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IMPROVEMENTS IN GEOTHERMOMETRY

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IMPROVEMENTS IN GEOTHERMOMETRY

Alkali and alkaline earth geothermometers are useful for estimating geothermal reservoir temperatures, though a general theoretical basis has yet to be established and experimental calibration needs improvement. Equilibrium cation exchange between feldspars provided the original basis for the Na-K and Na-K-Ca geothermometers (Fournier and Truesdell, 1973), but theoretical, field and experimental evidence prove that neither equilibrium nor feldspars are necessary. In this report, we summarize evidence in support of these observations, concluding that these geo-thermometers can be expected to have a surprisingly wide range of applicability, but that the reasons behind such broad applicability are not yet understood.

Early experimental work proved that water-rock interaction ares are slow at low temperatures, so experimental calibration at temperatures below 150° is impractical. Theoretical methods and field data were used instead for all work at low temperatures. Experimental methods were emphasized for temperatures above 150°C, and the simplest possible solid and solution compositions were used to permit investigation of one process or question at a time. Unexpected results in experimental work prevented complete integration of the various portions of the investigation.

Important assumptions underlying chemical geothermometers include (Fournier, 1977; Fournier, White and Truesdell, 1974):

(1) Temperature dependent water-rock reactions in the reservoir fix the absolute (silica) or relative concentrations of dissolved indicator constituents in the formation water.

(2) The water and rock are at equilibrium with respect to the indicator reaction.

(3) There is an adequate supply of each reactant.

(4) Unless specifically accounted for, no re-equilibration, mixing or boiling occurs after the water leaves the reservoir en route to the sampling point.

Na-K-Ca GEOTHERMOMETER: BASIS

The Na-K-Ca geothermometer (Fournier and Truesdell, 1973) is based on assumed equilibrium among K, and Na, Ca aluminosilicates (Fournier and Truesdell, 1973; Fournier, White and Truesdell, 1974; Truesdell, 1976; Fournier, 1977; Shikazono, 1976; Fournier, 1981). The indicator reactions originally proposed can be summarized in one expression.

$$K^+ + Solid1 = xNa^+ + yCa^{2+} + Solid\ 2 \tag{1}$$
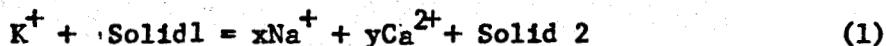
If [i] is the thermodynamic activity of species i, whether i is a solute or a solid (Garrels and Christ, 1965) and (i) is the corresponding concentration,

$$\dot{K} = \frac{[Na^+]^x [Ca^{2+}]^y}{[K^+]} \cdot \frac{[Solid\ 2]}{[Solid\ 1]} \tag{2}$$

1

Preservation of electroneutrality requires that

$$x + 2y = 1 \quad \text{or} \quad x = 1 - 2y \tag{3}$$

and, if we define two more quantities

$$K^* = K \frac{[\text{Solid 1}]}{[\text{Solid 2}]} \tag{4}$$

$$\beta = 2y \tag{5}$$

Equation 2 can be stated in the form used by Fournier and Truesdell (1973),

$$\log K^* = \log \left[\frac{(Na^+)}{(K^+)} \right] + \beta \log \left[\frac{(Ca^{2+})^{\frac{1}{2}}}{(Na^+)} \right] \tag{6}$$

As a first approximation, over narrow temperature range the Van't Hoff equation (Garrels and Christ, 1965) should describe the temperature dependence of K and K^*.

$$\log K_T^* = \log K^* (\text{ref}) + \frac{h}{2.3R} \left(\frac{1}{T(\text{ref})} - \frac{1}{T} \right) \tag{7}$$

$T = t + 273.16$. The quantity h is the enthalpy change associated with reaction 1 at the reference temperature $T(\text{ref})$.

Combining 6 and 7

$$\log \left[\frac{(Na^+)}{(K^+)} \right] = \log K^*(\text{ref}) - \beta \log \left[\frac{(Ca^{2+})^{\frac{1}{2}}}{(Na^+)} \right] + \frac{h}{2.3R} \left(\frac{1}{T(\text{ref})} - \frac{1}{T} \right) \tag{8}$$

Equations 7 and 8 suggest that $\log (K^*)$ should vary linearly with $1/T$. Fournier and Truesdell (1973) found this to be approximately true in two temperature ranges if

$$\beta = 4/3 \quad \text{for} \quad t < 100°C$$

$$\beta = 1/3 \quad \text{for} \quad t > 100°C$$

After empirical calibration, the geothermometer takes the form (Fournier, 1977, 1981),

$$\log K^* = \frac{1647}{t + 273} - 2.24 \qquad (9)$$

Corresponding to these calibration constants, $\log(K^*, \text{ref}) = 3.28$ and $h = -7.53$ kcal.

This derivation emphasizes additional implicit assumptions or pre-requisites to the success of the geothermometer. These are (numbered to continue the list in the first paragraph):

(5) $[i] = (i)$, i.e., the effects of non-ideality and speciation or complexing cancel or are negligible.

(6) β (or x and y) must be constant for all temperatures and, at each temperature, β, K, h, and the ratio of the activities of solid 1 and solid 2 must be the same for all rock-water systems to which the geothermometer is applied.

This requirement should be very restrictive. Its implications are discussed in several contexts below.

(7) No species other than those involved in the indicator reactions participate in reactions with the same solids; otherwise the set of equations used to derive the geothermometer would be incomplete.

There is empirical evidence that not all of these conditions (1-7) are always satisfied. There is a great deal of scatter in the original calibration curves (figure 6 in Fournier and Truesdell (1973) or figure

3

3 in Fournier (1977)). The Na-K-Ca geothermometer has proven more reliable than the simpler Na-K geothermometer for low temperatures, particularly at temperatures below 100°C (Fournier, 1977), but remaining uncertainty has prompted many proposed refinements.

Refinements

High CO_2 water may yield high estimated temperatures. Paces (1975) suspects that many rock-water systems may not have reached equilibrium, particularly in high CO_2 systems. He has proposed a correction to the Na-K-Ca geothermometer for use below 70°C when log (P_{CO_2}) exceeds -4. Goff and Connolly (1978) applied Paces' correction to waters from three different rock types, all different from the granitic rocks upon which Paces' work was based, and found it wanting. Instead, they found that the discrepancy between predicted and measured temperatures varied systematically with salinity and rock type.

High magnesium waters may yield false Na-K-Ca temperatures as well. Fournier and Potter (1979) have proposed a correction for interference by magnesium.

High salinity (Goff and Connolly, 1978; Fouillac and Michard, 1981), precipitation of calcium carbonates or sulfates (Fournier and Truesdell, 1973; Swanberg, 1974), strong acidity (Swanberg, 1974) or the high aluminum concentrations likely to result from high acidity (Fournier and Truesdell, 1973) may all result in false predicted temperatures.

Temperatures predicted by several geothermometers are compared with discharge temperatures and occasionally bore hole temperatures in figures 1-3. References for water analyses are listed below in the text. These figures illustrate several points, including the disturbing scatter already mentioned. Scatter is reduced by use of the Mg and CO_2 corrections.

The exact correspondence of some predicted and discharge temperatures with
the Na-K-Ca-Mg geothermometer is misleading. Under some circumstances the
computation protocol prescribes adoption of the discharge temperature
directly as the aquifer temperature. The CO_2 correction apparently
overcorrects systematically when used with limestones.

Because most of the measured temperatures in these examples are
discharge, rather than aquifer temperatures, our conclusions must be
considered suggestive rather than conclusive.

GEOTHERMOMETRY VIA MODEL CALCULATIONS

As suggested by Fournier (1981) and, indirectly by Michard et al.
(1980) reservoir temperatures might be estimated by analysing the temperature
dependence of the saturation indices of minerals likely to be present in
the reservoir, using the observed analytical composition of the water and
a computer code such as WATEQ2 (Ball et al., 1980), EQ3 (Wolery, 1979) or
PHREEQE (Parkhurst et al., 1980). Saturation indices for the minerals
controlling solution compositions should approach zero at the reservoir
temperature if equilibrium is reached.

Figure 4 illustrates the temperature dependence of saturation indices
for several minerals likely to be involved in geothermometric indicator
reactions for a single spring water discharging at 85.5°C. Saturation
indices converge toward zero near 140°. This is close to the Na-K-Ca
and quartz temperatures, but higher than Mg or CO_2 corrected temperatures,
and not surprisingly, higher than the discharge temperature. Unfortunately
we do not know the reservoir temperature in this case. (SI's for hallo-
site and wairakite approach zero at T < 75°C; analcime and muscovite
are highly supersaturated for all temperatures.)

Chen (1975) reports complete analyses for some thermal waters in Taiwan. In a few cases, bore-hole temperatures are provided. Saturation indices calculated for temperatures up to 175°, using MNQL98, are summarized in figures 5, 6 and 7. Well IT4 and Jentze Spring are in the Tuchang geothermal field, tapping an aquifer in Miocene slates. Lushan spring is 50 to 70 km to the south-southwest, and also taps an aquifer in Miocene slates.

Aquifer temperatures estimated with several geothermometers and discharge or bore-hole temperatures are listed in Table 1. In each case, within the expected range of computation error discussed in Appendix A, MNQL98 places quartz, albite, K-spar and kaolinite at equilibrium in a temperature range within 10-20° of the Na-K-Ca and quartz temperatures and very close to the 144° bore-hole temperature in well IT4.

Calculations of this sort have serious weaknesses.

(1) The probability that gaseous constituents such as CO_2 will be lost between reservoir and sampling point, or during sampling, is high (Fournier and Truesdell, 1973), so pH calculations are suspect (Truesdell and Singer, 1971).

(2) Thermodynamic data are lacking for many important complexes and minerals (Fournier, 1981), and the data available are often uncertain. Uncertainty is illustrated by two very carefully selected free energies of formation for kaolinite: -905.6 kcal/mole (Helgeson et al., 1978) and -908.1 (Hemingway, Roble and Kittrick, 1978).

(3) Most computation codes neglect the fact that many minerals are solid solutions (Fournier, 1981), thus that their activities may be variable and not well represented by the thermodynamic properties of end-members

(Garrels and Christ, 1965). Bird and Norton (1981) have developed methods and data with which this deficiency can be overcome for the Salton Sea system.

(4) Non-ideality corrections are inexact (Garrels and Christ, 1965).

(5) Water analyses are often incomplete, omitting constituents which may be indirectly related to indicator reactions, yet significant in fixing pH, for example. Too often, aluminum is neglected in the analysis, thus precluding use of the most abundant minerals in any system.

In our MNQL98 calculations, additional uncertainty is introduced through use of the Van't Hoff appoximation to adapt equilibrium constants to temperature. We expect increasing error as temperature increases above 50°C with predicted temperatures probably low. As shown in Table A1b quartz temperatures estimated with MNQL98 may be low by as much as 25° at 125°. We do not intend our MNQL98 calculations to be correct at these temperatures. We present them here only to illustrate the method. More sophisticated computation codes should be used in subsequent work.

In spite of the many difficulties, such calculations may help in selecting among geothermometers. If a realistic assemblage of minerals approaches equilibrium at a temperature close to one or more chemical geothermometer temperatures, the agreement should lend confidence to the estimated reservoir temperature. More complete water analyses are probably worthwhile.

Na-K-Ca GEOTHERMOMETRY

Evaluation of β, $\log(K^*)$, and h

The constant β (equations, 5, 6, 8 etc.) should have a single value for all t < 100 regardless of rock type. K^* should vary with T, but should be independent of rock type. We have tested these requirements by selecting waters from narrow ranges of temperature, from each of three distinct types of rock, and using equation 5 in a least squares regression program to evaluate β and $\log (K^*)$ for each temperature band and rock.

Multiple regression of $\log ((Na)/(K))$ against both

$$\log \left(\frac{(Ca^{2+})^{1/2}}{(Na^+)} \right)$$

and

$$\frac{1}{2.3R} \left(\frac{1}{T(ref)} - \frac{1}{T} \right)$$

Using T(ref) = 298.16 utilizes all temperatures, provides another estimate of β, and estimates of K^*(ref) and h. This has been done for each type of rock for which we have enough cases for statistical reliability.

We will describe the data first, then discuss results.

Andesites

Seki et al. (1980) report water temperatures and analyses from bore holes and seeps in the Seikan Undersea Tunnel complex between Honshu and Hokkaido, Japan. The tunnel penetrates mainly andesitic rocks. Many waters are mixtures of meteoric water and seawater; chloride contents above about 80 ppm indicate a mixture of seawater (Mizukami, Sakai, and Matsubaya, 1977). The effect of seawater contamination on the Na-K-Ca geothermometer is illustrated in figure 8. The solid line in figure 8 is the least squares trend of waters not contaminated by seawater.

Contaminated waters, i.e. those containing more than 80 ppm chloride, are not used in the analyses to follow.

White, Hem and Waring (1963) present selected analyses from a variety of andesitic rocks, reporting discharge temperatures.

Wells, Childs, and Downes (1977) report detailed analyses of three cold spring waters issuing from andesitic rocks. These springs are depositing amorphous aluminosilicates.

We have estimated β and K^* in two relatively narrow temperature bands. Data in the range $5 < t < 32°C$ are plotted in figure 9 and in the range $77 < t < 100$ are plotted in figure 11. Values of β and $\log K^*$ determined through least squares linear regression are listed in Table 2.

Data for the temperature range $60-73°$ are shown in figure 10, but are too sparse to permit regression. These data support the claim cited earlier that the geothermometer might be unreliable with acid sulfate waters. Estimates of β, $\log K^*$ and h are listed in Table 2.

Serpentinites

White, Hem, and Waring (1963) include some waters from serpentinites in their compilation. Unfortunately, the brief geologic descriptions hint that these waters may be mixed with others from nearby shales or sandstones. We have not used these waters in estimation of β or K^* but do include them in the following figures.

Barnes, O'Niel, Rapp, and White (1973) present a detailed study of several waters from serpentinites, including four which may not be contaminated by waters from other rocks, though the pH's of these waters seem low for serpentinites.

The data are summarized in figure 12. β and $\log (K^*)$ are listed in Table 2.

Limestones

White, Hem, and Waring (1963) include waters from several limestones and dolomites in their compilation.

Helz and Sinex (1974) reported analyses from thermal springs in Virginia. Waters with temperatures below 25° are thought to be mixed (Helz and Silex, 1974; Helz, oral communication, 1981) and are not considered in estimating β and K^*.

The data are summarized in figures 13 and 14; values of β and $\log(K^*)$ are listed in Table 2 for the lower temperature range only.

The Magnitude of β

Values of β estimated using 'constant' temperature data are apparently nearly independent of temperature and rock type, as required. The value of β is, however, closer to 1.00 than to the 4/3 customarily utilized (Fournier, 1973) in the Na-K-Ca geothermometer for temperatures less than 100°C.

Mechanisms

Mizukami, Sakai, and Matsubaya (1977) argue convincingly that the relative activities of Na, K and Ca in the formation waters encountered in the Seikan tunnel complex are fixed by ion exchange on montmorillonites. A value of β = 1.00 may be consistent with simultaneous Na/K and Na/Ca exchange or perhaps with simple K/Ca exchange. It is possible to derive a relationship analogous to equations 6 and 8 using cation exchange equilibria. We will use the formalism adopted by Bruggenwert et al. (1979). Barred species are exchangeable ions associated with or bound to a single solid such as a clay. The reactions and equilibrium constants needed are

$$\overline{Na} + K^+ = \overline{K} + Na^+ \; : \; K_1 = \frac{[\overline{K}][Na^+]}{[\overline{Na}][K^+]} \qquad (10)$$

$$\overline{Na} + \frac{1}{2} Ca^{2+} = \frac{1}{2}\overline{Ca} + Na^+ \quad : \quad K_2 \frac{[\overline{Ca}]^{\frac{1}{2}}[Na^+]}{[\overline{Na}][Ca^{2+}]^{\frac{1}{2}}} \tag{11}$$
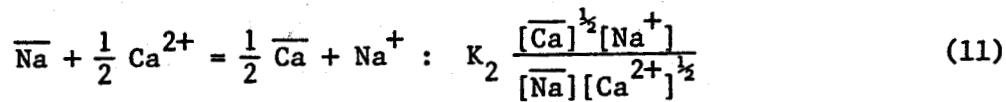
The enthalpy changes for reactions (10) and (11) are h_1 and h_2, respectively.

Combining K_1 and K_2 to eliminate $[\overline{Na}]$ and converting to logarithmic form:

$$\log\left(\frac{[Na^+]}{[K^+]}\right) = \log\left(\frac{K_1}{K_2}\right) + \log\left(\frac{[\overline{Ca}]^{\frac{1}{2}}}{[\overline{K}]}\right) - \log\frac{[Ca^{2+}]^{\frac{1}{2}}}{[Na^+]} \tag{12}$$

$$\log K^* = \log\left(\frac{K_1}{K_2}\right) + \log\left(\frac{[\overline{Ca}]^{\frac{1}{2}}}{[\overline{K}]}\right) \tag{13}$$

Introducing the Van't Hoff equation to provide temperature dependence

$$\log\left(\frac{(Na^+)}{(K^+)}\right) = \log K^*(ref) - \log\left(\frac{(Ca^{2+})^{\frac{1}{2}}}{(Na^+)}\right) + \frac{h_2 - h_1}{2.3R}\left(\frac{1}{T(ref)} - \frac{1}{T}\right) \tag{14}$$

The same relationship can be derived from binary K/Ca exchange,

$$\frac{1}{2}\overline{Ca} + K^+ = \overline{K} + \frac{1}{2} Ca^{2+} \quad : \quad K_3 = \frac{[\overline{K}][Ca^{2+}]^{\frac{1}{2}}}{[\overline{Ca}]^{\frac{1}{2}}[K^+]} \tag{15}$$

Expressing equation 15 logarithmically, adding $\log[Na^+]$ to both sides and rearranging,

$$\log\left(\frac{[Na^+]}{[K^+]}\right) = \log K_3 + \log\frac{[\overline{Ca}]^{\frac{1}{2}}}{[\overline{K}]} - \log\frac{[Ca^{2+}]^{\frac{1}{2}}}{[Na^+]} \tag{16}$$

$$\log K^* = \log K_3 + \log\frac{[\overline{Ca}]^{\frac{1}{2}}}{[\overline{K}]} \tag{17}$$

11

$$\log\left[\frac{[Na^+]}{[K^+]}\right] = \log K_3^*(\text{ref}) - \log\left[\frac{[Ca^{2+}]^{\frac{1}{2}}}{[Na^+]}\right] + \frac{h_3}{2.3R}\left[\frac{1}{T(\text{ref})} - \frac{1}{T}\right] \quad (18)$$

Even if solution-phase non-ideality is negligible or accounted for, equations 6 and 8 are linear only if the activities of Solid 1 and Solid 2 are invariant. Similarly, equations 12-18 are linear only if the exchangeable ion composition of the solid phase is constant. That is, if the ratio of the activities of exchangeable Ca^{2+} to Na^+ is invariant. Mizukami, Sakai, and Matsubaya (1977) have pointed out that if the total exchange capacity of the aquifer material is large relative to the total ionic content or salinity of the formation water, the composition of the rock may remain relative constant. This condition may not be uncommon within any one formation, but if $K^*(\text{ref})$ is to be a single constant for all aquifers, as required for a generally applicable geothermometer, this ratio must have approximately the same value in all rocks, not only within one aquifer! This is obviously unlikely, and much of the scatter in regressions may be attributable to variability in the compositions of aquifer materials.

