.165 Al_2O_3
H-Nontronite	$H_{0.33}Fe_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1058235.0	H-Nontronite = Pyrophyllite + 0.165 H_2O_{ex} + Fe_2O_3 - Al_2O_3 + 0.165 Al_2O_3 - 0.33 SiO_2
Na-Nontronite	$Na_{0.33}Fe_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1077507.0	Na-Nontronite = Pyrophyllite + 0.165 Na_2O_{ex} + Fe_2O_3 - Al_2O_3 + 0.165 Al_2O_3 - 0.33 SiO_2
K-Nontronite	$K_{0.33}Fe_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1079592.6	K-Nontronite = Pyrophyllite + 0.165 K_2O_{ex} + Fe_2O_3 - Al_2O_3 + 0.165 Al_2O_3 - 0.33 SiO_2
Ca-Nontronite	$Ca_{0.165}Fe_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1078728.0	Ca-Nontronite = Pyrophyllite + 0.165 CaO_{ex} + Fe_2O_3 - Al_2O_3 + 0.165 Al_2O_3 - 0.33 SiO_2
Mg-Nontronite	$Ca_{0.165}Fe_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1074883.5	Mg-Nontronite = Pyrophyllite + 0.165 MgO_{ex} + Fe_2O_3 - Al_2O_3 + 0.165 Al_2O_3 - 0.33 SiO_2

Upon beginning the present work, it was realized that sufficient information was available from the previously used procedure to calculate estimates of the Gibbs free energies of the corresponding fully dehydrated forms (e.g., by using silicate Na_2O in place of exchangeable Na_2O). The results of these calculations are given in Table 2. We note that the corresponding data for entropy, heat capacity, and molar volume estimated in the YMP work (BSC, 2007a) would apply to these dehydrated forms.

Table 2. Gibbs Energy Data for 20 Idealized, Fully Dehydrated Smectite End-Members. The data shown here were derived in the present work.

Name	Formula	ΔG_f°, cal/mol	Reference Reaction
dehy-H-Beidellite	$H_{0.33}Al_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1260762.7	dehy-H-Beidellite = Pyrophyllite + 0.165 H_2O + 0.165 Al_2O_3 - 0.33 SiO_2
dehy-Na-Beidellite	$Na_{0.33}Al_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1278744.7	dehy-Na-Beidellite = Pyrophyllite + 0.165 Na_2O + 0.165 Al_2O_3 - 0.33 SiO_2
dehy-K-Beidellite	$K_{0.33}Al_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1281777.2	dehy-K-Beidellite = Pyrophyllite + 0.165 K_2O + 0.165 Al_2O_3 - 0.33 SiO_2
dehy-Ca-Beidellite	$Ca_{0.165}Al_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1278613.6	dehy-Ca-Beidellite = Pyrophyllite + 0.165 CaO + 0.165 Al_2O_3 - 0.33 SiO_2
dehy-Mg-Beidellite	$Mg_{0.165}Al_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1275634.0	dehy-Mg-Beidellite = Pyrophyllite + 0.165 MgO + 0.165 Al_2O_3 - 0.33 SiO_2
dehy-H-Saponite	$H_{0.33}Mg_3Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1324953.7	dehy-H-Saponite = Talc + 0.165 H_2O + 0.165 Al_2O_3 - 0.33 SiO_2
dehy-Na-Saponite	$Na_{0.33}Mg_3Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1342935.7	dehy-Na-Saponite = Talc + 0.165 Na_2O + 0.165 Al_2O_3 - 0.33 SiO_2
dehy-K-Saponite	$K_{0.33}Mg_3Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1345968.2	dehy-K-Saponite = Talc + 0.165 K_2O + 0.165 Al_2O_3 - 0.33 SiO_2
dehy-Ca-Saponite	$Ca_{0.165}Mg_3Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1342804.6	dehy-Ca-Saponite = Talc + 0.165 CaO + 0.165 Al_2O_3 - 0.33 SiO_2
dehy-Mg-Saponite	$Mg_{0.165}Mg_3Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1339825.0	dehy-Mg-Saponite = Talc + 0.165 MgO + 0.165 Al_2O_3 - 0.33 SiO_2
dehy-H-Montmorillonite	$H_{0.33}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2$	-1251665.0	dehy-H-Montmorillonite = Pyrophyllite + 0.165 H_2O + 0.33 MgO - 0.165 Al_2O_3
dehy-Na-Montmorillonite	$Na_{0.33}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2$	-1269647.1	dehy-Na-Montmorillonite = Pyrophyllite + 0.165 Na_2O + 0.33 MgO - 0.165 Al_2O_3
dehy-K-Montmorillonite	$K_{0.33}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2$	-1272679.5	dehy-K-Montmorillonite = Pyrophyllite + 0.165 K_2O + 0.33 MgO - 0.165 Al_2O_3
dehy-Ca-Montmorillonite	$Ca_{0.165}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2$	-1269516.0	dehy-Ca-Montmorillonite = Pyrophyllite + 0.165 CaO + 0.33 MgO - 0.165 Al_2O_3