Under circumstances permitting linearity in equations 12-18, comparison of these equations with 6 and 8 illustrates that an ion exchange mechanism is compatible with $\beta = 1.0$ for temperatures $<75°C$.

If the value of β is exactly 1.00, sodium drops out of the indicator reaction, and a K-Ca geothermometer should be equally as useful as the Na-K-Ca geothermometer.

At any specific temperature, the factor β in equation 8 is determined by the net water/rock reaction. Fournier and Truesdell (1973) noted

that "a net reaction cannot be deduced only from the composition of water

flowing from a rock or only from the mineralogy of an alteration assemblage.

One must know either the change in composition of water as it flows through

a given volume of rock or the change in bulk composition of that given

volume of rock in response to water-rock reactions". Rarely do we have

the information necessary to determine the net reaction. However, in the

case of the Seikan Tunnel, Japan (Seki et al., 1980) where seawater-meteoric

water mixtures flow through andesitic volcanics, such information is

available.

From samples collected from the Seikan tunnel, net mass fluxes for

Na, K and Ca can be deduced qualitatively. A net mass flux is the differ-

ence between an absolute mass flux leaving the rock and an absolute mass flux

into the rock. From the data presented by Seki et al. (1980), the net

mass flux of Ca^{2+} is greater than zero even for weakly interacted fluids.

The net mass flux of K^+, however, is less than zero. For weakly interacted

solutions, the net mass flux of Na^+ is either zero or slightly negative.

These results signify that dissolution mass fluxes out of Ca-bearing

reactants is greater than growth mass fluxes into Ca-bearing products.

On the other hand, growth mass fluxes into K-bearing products must be

greater than dissolution mass fluxes out of K-bearing reactants. In the

case of Na^+, either equilibrium exists between solution and rock or growth

and dissolution fluxes into and out of Na-bearing phases must be equal.

The nearly zero net mass flux for Na^+ in the Seikan tunnel indicates

that Na^+ is not involved in the overall reaction controlling water chemistry.

This leads, via equations 1 to 5, to a value of β equal to 1.0 or a little

larger, perhaps as large as 4/3. If β were 4/3 the following overall net

reaction describes the process:

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$$K^+ + \frac{1}{3} Na^+ + \text{dissolving phases} \rightarrow \frac{2}{3} Ca^{2+} + \text{growing phases}$$

which is consistent with low temperature (<75°C) water/rock interactions worldwide. . If the Seikan Tunnel is representative of flowing systems in general, then irreversible reactions are responsible for empirical geothermometric relationships. In this case, K^* represents a steady-state Q^*, or ion activity product, and β an irreversible reaction stoichiometric coefficient controlled by relative reaction rates.

The Magnitude of K^*(ref) and h

If the indicator reaction involves only pure solids of invariant composition, K^*(ref) and h should be comparable to the corresponding equilibrium constants and enthalpies of reaction. However, if the indicator reaction is an exchange reaction, K^*(ref) contains the ratio of the activities of the adsorbed exchangeable ions involved. Still, h may be comparable to the enthalpy of the exchange process.

Bruggenwert and Kamphorst (1979) and Maes and Cremers (1979) have compiled exhaustive reviews of clay and soil cation exchange literature. Breck (1974) published a review of the cation exchange behavior of zeolites. Observed ranges of exchange constants and enthalpies for cation exchange reactions are listed in Table 3.

Fournier (1981) gave two examples of possible indicator reactions involving cation exchange among feldspars and alteration of feldspars. Using critically selected thermodynamic data (Helgeson et al., 1978) we have calculated the equilibrium constants and enthalpy changes associated with these and similar reactions; results are given in Table 3.

Comparing the Van't Hoff enthalpies derived from the Na-K-Ca geothermometer (Fournier, 1977) and from our work with individual rock types

(see Table 2a,b) with the enthalpy changes listed in Table 3, it appears

unlikely that a simple clay cation exchange reaction is responsible for

fixing Na, K, Ca ratios.

A reaction among feldspars or an alteration reaction involving a

larger enthalpy change is more likely. Fournier (1979) concluded that ion

exchange among feldspars probably dominated for t > 100°C and that reaction

involving clays and or zeolites dominated for t < 100°C. These observations

are consistent with the MNQL98 calculation represented in figs. 4-7 as well.

Additional Reactions

We have evaluated several additional reactions in search of reactions

that can account for the empirical relationships that are the basis of

the Na-K-Ca geothermometer. To fully evaluate chemical controls on the geothermo-

meter, the complex system Na_2O, K_2O, CaO, Al_2O_3, SiO_2 and H_2O needs

to be considered. The stable phases in this system over the temperature range

of geothermal systems (50-300°C) are grossular, clinozoisite, albite,

paragonite, muscovite, K-feldspar, and quartz (Giggenbach, 1981). Only

five of these phases need be present to fix the solution composition at a

given temperature and pressure.

The fundamental geothermometric reaction has been proposed to be

between two alkali feldspars (Fournier and Truesdell, 1973):

$$\underset{\text{albite}}{NaAlSi_3O_8} + K^+ \overset{K_1}{=} \underset{\text{K-spar}}{KAlSi_3O_8} + Na^+ \tag{19}$$
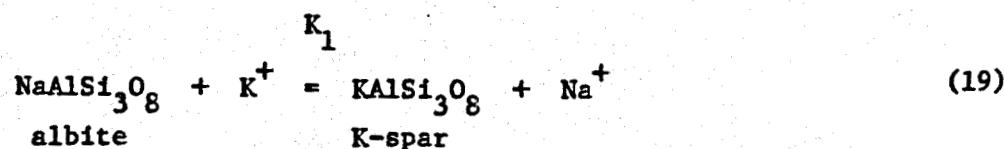
Any of a variety of other reactions involving both stable and metastable

aluminosilicates may be considered to introduce Ca^{2+};

15

$$\tfrac{1}{2} CaAl_2SiO_{12} \cdot 2H_2O + SiO_2 + Na^+$$
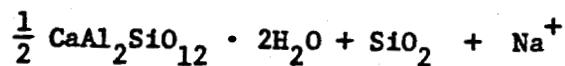
wairakite (or laumontite)   quartz

$$\overset{K_2}{=} NaAlSi_3O_8 + \tfrac{1}{2} Ca^{2+} + H_2O \qquad\qquad (20)$$

albite

$$\tfrac{1}{4} Ca_2Al_3Si_3O_{12}(OH) + \tfrac{1}{8} NaAl_3Si_3O_{10}(OH)_2 + 9/4\ SiO_2 + Na^+$$

clinozoisite   paragonite   quartz

$$\overset{K_2}{=} \tfrac{9}{8} NaAlSi_3O_8 + \tfrac{1}{2} Ca^{2+} + \tfrac{1}{4} H_2O \qquad\qquad (21)$$

albite

$$\tfrac{1}{4} Ca_2Al_2Si_3O_{10}(OH)_2 + \tfrac{1}{8} NaAl_3Si_3O_{10}(OH)_2 + \tfrac{9}{4} SiO_2 + Na^+$$

prehnite   paragonite   quartz

$$\overset{K_2}{=} \tfrac{5}{4} NaAlSi_3O_8 + \tfrac{1}{2} Ca^{2+} + \tfrac{1}{2} H_2O \qquad\qquad (22)$$

albite
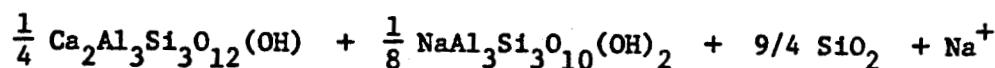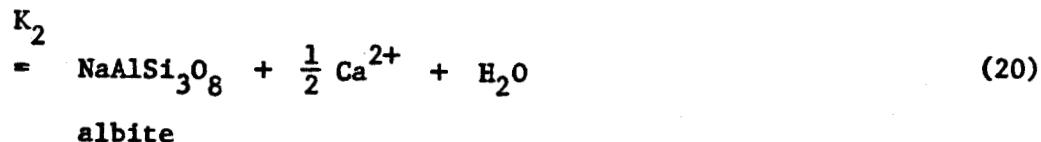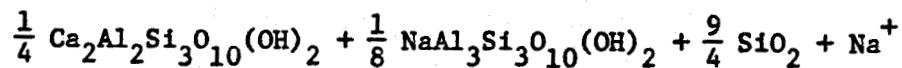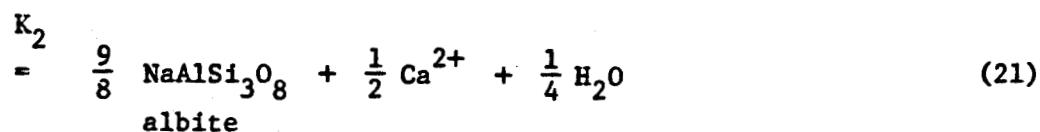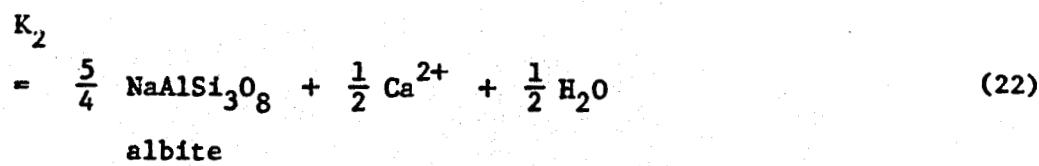
Two or more of these reactions are likely to occur simultaneously in any real system. The overall observed stoichiometry is not necessarily determined by an a priori principle. These reactions can, however, be combined in proportions which yield appropriate values of β with useful

results. The empirical Na-K-Ca geothermometric relationship in terms of component activities is then:

$$\log K_a^* = \log \left(\frac{a_{Na}}{a_k} \right) + \beta \log \left(\frac{a_{Ca}}{a_{Na}} \right)^{\frac{1}{2}}$$

$$= \log K_1 + \beta \log K_2 \qquad (23)$$

Equilibrium constants for a variety of such combined reactions were used to construct figures 15 and 16. An interesting example is a reaction between minerals constituting the most stable assemblage: clinozoisite, paragonite, quartz, albite and K-spar. For temperatures above 100°C, $\beta = 1/3$ (Fournier and Truesdell, 1973) and the overall reaction combining (22) and (23) must be

$$\frac{1}{12} Ca_2Al_3Si_3O_{12}(OH) + \frac{1}{24} NaAl_3Si_3O_{10}(OH)_2$$
$$\text{clinozoisite} \qquad\qquad \text{paragonite}$$

$$+ \frac{1}{4} SiO_2 + \frac{5}{8} NaAlSi_3O_8 + K^+ =$$
$$\text{quartz} \qquad \text{albite}$$

$$\frac{2}{3} Na^+ + \frac{1}{6} Ca^{2+} + \frac{1}{12} H_2O + KAlSi_3O_8 \qquad (24)$$
$$\text{K-spar}$$
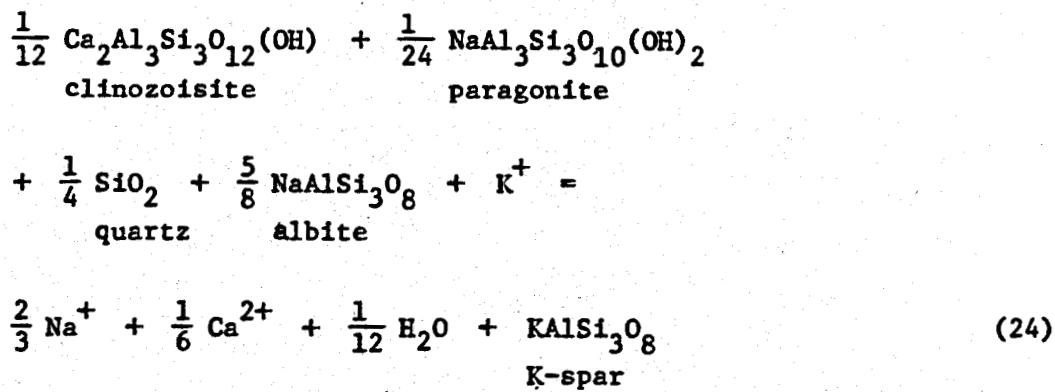
From figure 16 it can be seen that such reactions, with appropriate stoichio-
metric coeficients, can control activities of Ca, Na, and K at values con-
sistent with the geothermometer. What can also be observed is that many
metastable reactions will work equally well. All thermodynamic data at
the various temperatures were obtained from the SUPCRIT Data File (Helgeson
et al., 1978) via EQ3 (Wolery, 1979). The dashed limits represent the
range of calibrating data used by Fournier and Truesdell (1973).

Even though the stable assemblage and some common unstable minerals
may control solution compositions consistent with the geothermometer, none
of these solid phases were produced consistently in calibration experiments
using glass or rocks. Also since many of these phases are not found commonly
in geothermal systems, a variety of stable and metastable solids evidently
can generate similar cation ratios. The success of the Na-K-Ca geothermometer
must depend mainly on the coincidental similarity of K^* or Q^* values
produced in a wide variety of rocks interacted with many solutions at
nearly constant β.

NON IDEALITY AND COMPLEXING

In principle, chemical geothermometers should be computed using the
activities of free, uncomplexed species, not analytical, concentrations.
This is impractical (Fournier and Truesdell, 1973), but the possibility
that serious error is introduced by neglecting the difference should be
appraised. Figures 17 and 18 give some insight into the
degree to which correction of analytical concentrations to free
ion activities may affect geothermometers. Statistical tests
have not been made, but it appears that K^* may be significantly
sensitive to non-ideality, while β may not be. No firm conclusions are

justified at this time, except a reminder that the same degree of data reduction must be used in application of a geothermometer as was used in calibration.

EXPERIMENTAL CALIBRATION

Previous Experimental Studies

Experimental equilibration of whole rock with water or salt solutions insures known 'reservoir' temperatures; there is no doubt that the measured temperature is close to the temperature of equilibration. Limited reaction time, however, reduces the liklihood that equilibrium or steady state can be achieved.

Ellis and Mahon (1964) published results of experimental reaction between an andesite and pure water at temperatures from 150 to 350°C. Maximum reaction times were about 12 days. Dickson, Potter, Pohl, and Guillemette (1982, unpublished data, Stanford Geology Dept.) reacted an andesite and a basalt with NaCl solutions at 200 and 300°C for periods up to 60 days. The evolutions of Na-K, Na-K-Ca and silica temperatures is illustrated in figures 19 and 20. Na-K and silica temperatures approach apparent steady state only after 10 to 30 days. Steady-state Na-K and Na-K-Ca temperatures and quartz temperatures are compared with measured temperatures in Figure 21.

Present Experiments: Agitated Hydrothermal System

Experimental calibration of the geothermometer was initially thought possible by reacting feldspars under hydrothermal conditions until equilibrium Na/K ratios were obtained. Traditionally, experiments of this type have been conducted in agitated or closed tube hydrothermal apparatus.

Part of our experimental approach was to react oligoclase and microcline at temperatures from 75 to 300°C in Dickson type agitated hydrothermal apparatus. This type of apparatus allows for time dependent sampling of fluid without disturbance of the conditions of the experiment. In addition to the two feldspars, two zeolites, a synthetic Na-K Phillipsite and a natural analcime were reacted at temperatures of 75 and 150 degrees.

Procedure

The compositions of the four minerals used in this study, as determined by bulk chemical analysis, are listed in Table 4. The microcline and oligoclase were ground and sized to -100+200 mesh. The particles were then ultrasonically cleaned and etched using the procedure outlined in Holdren and Berner (1979). The analcime, from pocket fillings in basalt from Washington, was crushed and sized to <100 mesh. The analcime was not etched. The synthetic phillipsite was grown from solution at 90°C (Rona Donahoe, Geology Dept., Stanford University). The particle size of the phillipsite averaged 5 microns.

All experiments were conducted at an initial water to rock ratio of 10:1 using a 100 ppm NaCl solution as the starting fluid. Fluid samples were removed from the vessel at various times. These samples were analyzed for Na, K and Ca by atomic absorption. All Mg concentration proved to be below detection.

Results

The first experiment reacted the two feldspars with 100 ppm NaCl solution at 225°C for a period of 3 months. The results of this experiment are listed in Table 5 and are shown on figure 22. The calculated Na/K temperature is plotted as a function of time. The calcium concentration was below detection (< .1 ppm) in all of these experiments. The calculated temperature moves through a maximum initially and then approaches

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a steady state after several hundred hours. At the termination of the experiment the run was quenched rapidly to room temperature. Additional fluid samples were taken over several weeks. Only a slight drop in calculated temperature was observed.

The second experiment was run at a temperature of 75° and subsequently heated to 150°. The results of this experiment are listed in Table 5 and are shown on figure 23. The calculated temperature increases significantly above the run temperature and goes through a maximum at about 400 hours. Upon increasing the temperature to 150° the calculated temperature goes through a maximum and then may approach steady state at about 230°.

The results of the next experiment are listed in Table 5 and are shown on figure 24. After a short period at 300°C the temperature was dropped to 150°. As in the previous experiment the change in actual temperature is accompanied by an increase in the calculated temperature. The steady state value approached is approximately the same as that in the previous experiment, near 225°.

In addition to the feldspar -100 ppm NaCl experiments, two experiments using the zeolites were run. The results of these experiments are listed in Table 6. The temperatures calculated from the Na/K ratios do not even closely correspond with the experimental temperatures. Ion exchange reactions between zeolites should be relatively rapid as the results of these experiments suggest, however the synthetic phillipsite is control-ling K concentrations at elevated levels.

Present Experiments: Flow Through System

The flow of a dilute NaCl solution through oligoclase and K-feldspar models the flow of high Na/K ratio solution produced at low temperature through a feldspar-bearing reservoir at higher temperatures. The factors controlling attainment of equilibrium Na/K ratios are determined

by varying the flow rate and core length.

Procedure

The flow through experiments were conducted in an apparatus of a new design. A schematic of the apparatus is shown in Figure 25. Fluid flow rate is precisely controlled using a stepping motor flow rate controller. Details of the flow through system are included in Potter (1981). A paper presenting further information is in preparation.

The cores used in these experiments consist of teflon or teflon lined stainless steel tubing packed with an equal mixture of the etched oligoclase and microcline. The cores are 0.5 cm in diameter and range from 15.2 to 152 cm in length. Experiments were performed at flow rates from .001 ml/min to 1 ml/min. Two temperature and pressure conditions were used 90°C and 1 bar and 200°C and 140 bars. Inlet fluid was a 100 ppm NaCl solution.

In all, over 30 flow-through experiments were completed within the contract period. A substantial part of these experiments were performed in the last few months due in part to the difficulty in developing a reliable and precise flow rate controlling device. The experiments were designed to study the effects of changes in core length and changes in inlet fluid composition as well as changes in temperature.

Results

Of primary importance to these experiments is the attainment of steady state outlet solution concentrations. Fluid samples were taken at various times and analyzed for Na and K. Steady state was attained in most experiments. Steady state compositions were rapidly attained in the 200° experiments while the slowest approach was observed at 90°. An example of the time dependence is shown in figure 26. The steady state outlet Na and K concentrations are listed in Table 7 along with core length, flow

rate, temperature, salinity, log Na/K ratio and Na-K temperature.

Several experiments were run varying both flow rate and core length at 90°C. The results of these experiments are summarized in Figure 27. The calculated Na/K temperatures are plotted as a function of core length. The apparent effect of core length is negligible relative to the much larger effect of flow rate. Flow rate has a strong effect on the absolute concentrations of Na and K as well as the calculated Na/K temperatures. The calculated Na-K temperatures as a function of flow rate are plotted on Figure 28. The calculated Na/K temperature ranges from < .0 to >325° for the 90° experiments and from 300-450° in the 200° experiments; only fortuitously do the Na/K and experimental temperatures agree at any one flow rate.

The absolute steady state Na and K concentrations are plotted against log flow rate in figures 29 and 30 for 100 ppm NaCl experiments at 90°. The steady state concentrations of Na and K decrease with increasing flow rate until flow rates exceed 0.01 ml/min, after which they remain constant. At 200° (fig. 30) these concentrations decrease continuously and linearly with log flow rate. Extrapolating to high flow rates, both Na and K would reach their input levels at the same flow rate, suggesting that flow rate itself has a direct influence on the steady state achieved. The implications of this will be discussed later.

Discussion

Agitated experiments

The results of the agitated experiments are somewhat disappointing. In nearly every experiment, especially at the lower temperatures a low Na/K ratio was set early, presumably by the rapid dissolution of micro-cline. The ability of the system to recover is limited by reaction kinetics. Times required to obtain true, steady state conditions may be

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in excess of 12 months at lower temperatures.

The results obtained from these agitated experiments are similar in behavior to those of Potter (1981) in which rhyolite glass was reacted with NaCl solutions at 300°C for a period of 60 days. The Na/K ratio was set initially at very low values. With time the ratio increased and approached a value in agreement with the experimental values determined by Hemley (1967) and Orville (1963) for feldspar exchange. The rhyolite glass first altered to zeolites and clay; Na and K feldspars later formed as very fine crystals (5-10 μm). These experiments show that long reaction times are needed to insure formation of the expected feldspars and that these apparently must be present to set the Na-K ratio in accord with the geothermometer.

In all of the oligoclase-microcline experiments performed in this study the K concentration   rose to levels above the equilibrium value, then decreased. These metastable high levels increase with temperature. The lengths of time taken to observe the decrease in K concentration decreases with increasing run temperature (position of K concentration maxima). The rate of growth of a K-bearing phase in quantities appreciable enough to affect the K concentration in the bulk solution is a strong function of temperature. However, the dissolution reaction which liberates K into solution is rapid at all temperatures. Even at 75°, the K concentration from the feldspar experiment is well above the value in equilibrium at this temperature and Na concentration.

This supports our contention that the Na-K geothermometer relation is controlled by relative reaction rates, primarily because of the sluggishness of secondary mineral growth at low temperatures. If fluid flow in a hydrothermal system is rapid, the degree of reequilibration of the Na-K ratio would be negligible.

The experiments run using the synthetic phillipsite and analcime were done to test whether zeolites are capable of setting Na/K ratios near those of the geothermometer. We found, however, that the ratios were much too low; temperatures calculated from these ratios are ridiculously high, reaching values in excess of 1500°C. In one short experiment the synthetic phillipsite was reacted alone at 75° and the solution was found to have a Na/K ratio of 0.36 or a Na/K temperature of 2700°C.

We believe we have made some experimental advances in understanding the mechanisms involved in the Na/K geothermometer. However, much remains to be done on the experimental calibration of the geothermometer. We can recommend some improvements that might be followed in order to provide a reasonable calibration.

(1) Start with fine grained (5-20 μm) minerals grown during laboratory alteration reactions of synthetic and natural glasses and rocks. Use of synthetic materials provides better control over composition and phase purity.

(2) Expect to run experiments for periods exceeding one year to obtain steady state.

(3) Vary starting concentrations of Na and K to test for reversibility.

Flow through experiments

One of the fundamental tenets of Na-K geothermometry is that base exchange of alkalies between coexisting feldspars is the major control of Na/K ratios in most natural waters. When such reactions are written, i.e. $KAlSi_3O_8 + Na^+ \rightleftarrows NaAlSi_3O_8 + K^+$, reversibility is usually assumed. However, the reliability of the Na-K geothermometer depends to a large extent on reequilibration of fluid with feldspars in the rock

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as the solution flows to the surface, either in springs or wells. If reaction kinetics are sluggish enough, such reequilibration will not occur, and Na/K ratios will accurately reflect reservoir temperatures. However, if convection rates in a geothermal system are large and high Na/K ratio solutions enter the reservoir, sluggish reaction kinetics may retard attainment of the Na/K ratio appropriate for the reservoir temperature.

It is important, therefore, to know something abouth the rate of equilibration of feldspars with solution in flowing systems at various temperatures. The flow-through experiments were designed to measure steady-state Na/K ratios as a function of both temperature and flow rate.

The observed increase of K^+ in flowing solution to high levels as flow rates decrease is entirely a non-equilibrium effect. Similar excursions of the concentration of K^+ have been observed in both experimental and natural settings. Concentrations of K^+ higher than appropriate for equilibrium conditions were noted by Dickson and Potter (1982) and Charles (1979) in experiments reacting rhyolite and granodiorite, respectively, with solution. In the hot dry rock experiments at Fenton Hill, New Mexico, Grigsby et al. (1980) noted that when the reservoir temperature decreased from ~300°C to 150°C, Na/K ratios were maintaned at values which were consistently too low and reflected only the highest measured reservoir temperature.

In a real geothermal system if Na/K ratios are too low, some albite may dissolve irreversibly.

$$2H_2O + NaAlSi_3O_8 \rightleftharpoons Na^+ + Al(OH)_4^- + 3SiO_2(aq) \qquad (25)$$
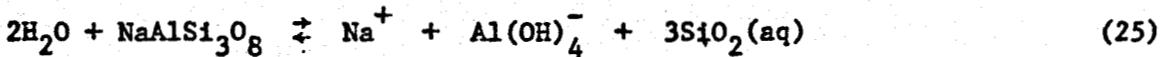
and some K-spar may grow irreversibly:

$$K^+ + Al(OH)_4^- + 3SiO_2(aq) \rightarrow KAlSi_3O_8 + 2H_2O \qquad (26)$$
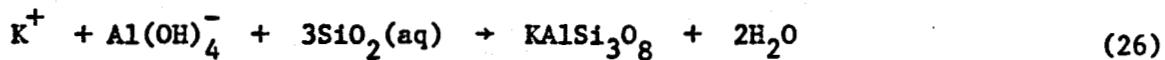
So that the net reaction becomes:

$$K^+ + NaAlSi_3O_8 \rightarrow KAlSi_3O_8 + 2H_2O \qquad (27)$$
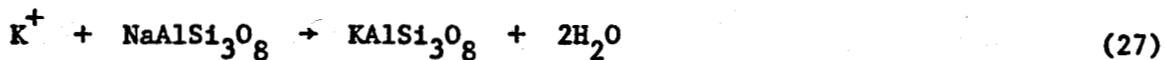
The net reaction proceeds until equilibrium Na/K values are attained. However, if reaction kinetics are sluggish, non-equilibrium Na/K values may be maintained for long times, especially in flowing systems. For example, if growth rates of K-spar in (26) are small relative to dissolution rates of albite in (25) then lower Na/K ratios than equilibrium values may be maintained. The same result will occur if K-spar growth rates are sluggish and an inflowing solution has an Na/K ratio too low for the temperature and pressure.

The positive net mass flux of K^+ from the cores in all flow-through experiments demonstrate that dissolution rates of K-spar exceed growth rates. Along each core a net dissolution region exists near the inlet end, and a net growth region exists near the outlet end if flow rates are small enough at large path lengths. Evidently, in our experiments, only dissolution occurred since K^+ contents never approach equilibrium values over the entire range of flow rates and path lengths.

The results of the flow-through experiments indicate that dissolution of K-spar dominates the chemistry of the outlet fluid. For feldspar samples prepared in the same way, Berner and Holdrchon (1979) found that feldspar dissolution kinetics followed a linear rate law. Such rate behavior can account for the results shown in Figures (29) and (30) since

$$C_K^{out} = \frac{K^{linear}}{U_v} \quad . \qquad (28)$$

where C_k^{out} is the outlet concentration of K^+ (mg/ml), K^{linear} (ml/mm) is a linear rate constant and U_v is the volumetric flow rate (my/min). Thus the outlet K^+ concentration increases as flow rate decreases. The non-linearity observed in figures (29) and (30) results from the fact that

$$K^{linear} = f(U_v) \qquad (29)$$

Therefore, C_k^{out} values will be lower at low flow rates than would be the case if no flow rate dependence existed.

A paper on the flow-through experiments discussing the results in detail is being prepared. These results show that the rate constant is dependent on flow rate, $K(U_v)$ and is given by the following expression:

$$K(U_v) = \frac{\Delta C_i}{2.303 \log (U_v^o/Uv)} \qquad (30)$$

where ΔC_i is the difference between outlet and inlet concentrations of i and U_v^o is the flow rate intercept at $\Delta C_i = 0$. The rate constants at 90° and $200°C$ are 7.8×10^{-5} and 0.192 mg/min, respectively; and U_v^o values are 0.025 and 200 ml/min. Thus, the effect of flow rate on reaction rates is greater at higher temperatures.

Because of the linear rate behavior observed in flow-through experiments, equilibrium Na/K ratios cannot be attained. The sluggish reaction kinetics observed at low flow rates even at high temperature

suggest that upon flow of geothermal reservoir fluids to the surface, reequilibration should not occur. Thus, Na/K ratios should reflect maximum temperatures encountered along the flow path.

CONCLUSIONS

Empirical data suggest that rocks very poor in feldspars may obey the same geothermometer as do feldspar-rich rocks, suggesting that reactions involving feldspars may not be essential. Empirical data also suggest that the value of β may be closer to 1.0 than to 4/3 as specified in earlier work for temperatures below 100°C.

Values of β and K^* derived from a wide variety of rock types are consistent with ion exchange mechanisms but the temperature dependence (h) is too large for clay-type ion exchange. The extreme variety of rocks which apparently obey the geothermometer, 2) mass flux calculations at one site (Seikan tunnel), 3) lack of evidence for equilibrium of realistic mineral assemblages in model calculations, and 4) experimental studies, all suggest that either very wide varieties of reactions coincidentally lead to the same ranges of values of β, K^* and h, or that the geothermometer reflects a coincidentally ubiquitous steady state set by competing, non-equilibrium reactions.

This is encouraging in the sense that it suggests an extremely wide range of possible applications for chemical geothermometers – beyond contexts in which feldspars are likely to control chemistry. On the other hand, these observations are disturbing because they emphasize how little we understand the mechanisms underlying the geothermometer and this in turn implies that we cannot state with confidence when a geothermometer will be accurate and when it will fail. All of this reinforces the advice of earlier workers that agreement among several geothermometers, interpreted with maximum understanding of the site is essential.

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TABLE 1. Chemical Geothermometry for Three Thermal Waters from Taiwan.

	Tuchang Field		
	Jentze Spr.	Well IT4	Lushan Spr.
Discharge temp, °C	98	144[a]	88
Na/K temp[b]	112	106	134
Na/K/Ca temp	147	140	153
Na/K/Ca/Mg	144	66	49
Quartz temp (Fournier)	155	164	141
Quartz temp (MNQL98)[c]	140	145	120
MNQL98 equilibration temperature range[c] and mineral assemblage	140-150 quartz albite K-spar analcime kaolinite	125-150 quartz albite K-spar analcime kaolinite calcite	110-120 quartz albite K-spar kaolinite muscovite

Notes: a. bore-hole maximum temperature

   b. see text for references and calibration

   c. probably low by 15 to 20 degrees, see Appendix 1.

TABLE 2a. "Isothermal" Estimates of β and Log (K^*) for Andesites, Serpentines and Limestones

Temperature, deg C	n	r	β	$\bar{P}(4/3)$	P(1.0)	Log(K^*)
Andesites						
5-32	16	.96	1.09	-(98)	-(70)	2.99
77-100	5	.90	1.03	-(60/70)	+	0.82
Serpentines						
17-52	4	.94	0.98	-(70/80)	+	1.55
Limestones and dolomites						
13-24	15	.90	0.90	-(99)	-(80)	2.80

Temperature = discharge temperature

n = number of cases considered

r = correlation coefficient

P(i) = positive if, by t test, cannot reject hypothesis that beta = 1 at any level of confidence greater than 50%

P(i) = negative if can reject same hypothesis at level of confidence in ()

TABLE 2b. Estimates of β, log (K^*), and h for Three Individual Rock-Types, Assuing Reaction 1.

	Temp	n	r	β	$\log(K^*)$	h	Note
Andesites	5–100	23	.85	1.13+.16	2.84	−13.9+2	
Limestones	10–49	22	.87	0.91+.18	2.60	−12.6+3	
Mixed	0–100			1.33	3.28	−7.5	(1)
	100–400			0.33	3.28	−7.5	(1)
	multiple regression results						
Andesites	5–32	16	.96	1.09	2.99		
	77–100	5	.90	1.03	0.82		
Serpentinites	17–52	4		0.98	1.55		
Limestones and dolomites	13–24	15	.90	0.90	2.80		
	"contant temperature" results						

n = number of cases considered

r = correlation coefficient

h = estimate of reaction enthalpy

Notes: 1.

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TABLE 3. Equilibrium Constants and Enthalpies of Reaction for
Illustrative Ion Exchange and Indicator Reactions

Reaction	β	Note 1	Log(K)	kcal/equiv.	Source (Note)
1. $NaZ + K^+ = KZ + Na^+$					
Z = montmorillonite		K'_N	.15 to .79	-.6 to -1.16	1,2
synth, zeolites		K'_N	-.1 to +.6	-1.4 to -2.4	3
chabazite		K'_N	1.2 to 1.3	-2.6	3
2. albite + K^+ = K-spar + Na^+		K	3.13	-6.81	4
3. $1/2CaZ + K^+ = KZ + 1/2Ca^{2+}$	1.0	K'_N			
Z = mont., ill., kaol., verm., musc.			-.1 to + 1.17	--	1
montmorillonite			-.6 to + .7	-.8 to -5.9	1,2(2)
synth zeolites			-2.2 to + .4	-2. to - 5.1	3(2)
4. 1/2 wairakite + Qz + Na^+ = albite + $1/2Ca^{2+} + H_2O$		K	2.26	-8.0	4
5. 1/2 wairakite + Qz + K^+ = K-spar + $1/2Ca^{2+} + H_2O$	1.0	K	5.5	-14.9	4
6. 2/3 anorth + 8/3Am + K^+ + 1/3 Na^+ = albite + $1/2Ca^{2+} + H_2O$	4/3	K	5.29	-18.9	4
7. 1/6 anorth + 2/3 Qz + K^+ + 2/3 albite = K-spar + 1/6 Ca^{2+} + 2/3 Na^+	1/3	K	1.34	-5.62	4

Sources: 1. Bruggenwert and Kamphorst, 1979; 2. Maes and Cremers, 1979; 3. Breck, 1974;
4. Helgeson et al., 1978.

Notes: 1. K'_N = equilibrium constant written in terms of equivalent fractions of adsorbed ions and molar
concentrations of dissolved ions. Variation includes effects of differences in solids, solution-
phase non-ideality, and non-ideality in behavior of adsorbed species, i.e. effects of loading.
K = normal thermodynamic equilibrium constant.