dehy-Mg-Montmorillonite	$Mg_{0.165}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2$	-1266536.4	dehy-Mg-Montmorillonite = Pyrophyllite + 0.165 MgO + 0.33 MgO - 0.165 Al_2O_3
dehy-H-Nontronite	$H_{0.33}Fe_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1058578.1	dehy-H-Nontronite = Pyrophyllite + 0.165 H_2O + Fe_2O_3 - Al_2O_3 + 0.165 Al_2O_3 - 0.33 SiO_2
dehy-Na-Nontronite	$Na_{0.33}Fe_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1076560.2	dehy-Na-Nontronite = Pyrophyllite + 0.165 Na_2O + Fe_2O_3 - Al_2O_3 + 0.165 Al_2O_3 - 0.33 SiO_2
dehy-K-Nontronite	$K_{0.33}Fe_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1079592.6	dehy-K-Nontronite = Pyrophyllite + 0.165 K_2O + Fe_2O_3 - Al_2O_3 + 0.165 Al_2O_3 - 0.33 SiO_2
dehy-Ca-Nontronite	$Ca_{0.165}Fe_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1076429.1	dehy-Ca-Nontronite = Pyrophyllite + 0.165 CaO + Fe_2O_3 - Al_2O_3 + 0.165 Al_2O_3 - 0.33 SiO_2
dehy-Mg-Nontronite	$Ca_{0.165}Fe_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1073449.5	dehy-Mg-Nontronite = Pyrophyllite + 0.165 MgO + Fe_2O_3 - Al_2O_3 + 0.165 Al_2O_3 - 0.33 SiO_2

For future work, we intend to obtain additional data to construct more accurate estimates of the thermodynamic properties of complex clays. A literature search is underway on ion exchange data for clays, both at 25°C (in part to reduce uncertainties, in part to treat more exchangeable ions such as Sr^{2+} and Cs^{+}) and at elevated temperature. Other literature search is addressing clay dehydration and other properties. We intend to carry forward the implicitly fully hydrated model as at least a point of comparison. However, the main goal of present and future work is to develop a corresponding model that explicitly treats the interlayer water and covers states of variable hydration and which reasonably explains a wide variety of types of physical measurements, including thermogravimetry and XRD studies of dehydration, ion exchange measurements, solubilities, and swelling pressures. We also intend to work in such insight as is possible from molecular dynamics studies (e.g., Cygan et al., 2004). The goal here would be do develop data for end-member compositions such as $Na_{0.33}Al_2Al_{0.33}Si_{3.67}O_{10}(OH)_2.n\ H_2O$, where n is likely to have a maximum value between 4.5 and 7.

Ransom and Helgeson (1993, 1994ab, 1995) develop an approach to dealing with variable hydration. It has some excellent features. However, it does not extend to a complete treatment of smectite thermodynamics in that it does not develop estimates of Gibbs energies for the various end member compositions that are discussed. Rather, it only addresses Gibbs energies of dehydration between fully hydrated and dehydrated end-members of otherwise fixed composition. Also, it doesn’t cover the full range of clay mineral compositions that is desired. However, it does show a path forward to extending the Tardy-Garrels type model thus far developed. They key is to develop an interlayer H_2O component in the manner of Ransom and Helgeson (1993, 1994b). Their interlayer H_2O is developed after the “zeolitic” H_2O component proposed earlier by Helgeson et al. (1978).

Tardy and Duplay (1992) go farther than Ransom and Helgeson (papers cited above) in that they address both interlayer water and the full thermodynamic stability of end-member clay compositions. Their approach provides a counterpoint to both aspects of the model we are working to develop, and various parts of their model may simply be incorporated into ours. Papers by Viellard (1994ab, 2000) is also of interest in this regard (his 2000 paper addresses interlayer water). Vidal and Dubacq (2011) have recently proposed a model for interlayer water and full stability that is also of great interest. One of the tasks that needs to be done is to compare and evaluate these models, as they have different ranges of focus and often have implications beyond what is addressed directly. There are, for example, implications of these models to high temperature ion exchange and swelling pressure behavior that are not fully developed or explored. This is a reflection of the complexity of the topic area. There appears to have been only rather limited penetration of such models into geochemical modeling and reactive transport simulation. In fact, there seem to be few computational tools available to readily assess the consequences of these models.

In summary, this remains a work in process. We intend to improve the existing data/models for complex clays by:

- Explicitly accounting for water in the exchange layers of smectites and vermiculites
- Accounting for a broader spectrum of physical measurements (e.g., basal spacing studies of clay dehydration, swelling pressure data, ion exchange data over a wide range of temperature)
- Including insights from molecular dynamics (MD) modeling regarding dehydration (in part via informal collaboration with R. Cygan's MD modeling group at SNL).
- Developing computational tools to evaluate existing and new models.

We expect the model to evolve as the work proceeds. The model will initially be fairly simple, and will become more complex as the need is shown by testing.

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