2. Equilibrium constants and enthalpies calculated by combining data for reaction 1 with data for
NaZ + 1/2Ca(2+) = 1/2CaZ + Na(+); all data from indicated sources.
Qz = quartz, Am = amorphous silica, anorth = anorthite.

Table 4. Mineral compositions in wt% of starting rocks from agitated and flow through experiments.

	Microcline Delaware Co.,PN	Oligoclase Risor, Norway	Analcime Lane Co.,OR	Na-K zeolite Synthetic
SiO_2	64.57	64.89	54.5	44.0
Al_2O_3	18.31	21.36	22.45	21.6
FeO	0.00	0.09	0.01	---
MgO	0.00	0.00	0.00	---
CaO	0.01	2.45	0.02	---
Na_2O	0.91	9.98	13.56	2.86
K_2O	15.19	0.39	0.03	18.1
BaO	0.06	0.03	0.02	---
H_2O^+	---	---	9.39[*]	6.86
H_2O^-	---	---	---	6.58[*]
Total	99.07	99.12	100.00	100.00

* By difference

Table 5. Concentrations of Na and K as well as log Na/K and Na/K temperatures for agitated experiments reacting feldspars at temperatures from 75 to 300°C.

Experiment (temperature)		Duration (hrs)	pH	Na (ppm)	K (ppm)	log Na/K	Na/K temperature
Oligoclase	1	0	6.86	40.9	4.09	1.0	183
Microcline	2	24	7.06	39.1	3.35	1.07	166
(75°C)	3	120	7.71	36.9	4.2	0.943	199
	4	336	7.98	39.5	5.6	0.846	229
	5	600	---	43.0	8.1	0.722	273
	6	1008	8.25	43.7	6.8	0.808	241
(150°C)	7	1008	8.01	46.3	6.5	0.85	228
"	8	1014	---	45.3	8.53	0.725	272
"	9	1038	7.74	45.0	8.03	0.748	263
"	10	1172	7.72	47.3	8.09	0.767	256
"	11	2276	---	52.3	7.36	0.852	227
Oligoclase	1	0	6.87	51.7	19.2	0.43	414
Microcline	2	24	7.12	65.3	18.0	0.558	344
(300°C)	3	168	7.01	64.2	18.6	0.548	349
	4	172	---	61.8	15.4	0.603	323
(150°C)	5	174	---	62.7	16.0	0.613	318
	6	175	---	58.9	17.0	0.538	354
	7	192	---	66.1	18.5	0.528	347
	8	198	7.42	59.9	15.0	0.599	325
	9	222	8.05	62.4	14.5	0.632	310
	10	342	8.16	61.4	13.3	0.662	297
	11	630	---	60.8	11.2	0.742	268
	12	1398	8.34	60.0	10.8	0.742	265
Oligoclase	1	0	7.42	49.2	9.7	0.705	279
Microcline	2	18	7.59	52.2	14.7	0.552	347
(225°C)	3	42	---	53.5	15.3	0.544	351
	4	90	8.04	53.5	15.2	0.545	351
	5	162	8.38	56.4	14.4	0.591	329
	6	402	8.58	58.3	15.1	0.587	330
	7	666	8.67	60.7	16.7	0.560	343
	8	1530	8.65	60.0	13.4	0.651	302
	9	1866	8.71	59.4	15.8	0.575	336
	10	2250	8.64	60.4	14.1	0.630	311
	11	2586	8.63	60.2	13.1	0.663	296
	12	2586	8.68	60.4	11.1	0.733	268

Table 6. Concentrations of Na and K as well as log Na/k and Na/K
temperatures for agitated experiments reacting zeolites
at 75°C, 200 bars pressure.

Experiment		Duration (hrs)	pH	Na (ppm)	K (ppm)	log Na/K	Na/K temperature (°C)
K-Na zeolite	1	0	10.4	28.8	42.5	-.169	1190
(75°C)	2	24	10.9	33.4	93.7	-.448	2810
"	3	68	10.9	34.6	93.6	-.432	2628
"	4	148	10.9	34.4	93.7	-.435	2661
"	5	388	10.9	34.9	95.3	-.435	2666
"	6	652	11.0	35.5	98.7	-.444	2763
K-Na zeolite	1	0	10.1	53.4	37.4	0.1547	636
analcime	2	24	10.3	---	---	---	---
(75°C)	3	168	10.3	43.2	63	-.164	1176
"	4	336	10.3	42.2	62.9	-.1733	1202
"	5	552	10.3	63.3	64.9	-.0108	854
"	6	864	10.3	31.4	65.0	-.316	1750
"	7	3192	10.1	42.6	84.8	-.299	1664
(150°C)	8	3288	10.2	43.0	126.3	-.468	3076
"	9	3720	10.2	44.1	124.9	-.452	2856

Table 7. Steady state concentrations of Na and K as well as log Na/K
and calculated Na/K temperatures for flow through experiments
at temperatures of 90 and 200 C.

Flow rate ml/min	Temp. C	Core Length (in)	Na	K	log Na/K	Na/K temperature
1.0	90	6	39.2	.116	2.5	−30.3
0.5	90	6	39.8	.18	2.31	−15.1
0.05	90	6	40.2	.334	2.04	10.0
0.01	90	6	39.9	.47	1.89	26.1
1.0	90	18	37.0	.19	2.29	−13.19
0.5	90	18	37.0	.20	2.27	−11.26
0.1	90	18	36.3	.321	2.05	9.08
0.005	90	18	39.9	5.1	0.89	214.6
0.001	90	18	44.4	10.1	0.643	305.4
1.0	90	60	37.2	.218	2.23	−8.1
0.5	90	60	38.8	.248	2.19	−4.6
0.1	90	60	37.0	.350	2.02	12.5
0.005	90	60	44.7	5.78	0.88	216
0.001	90	60	45.4	10.0	0.657	299
1.0	200	18	43.2	8.36	0.713	276.6
0.1	200	18	47.2	12.95	0.562	342.6
0.01	200	18	51.6	17.9	0.46	396.6
0.001	200	18	55.7	22.1	0.401	432.3
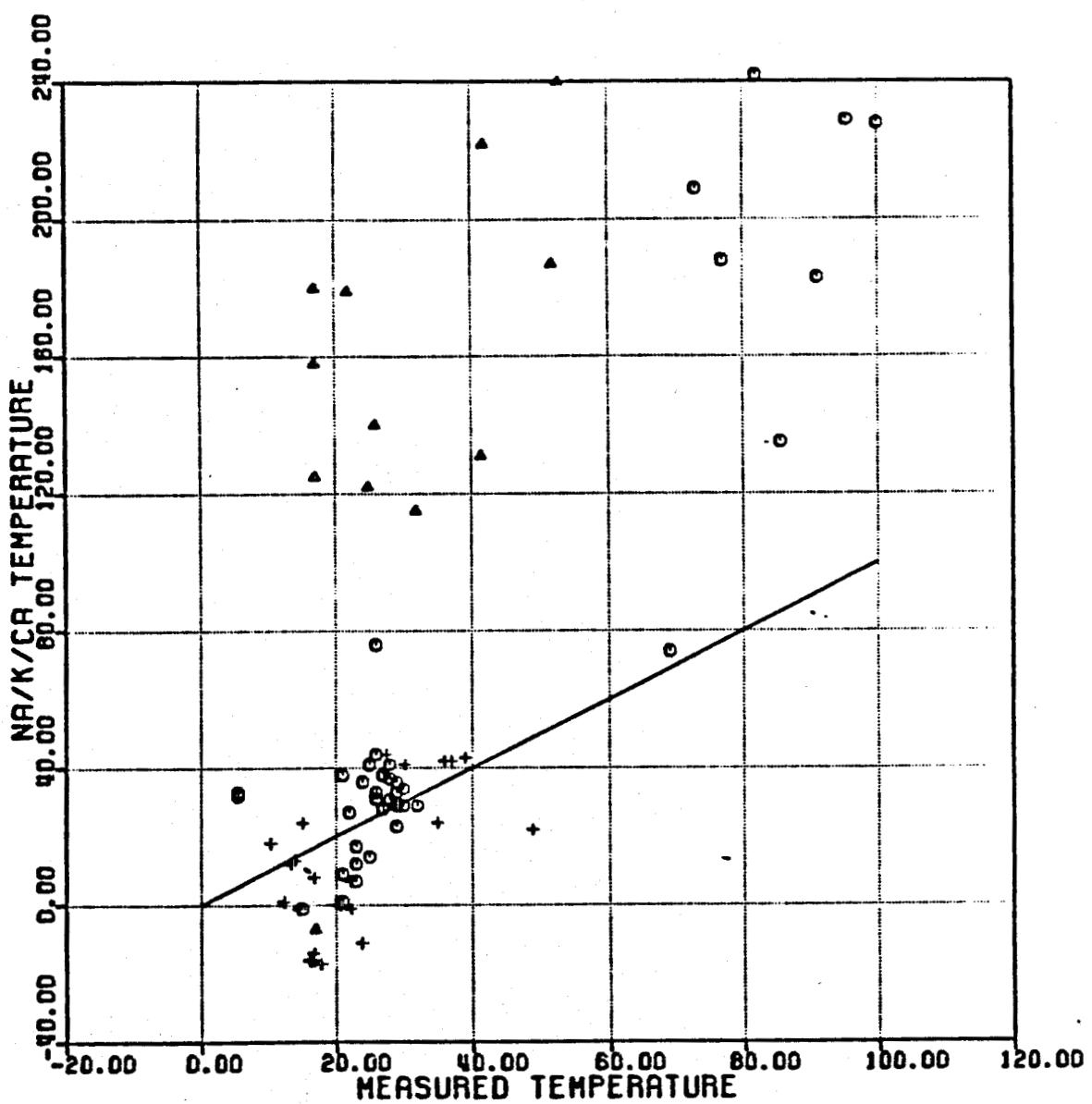
Figure 1. Na-K-Ca Geothermometer: Comparison of predicted and discharge temperatures for natural thermal waters.(see text for sources.)
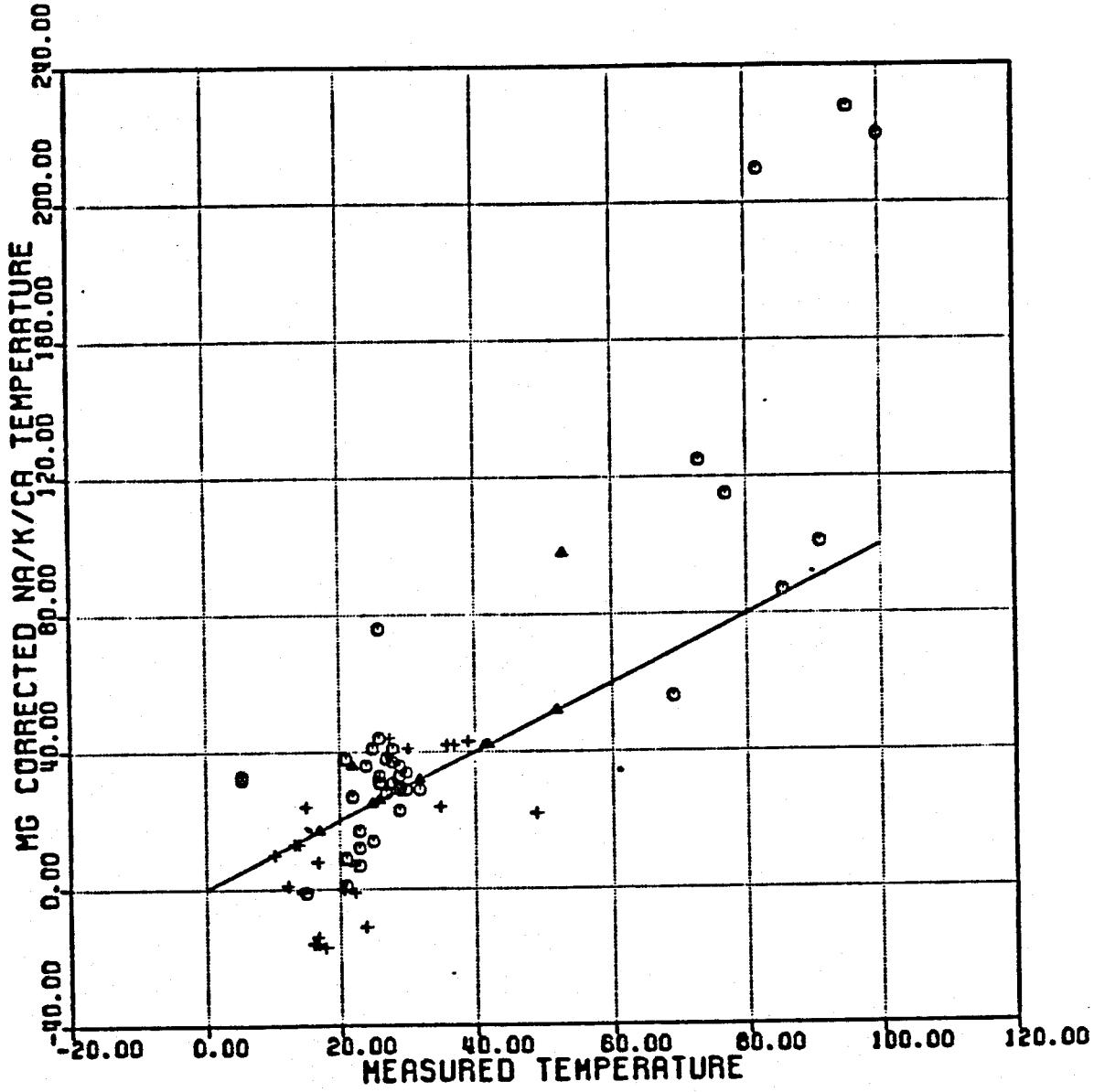
Figure 2. Na-K-Ca Geothermometer with Mg correction: Comparison of predicted and discharge temperatures.
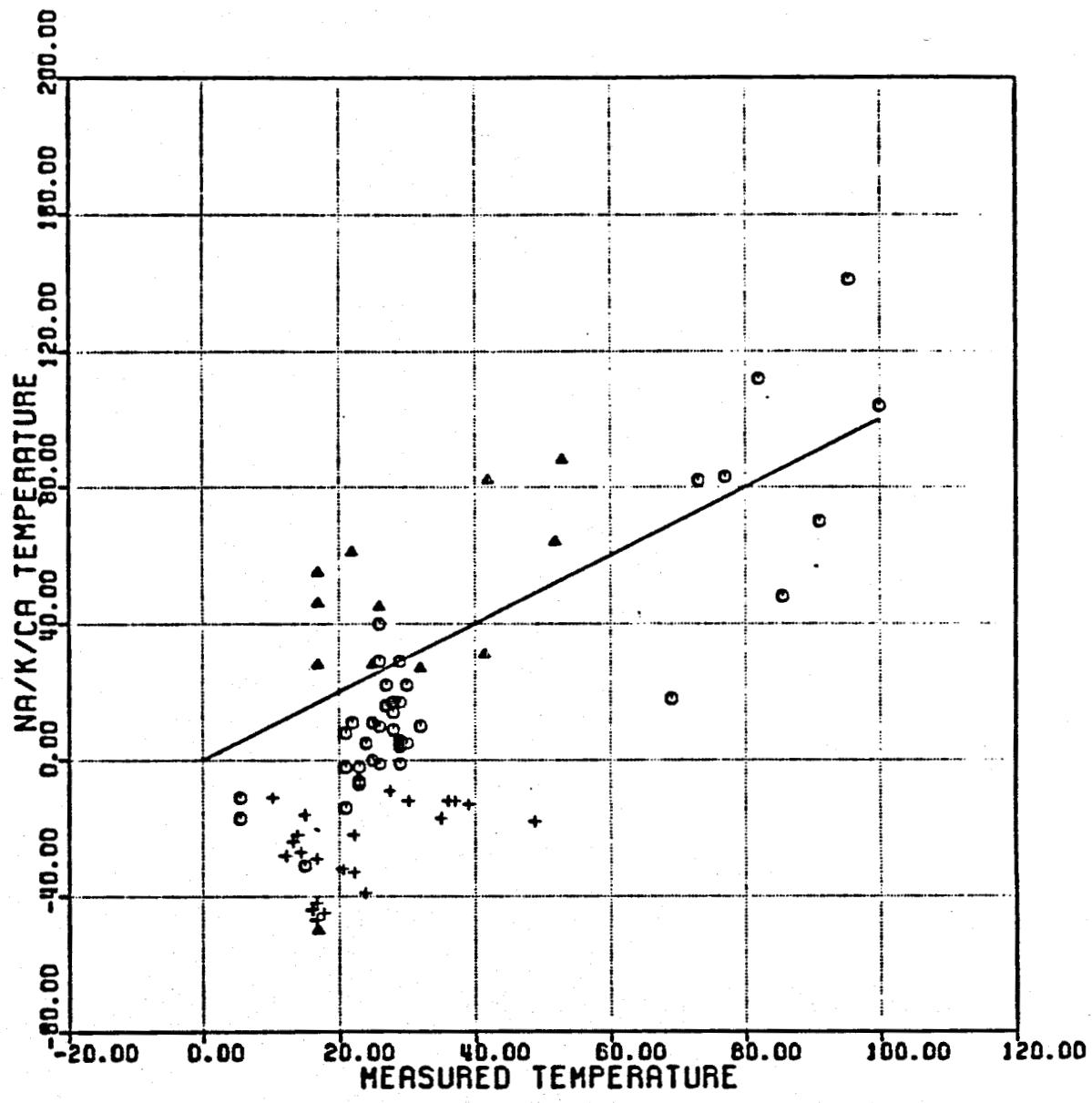
Figure 3. Na-K-Ca Geothermometer, CO_2 corrected:
Comparison of predicted and discharge temperatures

IMPOSED TEMPERATURE, DEG C
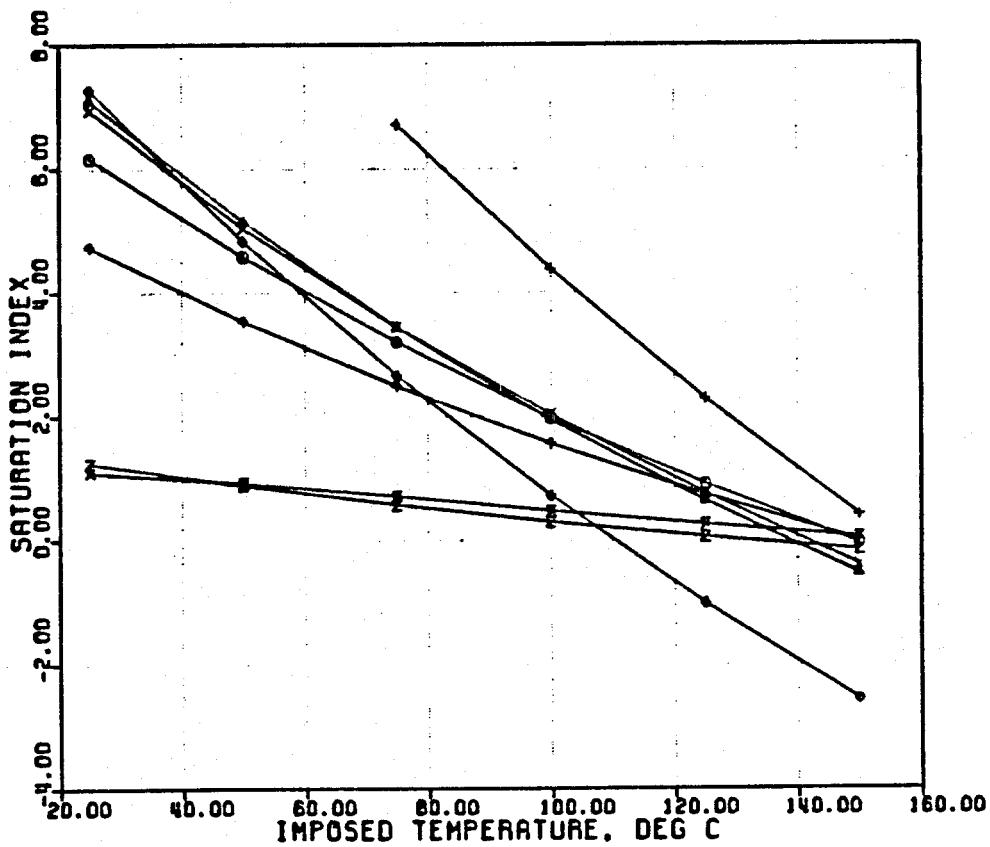
SATURATION INDEX

⊙	ALBITE	NA-K-CA TEMP = 135
▲	ORTHOCLASE	QUARTZ TEMP = 145 (H)
+	MUSCOVITE	QUARTZ TEMP = 133 (F)
✕	KAOLINITE (H)	.NA-K-CA-MG = 87
◇	LAUMONTITE	CO2-NA-K-CA = 48
✦	ANALCIME	DISCH TEMP = 85.5
✕	CALCITE	
Z	QUARTZ	

Figure 4. Temperature dependence of saturation indices: 85.5 $^{\circ}$ water, Te Aroha, North Island, New Zealand (White et al., 1963). A 229 ft. well penetrates alluvium overlying andesite.
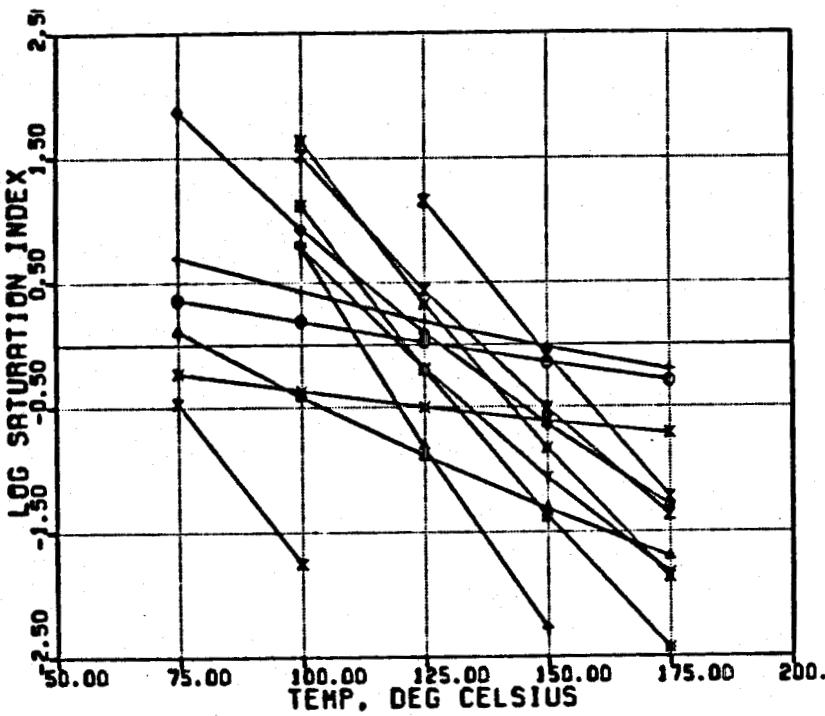
Figure 5. Temperature dependence of saturation indices;
Tuchang geothermal field, Taiwan, Well IT4.

Legend (Figure 5):
- ⊙ CALCITE.
- ▲ GIBBSITE.
- + QUARTZ.
- × AM-SILICA.
- ◆ ANALCIME.
- ✦ LAUMONTITE.
- ✕ WAIRAKITE.
- Z ALBITE.
- Y HIGH ALBITE.
- × K-SPAR.
- ✳ KAOLIN-H.
- ✕ KAOLIN-R.
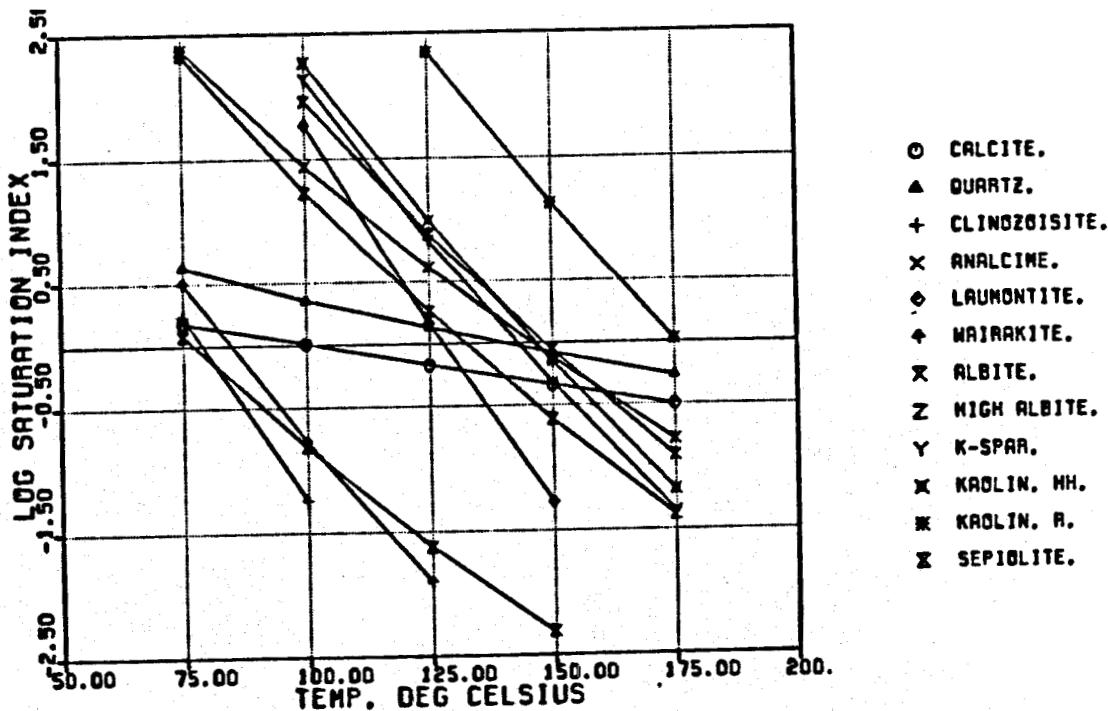
Figure 6. Temperature dependence of saturation indices;
Tuchang geothermal field, Taiwan, Jentze Spring

Legend (Figure 6):
- ⊙ CALCITE.
- ▲ QUARTZ.
- + CLINOZOISITE.
- × ANALCIME.
- ◆ LAUMONTITE.
- ✦ WAIRAKITE.
- ✕ ALBITE.
- Z HIGH ALBITE.
- Y K-SPAR.
- × KAOLIN, HH.
- ✳ KAOLIN, R.
- ✕ SEPIOLITE.

40
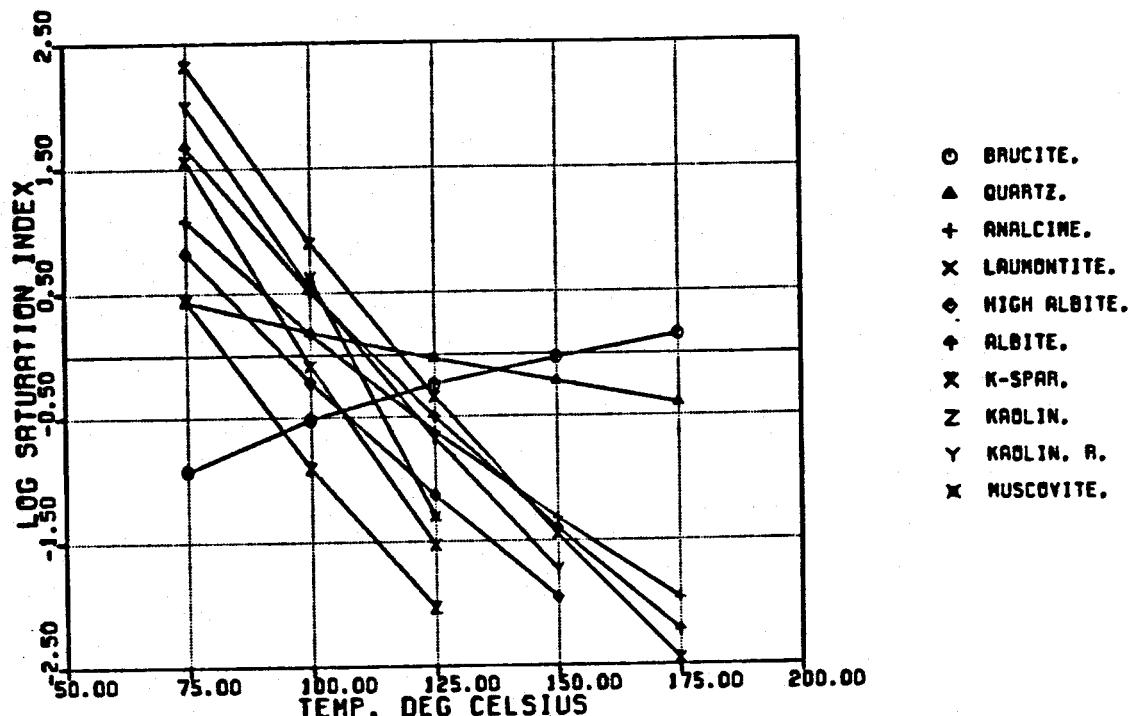
-Figure 7. Temperature dependence of saturation indices;
Geothermal waters of Taiwan, Lushan Spring

Legend for Figure 7:
- ⊙ BRUCITE.
- ▲ QUARTZ.
- + ANALCIME.
- ✕ LAUMONTITE.
- ◆ HIGH ALBITE.
- ♠ ALBITE.
- ✕ K-SPAR.
- Z KAOLIN.
- Y KAOLIN. R.
- ✕ MUSCOVITE.

Legend for Figure 8:
- ⊙ CL BELOW 80 PPM
- ▲ CL 81-199 PPM
- + CL 200-299 PPM
- ✕ CL 300-399 PPM
- ◆ CL 400-499 PPM
- ♠ CL ABOVE 500 PPM
- ✕ SEAWATER. RILEY AND CHESTER (1971)
- Z LST SQ FIT. NON-CONTAM. WATERS
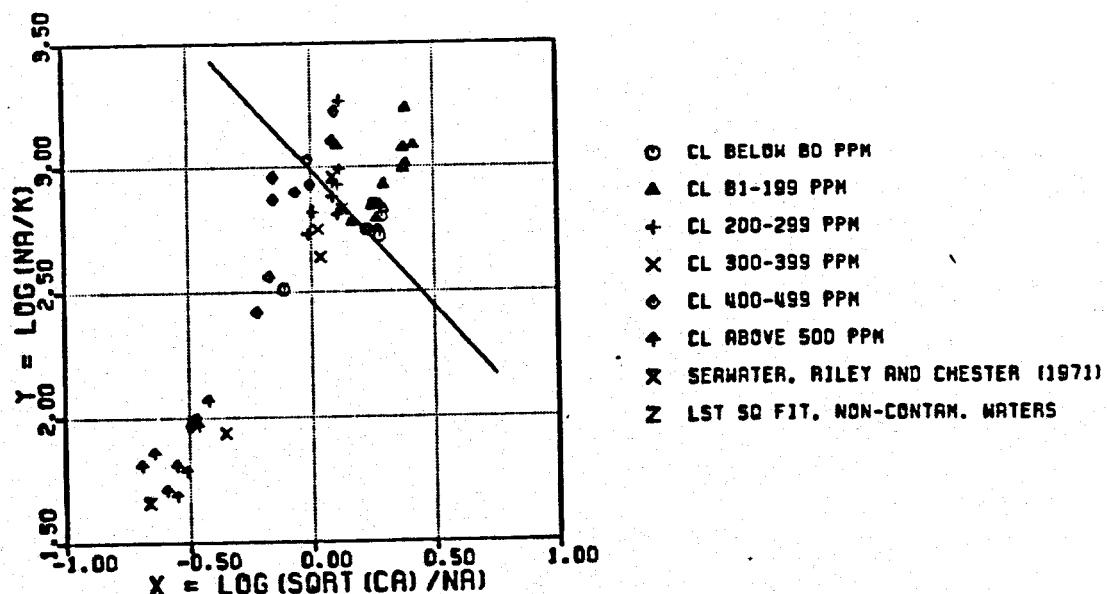
Figure 8. Tests of Equation 6; Seikan Tunnel Andesites,
effects of mixing meteoric and seawater. Solid line
represents least squares trend of uncontaminated meteoric
waters alone.

41
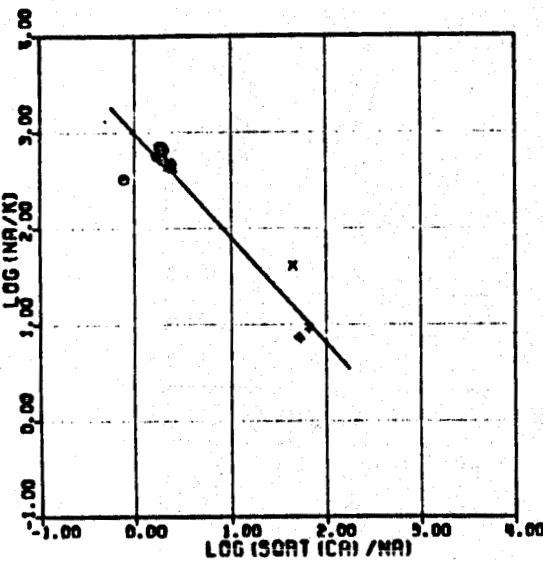
SEKI ET AL. 1980; SEIKAN TUNNEL, CL BELOW 80 PPM
SEKI ET AL. 1980; BORE HOLE B-B, CL BELOW 80 PPM
+ WELLS ET AL. 1977; SILICA SPRINGS, NEW ZEALAND
X WHITE ET AL. 1963; ASHBORO, NORTH CAROLINA
LST SQ FIT: Y VS X, BETA: 1.09

Figure 9: Estimation of beta and K*, Andesites, 5 to 32°C, solid line is least squares fit to all points.

WHITE ET AL. USGS PP 440-F; PH BELOW 9
WHITE ET AL. 1963; PH ABOVE 6

Figure 10: Estimation of beta and K*, Andesites, 60 to 73°C
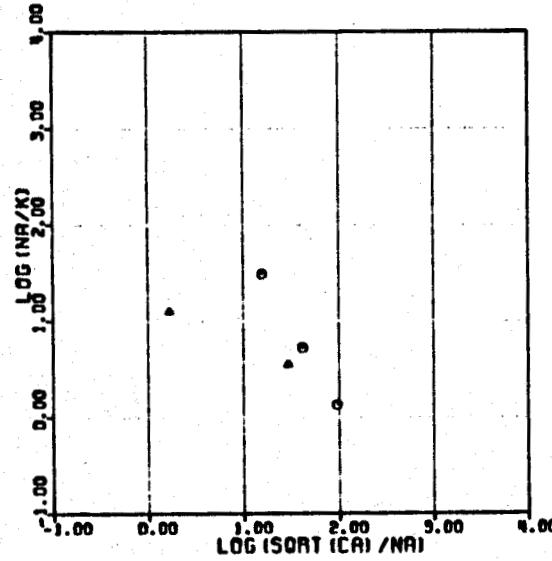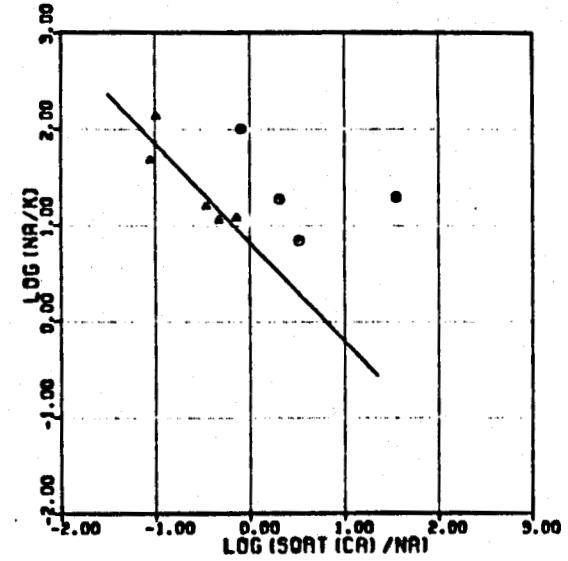
WHITE ET AL. 1963; PH BELOW 3.5
WHITE ET AL. 1963; PH ABOVE 5
LST SQ FIT: Y VS X; BETA = 1.09

Figure 11: Estimation of beta and K*, Andesites, 77 to 100°C, only waters of pH above 5 included in least squares fit (solid line).
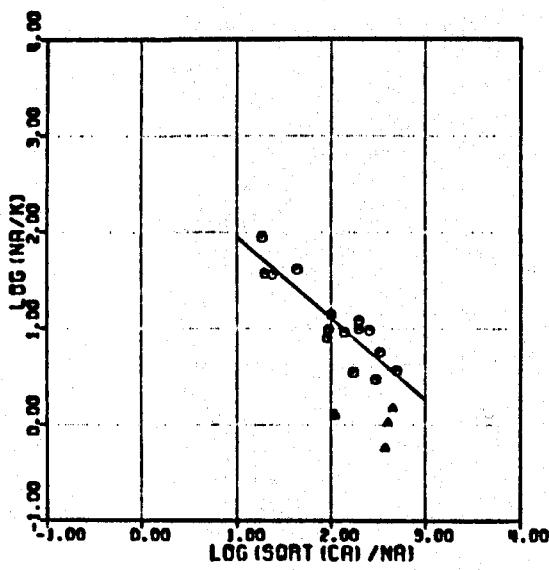
○ WHITE ET AL., 1963
▲ HELZ AND SILEX, 1974
    LST. SQ. FIT, OMITTING HELZ DATA, SEE TEXT

Figure 12: Estimation of beta and K^*, Limestones, 12 to 24°C.
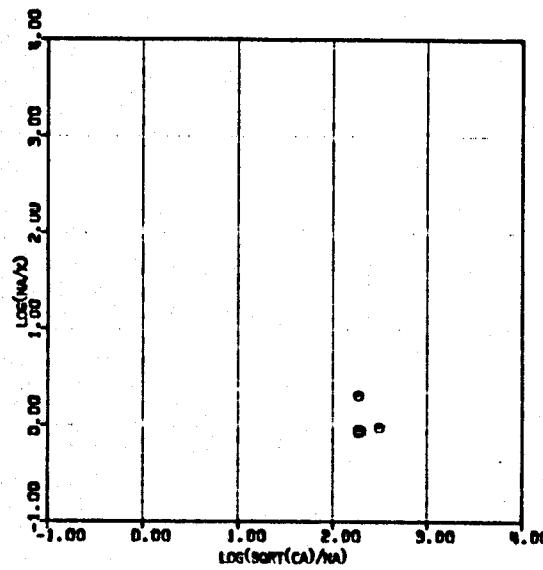
Figure 13: Estimation of beta and K^*, Limestones, 28 to 50°C.
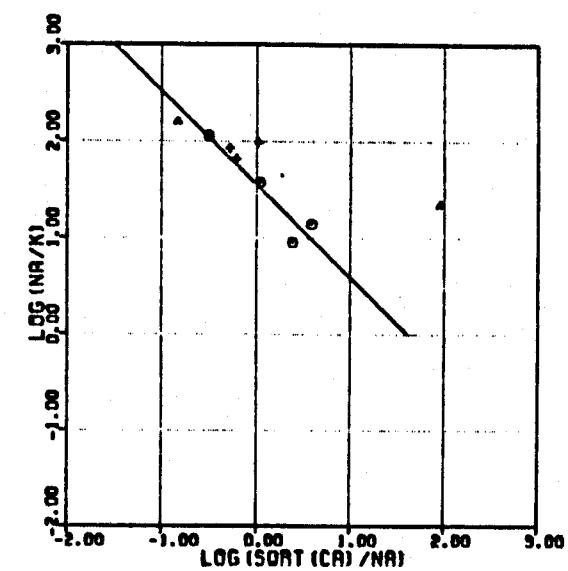
○ BARNES ET AL. 1973; AQUIFER SERP. ALONE
▲ BARNES ET AL. 1973; AQUIFER SERP. PLUS GRAYWACKE
+ WHITE ET AL. 1963; SERP., SANDSTONES AND SHALES
    LST. SQ. FIT, 'PURE' SERP. ONLY

Figure 14: Estimation of beta and K^*, Serpentines, 17 to 52°C.
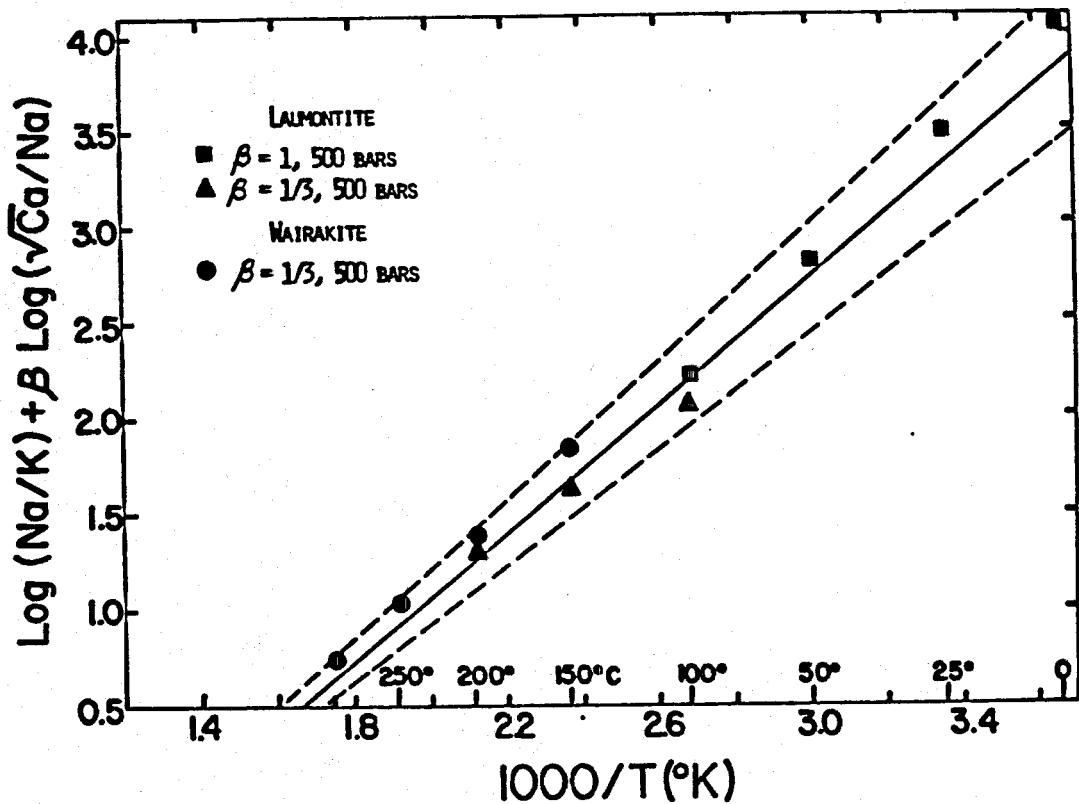
Figure 15. Calculated Na-K-Ca geothermometry relations for 2 feldspars
and laumontite or wairakite reactions (see text). Solid and
dashed lines are empirical curves from Fournier and Treusdell(1973).
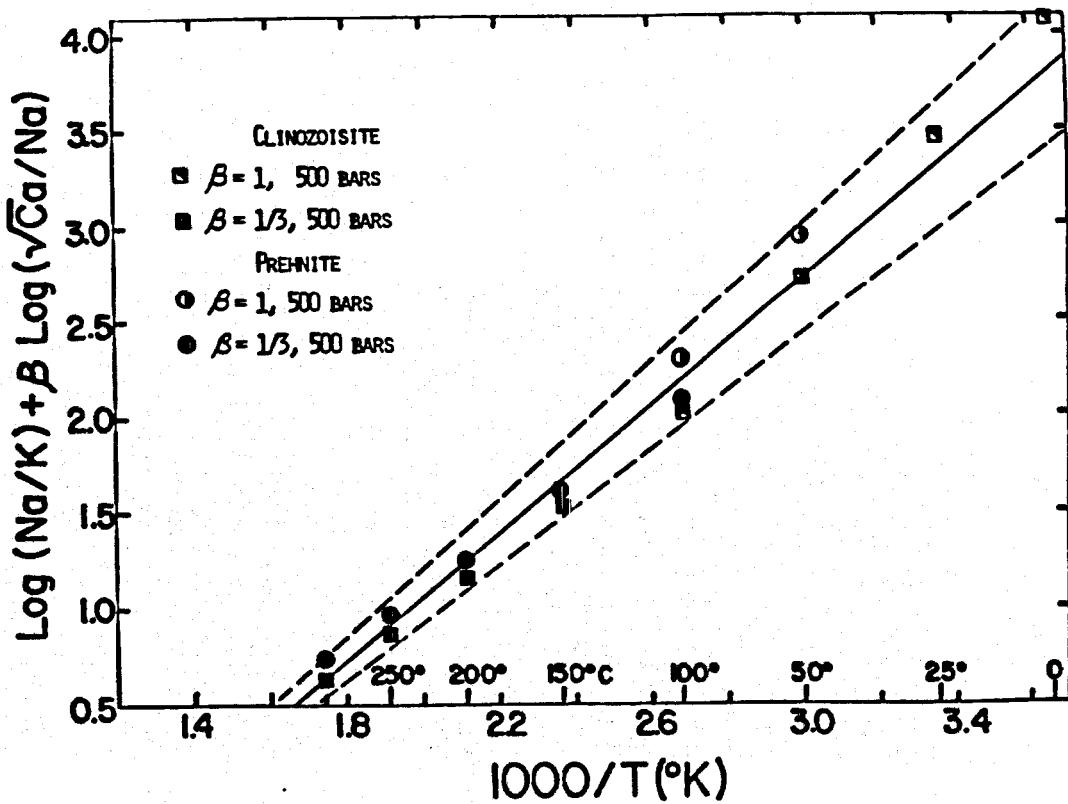
Figure 16. Calculated Na-K-Ca geothermometry relations for 2 feldspars
and clinozoisite and prehnite reactions. Solid and dashed
lines are empirical curves from Fournier and Truesdell(1973).
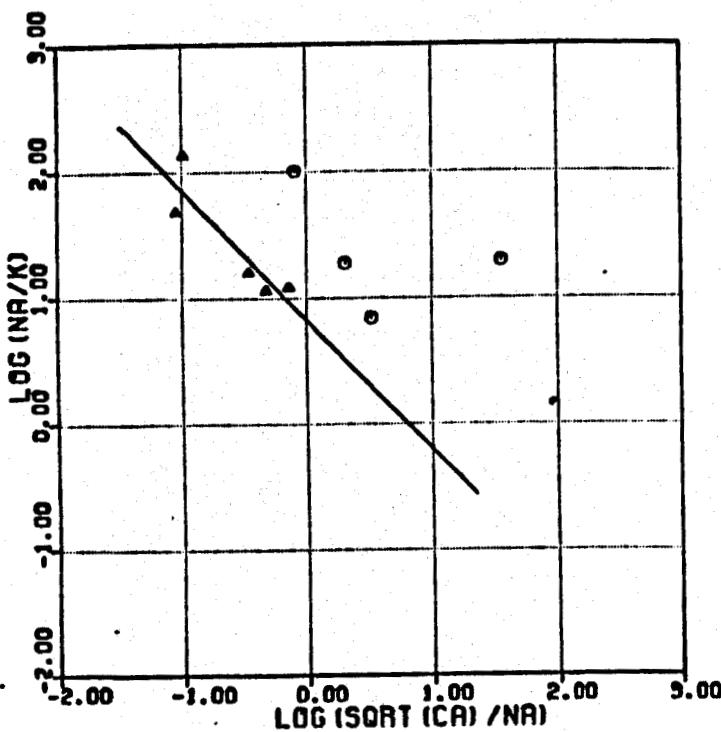
Figure 17. Estimation of beta and K* using raw, total metal concentrations in equation 6. Andesites, 77 to 100°C. Solid line is least squares fit to data for which pH is above 5.
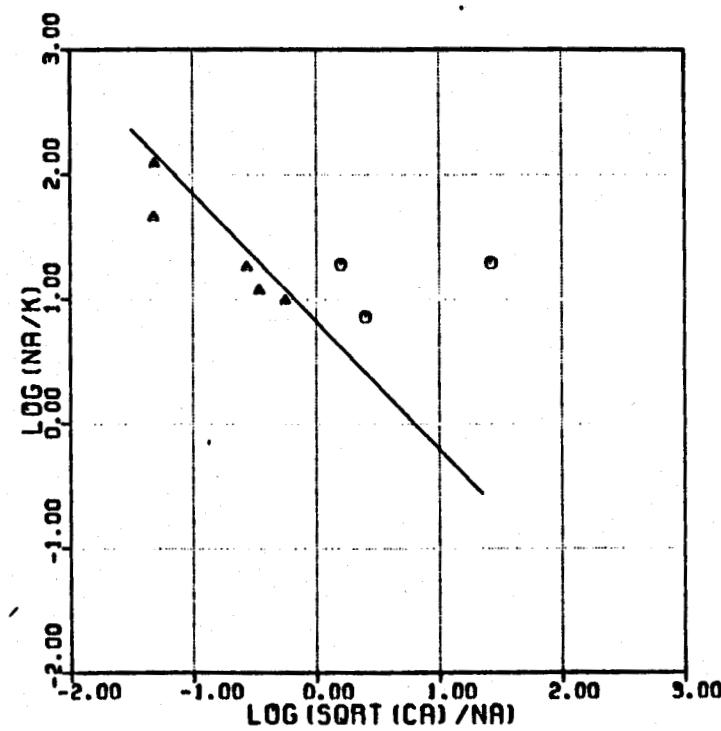
Figure 18. Estimation of beta and K* using computed free ion activities in equation 6. Andesites, 77 to 100°C. Solid line is least squares fit to data for which pH is above 5.
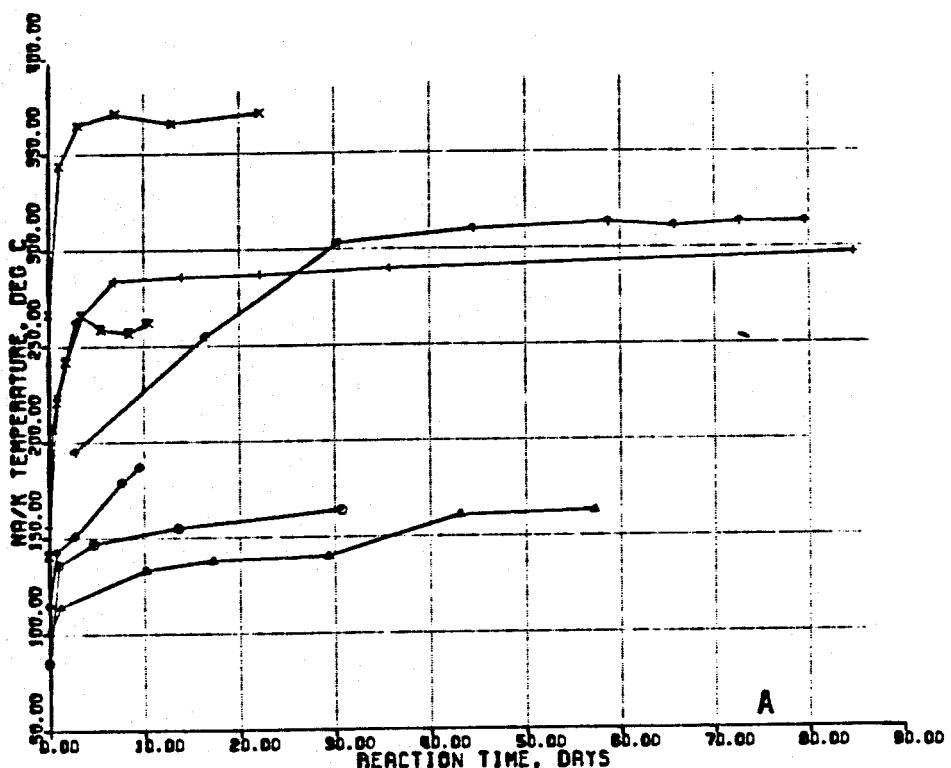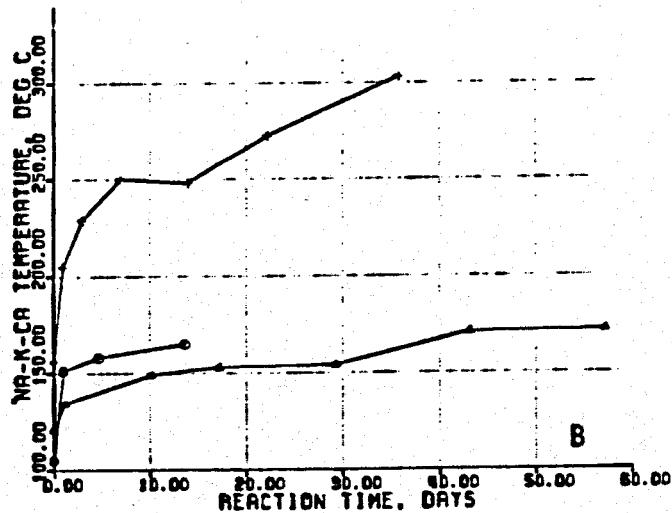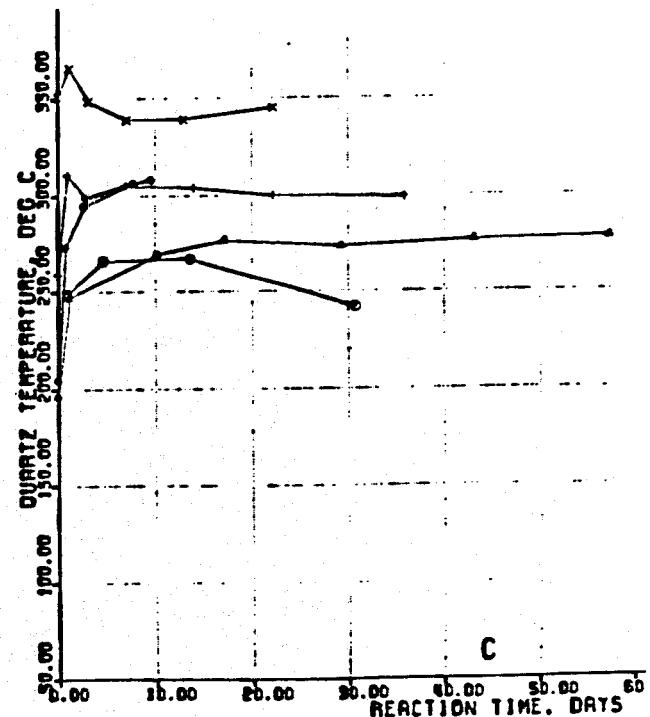
Figure 19. Evolution of geothermometer temperatures.
Holocrystalline and glassy andesites (Data from unpublished
water-rock experiments by Dickson, Potter, Pohl, and
Guillemette, Stanford University, 1981,1982).
A. Na-K temperature
B. Na-K-Ca temperature
C. Quartz temperature
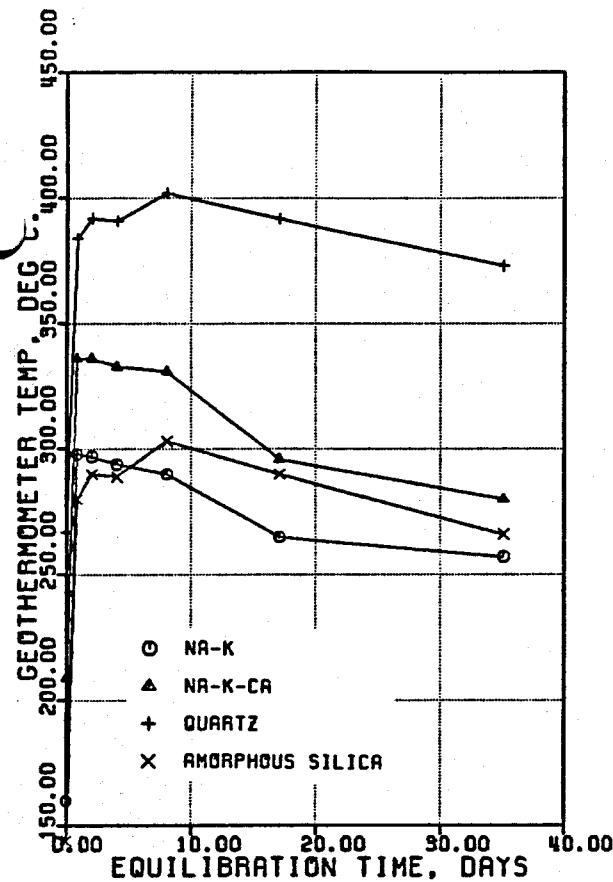
Figure 20. Evolution of geothermometer
temperatures. Basalt (Data from Guillemette,
Stanford University, 1982)
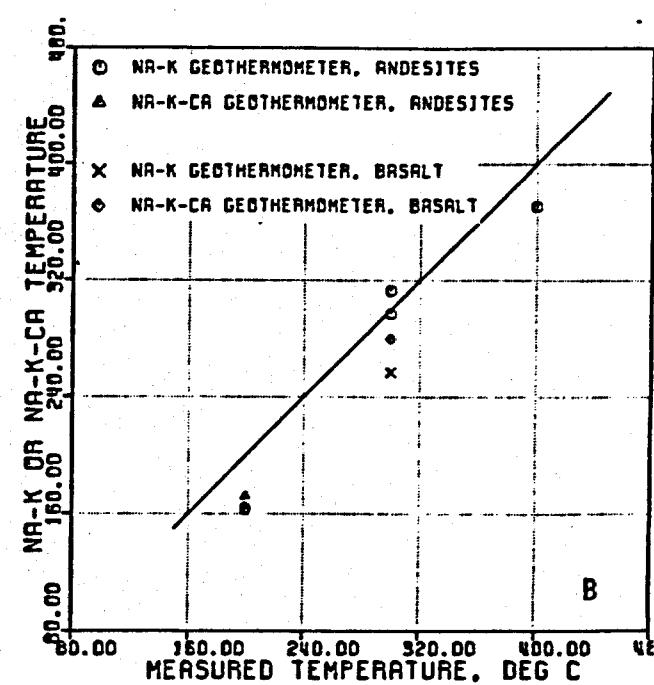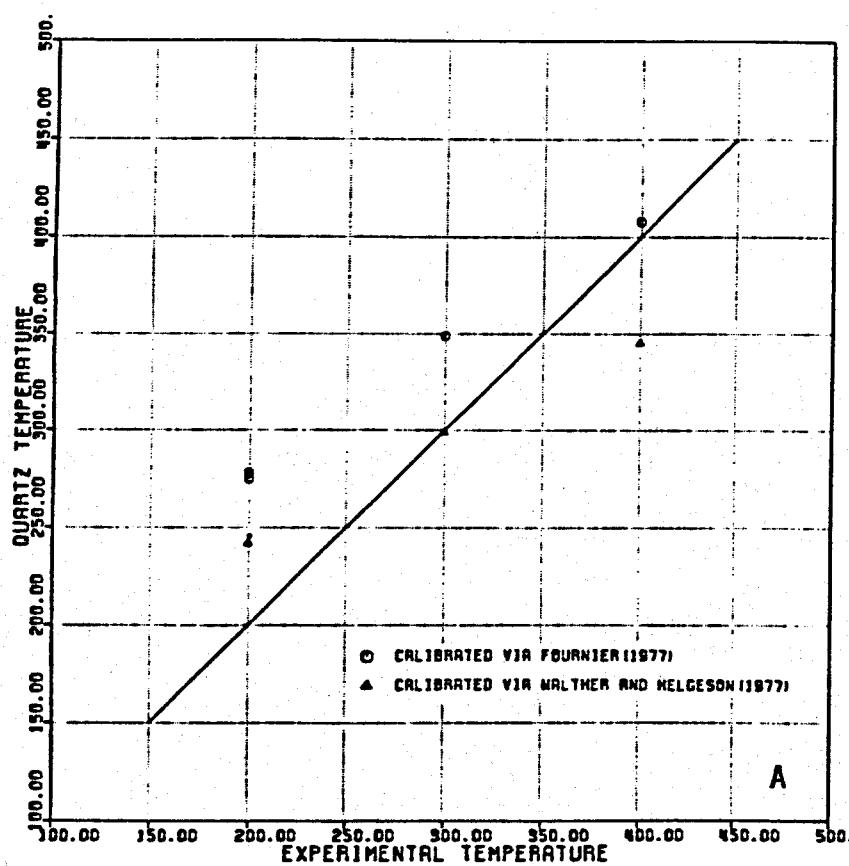
Figure 21. Comparison of Geothermometric and experimental
temperatures for experimental water-rock systems.
A. Quartz temperatures
B. Na-K and Na-K-Ca temperatures
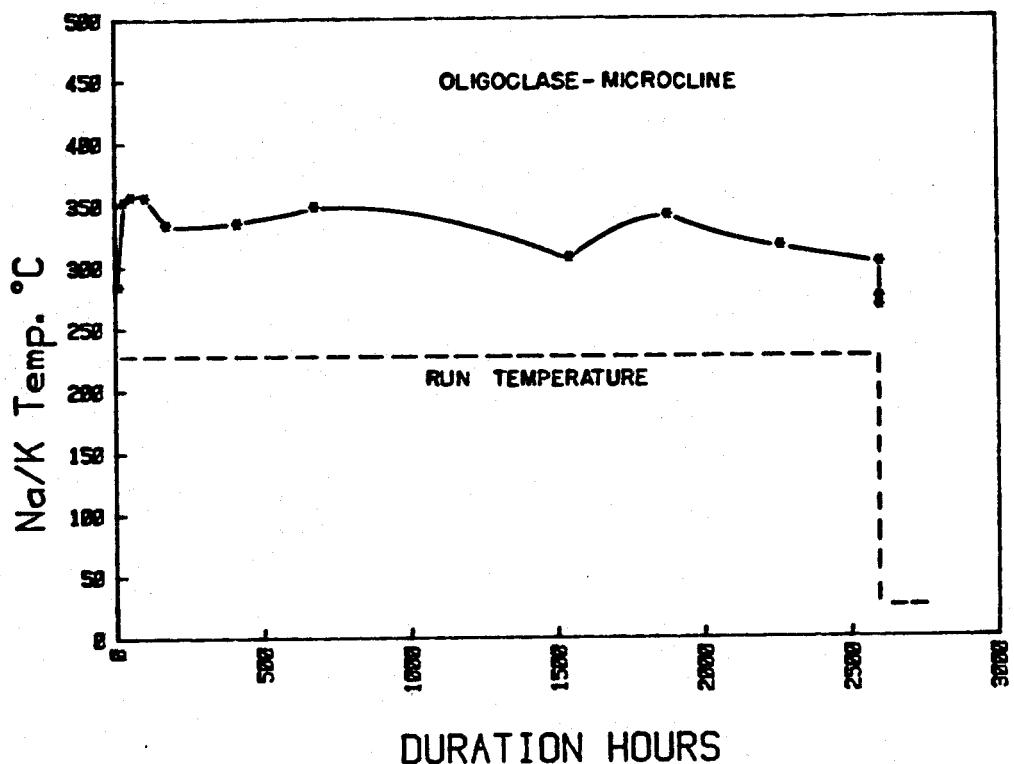
Figure 22. Na/K temperature experimental duration curve for agitated feldspar experiments at 225°C and 200 bars.
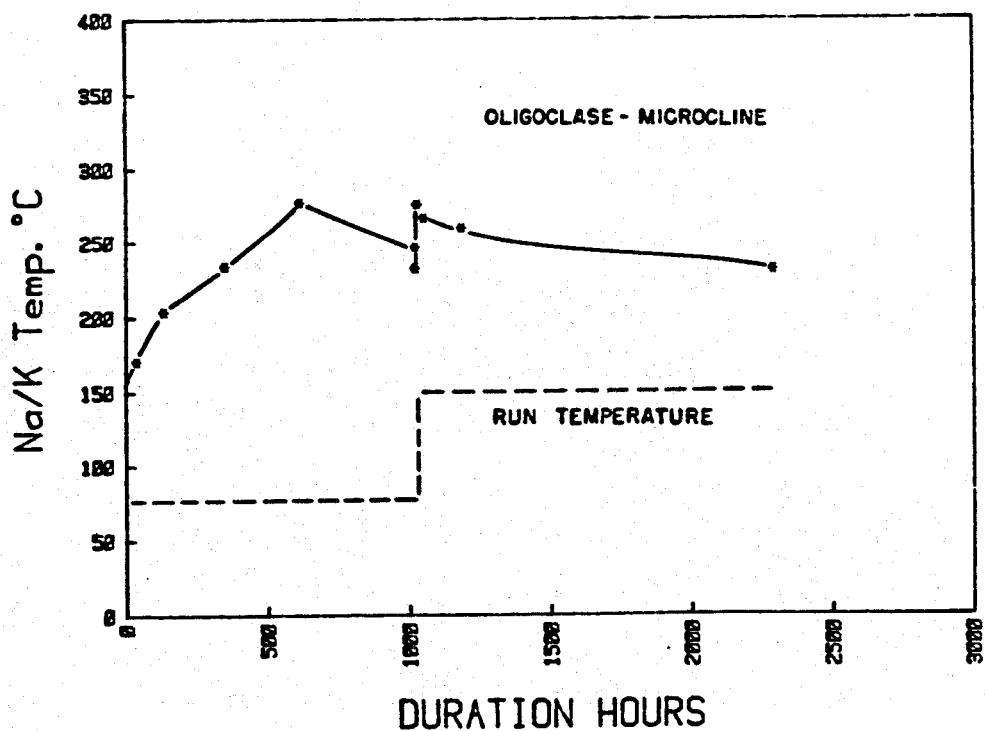

Figure 23. Na/K temperature-experimental duration curve for agitated feldspar experiment at 75 and 150°C, 200 bars.
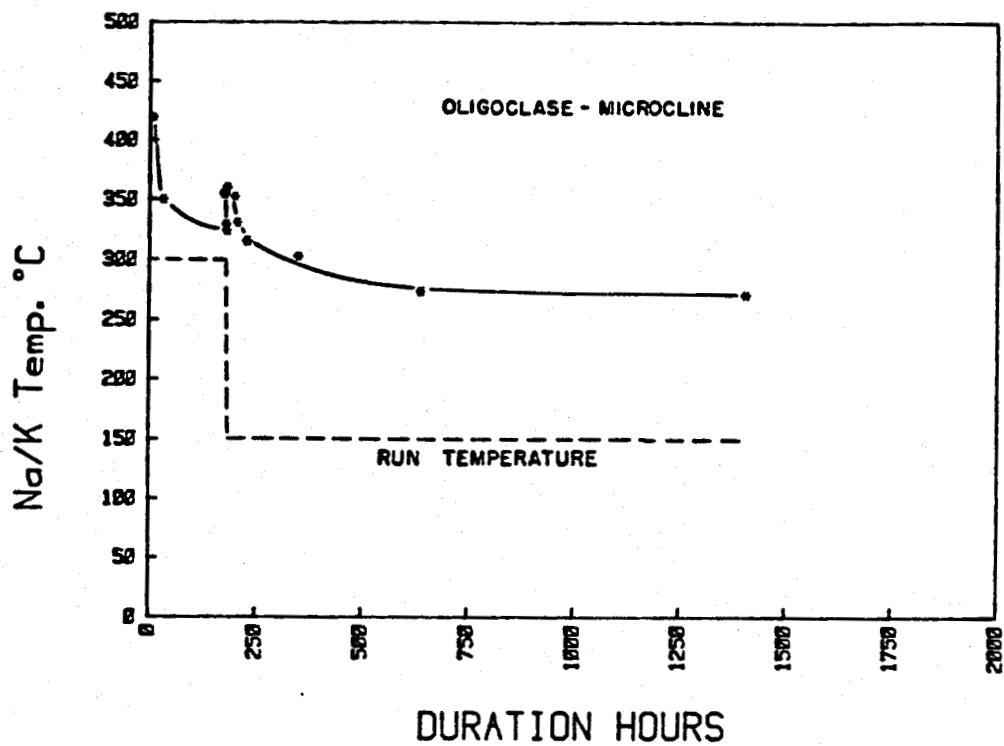
Figure 24. Na/K temperature –experimental duration curve for agitated feldspar experiment at 300° and 150°C, and 200 bars.
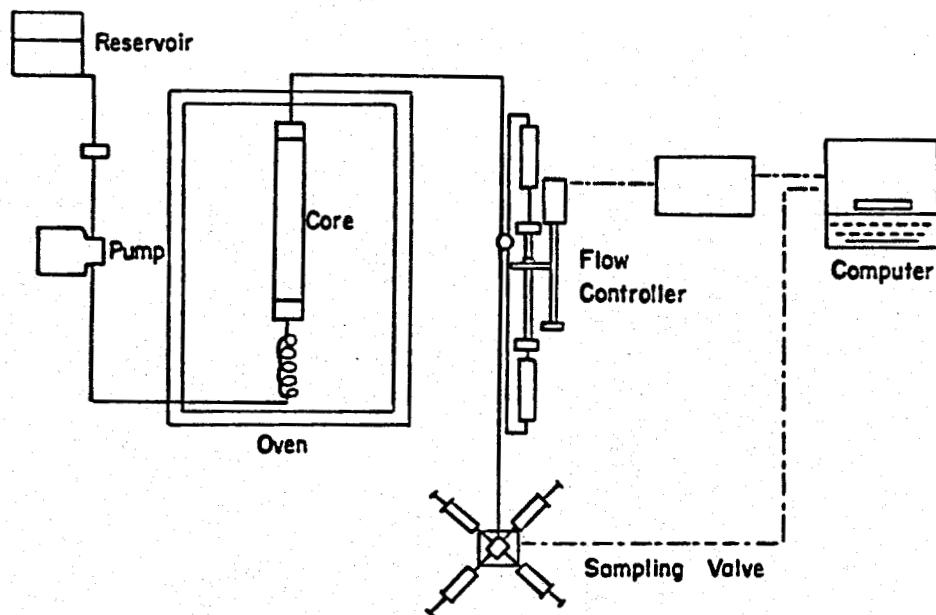

Figure 25. Schematic diagram of experimental flow through apparatus.
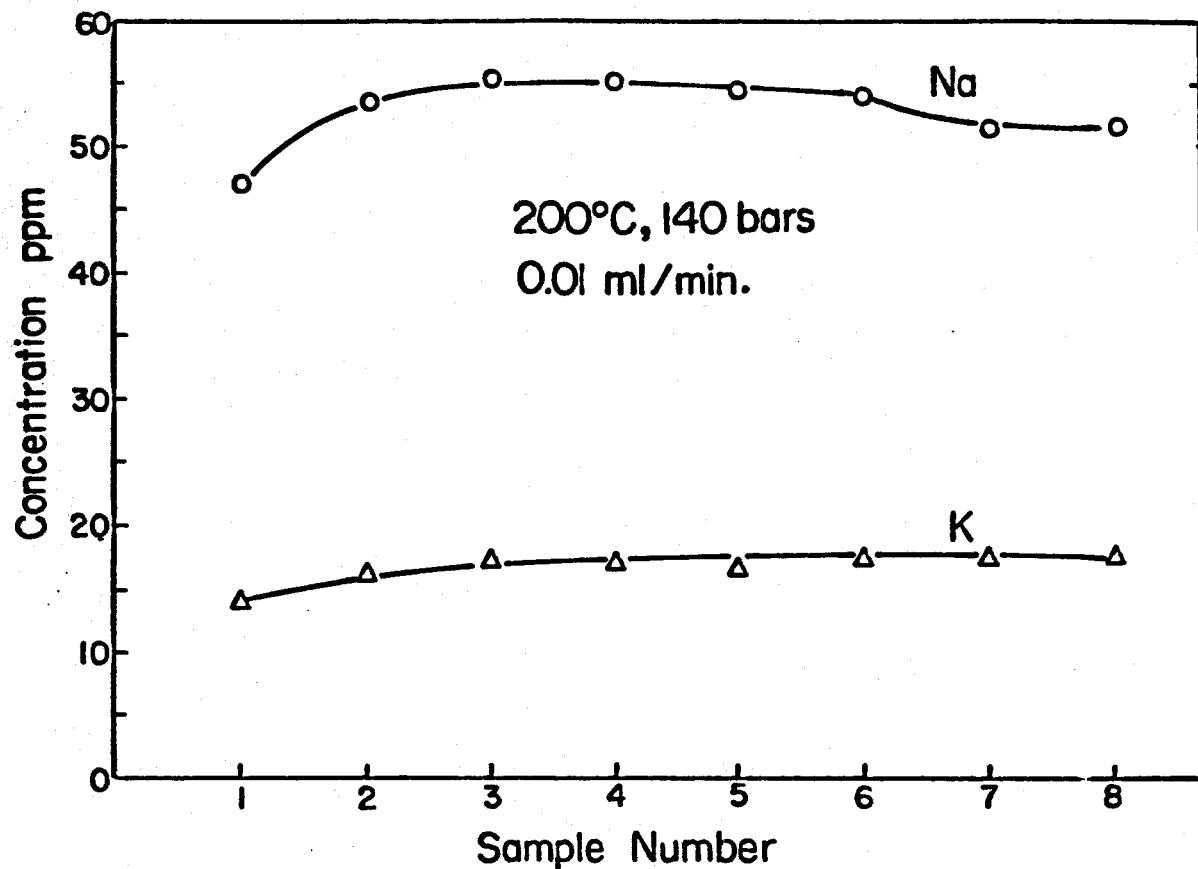
Figure 26. Concentrations of Na and K as a function of sample number for flow through experiment at 200°C, 140 bars.
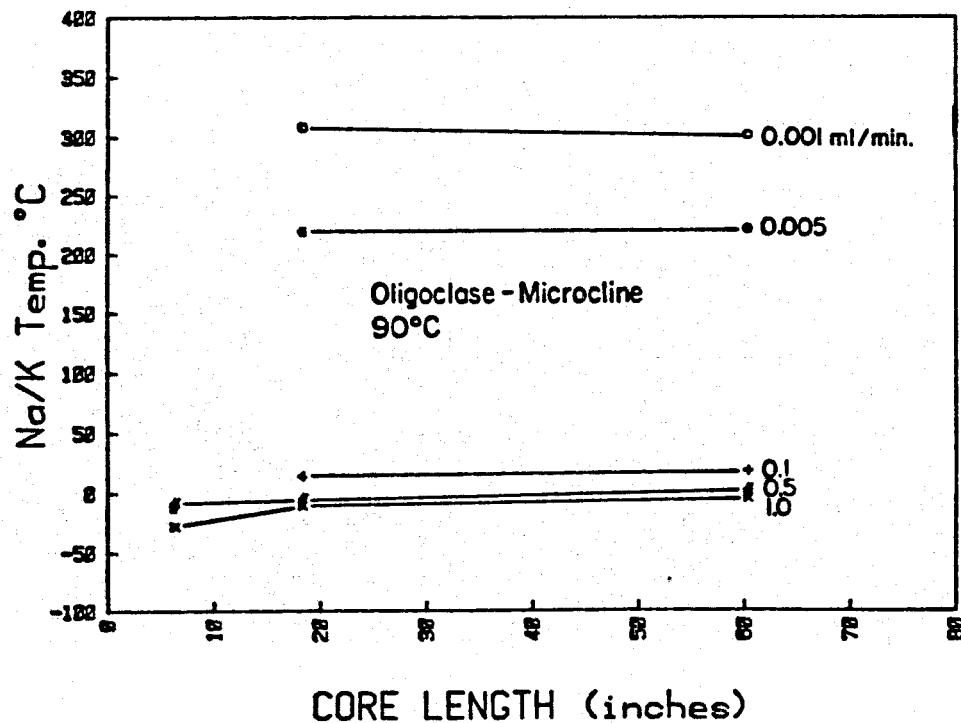

Figure 27. Calculated Na/K temperature as a function of experimental core length for feldspar experiments at 90°C, 1 atm.
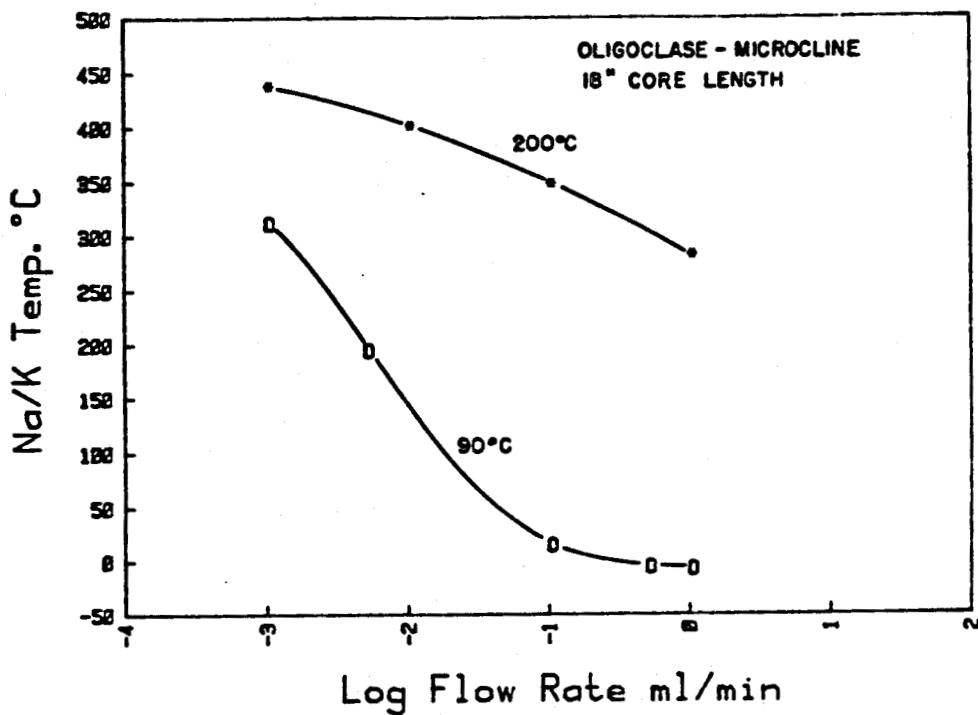
Figure 28. Calculated Na/K temperature as a function of log flow rate for 18"long feldspar experiments at 90 and 200°C.
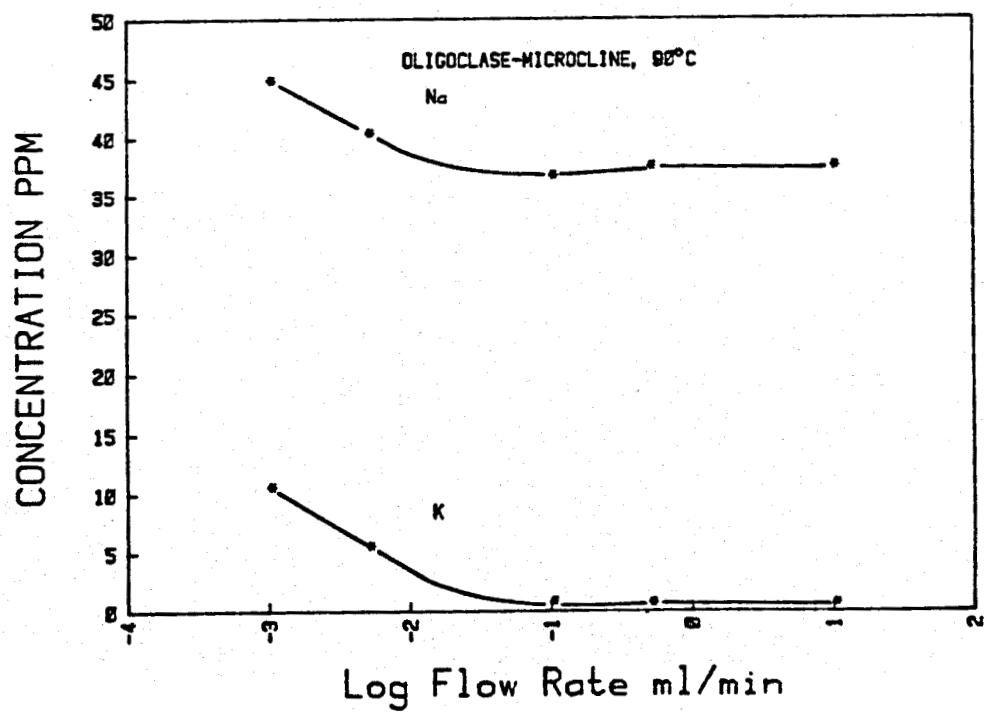
Figure 29. Concentrations of Na and K as a function of log flow rate for 18" long, 90°C experiment.

CONCENTRATION PPM

80

70

60

50

40

30

20

10

0

OLIGOCLASE-MICROCLINE, 200°C
18" CORE LENGTH

Na

K

4   -3   -2   -1   0   1   2
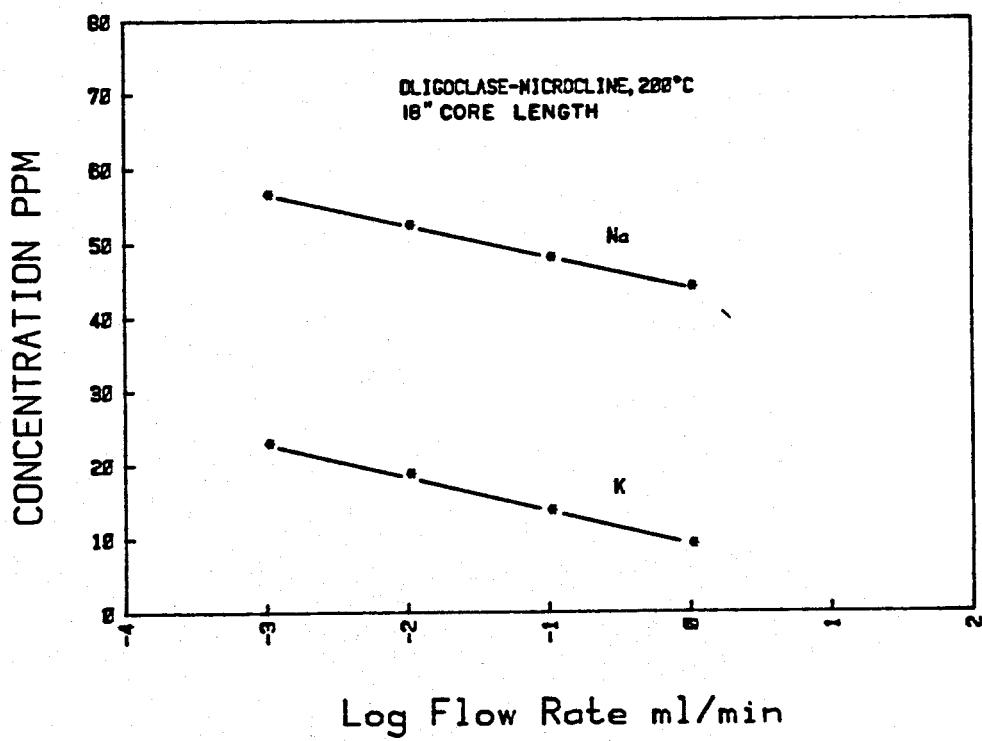
Log Flow Rate ml/min

Figure 30. Concentrations of Na and K as a function of log flow rate for
18" long 200°C experiment.

Appendix 1

CHEMICAL COMPUTATIONS: MINEQL AND MNQL98

Chemical computations were required in several contexts in this project. A wide variety of computer programs have evolved for this purpose. Nordstrom et al. (1979) have revived the characteristics of fourteen such programs. Among these programs, MINEQL is probably the most versatile, though originally designed for use at 25°C only. We have adapted MINEQL (Westall et al., 1976) to accommodate temperatures above 25 degrees Celsius by incorporating the Van't Hoff equation to correct equilibrium constants from 25 degrees to temperature and adding enthalpies of reaction to the thermodynamic data-base. The programming strategy was suggested by Leighton Wong and J.J. Morgan (Cal. Inst. Tech., 1981, personal communication).

Non-ideality corrections are made with the Davies equation.

$$- \log \gamma_i = A z_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - kI \right) \tag{1}$$

in which γ_i = single ion activity coefficient

$I = \sum_j C_j z_j^2$ = ionic strength

z_i = ionic charge

c_i = ionic concentration

The constant, A, is adjusted for temperature using data from Harned and Owen (1958); k is set to 0.3 (Stumm and Morgan, 1981).

Ionic strength and charge balances are computed internally. On demand, the program will iterate on ionic strength, computed after speciation. Charge imbalance is only reported. No attempt is made to

adjust the analysis to compensate for imbalance. The program in this form is referred to as MNQL98.

Thermodynamic data, i.e. stability constants for aqueous complexes and solubility products for solids, and the enthalpy changes associated with them, were selected from the following sources, with few exceptions.

(i) For weak acids and most complexes, Smith and Martell (1974).

(ii) For hydroxo- complexes, Baes and Mesmer (1974).

(iii) For silicate minerals, Helgeson et al. (1978).

Oiv. For all other solids, Robie, Hemingway, and Fisher (1978).

Neither MINEQL nor MNQL98 in their present forms can accommodate smectites or some zeolites because the programs are limited to minerals with four or few constituents. The solubilities of silicas and silicates must be related to $H_2SiO_4^{2-}$; values of K_{a1}, K_{a2} and the associated enthalpies of reaction were selected to duplicate the computed solubilities of quartz selected by Walther and Helgeson (1977) with reasonable precision at low temperatures. The free energies and enthalpies of formation of the species involved, as selected, are listed in Table Ala.

This thermodynamic data-set, referred to as W2THRM.SAV, should be considered tentative.

Limitations. All calculations made with MNQL98 and W2THRM.SAV are approximations. The non-ideality corrections and thermodynamic data are applicable with acceptable precision only to about 50 – 75°C. The use of the Van't Hoff equation assumes temperature independent enthalpies of reaction. While the enthalpies of reaction associated with some mineral assemblages of geochemical interest are approximately independent of temperature up to perhaps 200 degrees (Bird and Norton, 1981). We do not have this assurance for all reactions.

Errors. MNQL98 can be used to estimate reservoir temperatures by computation of saturation indices. This is described in detail in the text. The limitations described above lead to errors of unknown magnitude for all geothermometers. The illustrative calculations in Table Alb permit estimation of error in the quartz geothermometer when calculations are performed with MNQL98. The MNQL98 quartz temperature will be low by the amount of the error listed in Table Alb.

pH Calculations. Water analyses are introduced as the analytical, or "total dissolved" concentrations of each constituent present. Hydrogen is specified in one of two ways, either as a fixed pH or as HTOT, the total amount of acid or alkali needed to build the solution. Commonly, published analyses include a pH measured at or below discharge temperature. The pH at higher temperatures is not the same as the pH at the measurement temperature, because hydrolysis reactions are temperature dependent. It is assumed that the total dissolved concentrations of all constituents are independent of temperature, however. Given this assumption, pH dependent calculations at any temperature can be made as follows:

(i) Set the system temperature to the pH measurement temperature, fix pH at the measured pH, and compute HTOT with MNQL98.

(ii) To check, re-run MNQL98 at the temperature of pH measurement, fixing HTOT instead of pH, to calculate pH. The recomputed pH may differ from the measured pH if roundoff errors reduce precision of HTOT; repeat adjusting HTOT until recomputed pH matches measured pH.

(iii) To determine speciation or saturation indices at new temperatures, set temperature, fix HTOT, anf float pH.

During all calculations, precipitation and dissolution of solids are suppressed to prevent alteration of solution composition during computation.

Table Ala. Selected Free Energies and Enthalpies of Formation of Silicic Acid.

Species	ΔG°_f, kJ/mole	ΔH°_f, kJ/mole	Source
SiO2(aq)	−833.41	−881.57	(a)
H4SiO4(aq)	−1307.8 (b)	−1454.9	(c)
H3SiO4−	−1252.7	−1429.3	(d)
H2SiO42−	−1176.9	⊂1409.9	(d)

a. Walther and Helgeson, 1977.

b. $\Delta G(SiO_2(aq)) + 2\Delta G(H_2O,l)$

c. $\Delta H(SiO_2(aq)) + 2\Delta H(H_2O,l)$ + max. est. uncertainty suggested by Robie, Hemingway, and Fisher (1978).

d. Computed from H4SiO4(aq) data using dissociation constants and enthalpies of reaction from Busey and Mesmer (1977).

Table Alb. Computed Solutibilities of Quartz: MNQL98 Error

temp. °C	log(SiO_2(aq)) Walther and Helgeson (1978)	log(SiO_2(aq)) MNQL98	Quartz Geothermometer Error[a]
0	-4.50	-4.44	-3
25	-3.99	-4.00	nil
50	-3.63	-3.63	nil
75	-3.34	-3.37	+3
100	-3.10	-3.03	+5
125	-2.89	-2.79	+10
150	-2.72	-2.58	+15
175	-2.56	-2.39	+25

a. Walther/Holgeson quartz temperature is higher than MNQL98 temperature by "error".

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