IMPROVEMENTS IN GEOTHERMOMETRY

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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.

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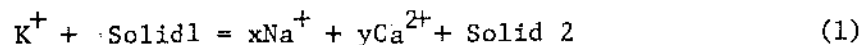
If [i] is the thermodynamic activity of species i, whether i is a solute or a solid (Garrels and Christ, 1965) and (i) is the corresponding concentration,

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

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

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

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

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

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 solid1 and solid2 must be the same for all rock-water systems to which the geo-thermometer 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

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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 hallosite and wairakite approach zero at T < 75°C; analcime and muscovite are highly supersaturated for all t.)

(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 Alb 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.

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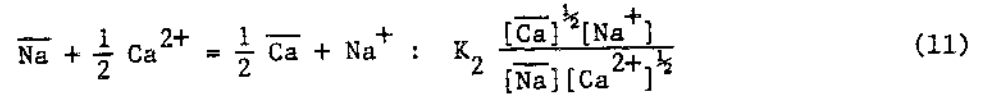
Data for the temperature range 60-73° are shown in figure 10, but are too sparse to permit regression. These data support the claim cited earlier that the geothermometer might be unreliable with acid sulfate waters. Estimates of β, $\log K^*$ and h are listed in Table 2.

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.

$$\overline{Na} + \frac{1}{2} Ca^{2+} = \frac{1}{2} \overline{Ca} + Na^{+} \ : \ K_2 \ \frac{[\overline{Ca}]^{\frac{1}{2}}[Na^{+}]}{[\overline{Na}][Ca^{2+}]^{\frac{1}{2}}} \tag{11}$$

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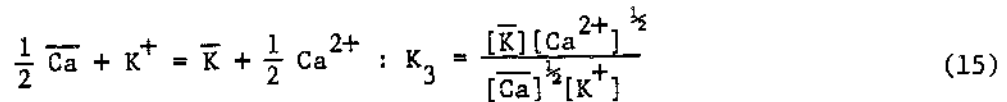
$$\log \left(\frac{[Na^{+}]}{[K^{+}]} \right) = \log\left(\frac{K_1}{K_2} \right) + \log \left(\frac{[\overline{Ca}]^{\frac{1}{2}}}{[\overline{K}]} \right) - \log \frac{[Ca^{2+}]^{\frac{1}{2}}}{[Na^{+}]} \tag{12}$$

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

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,

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

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

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

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

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
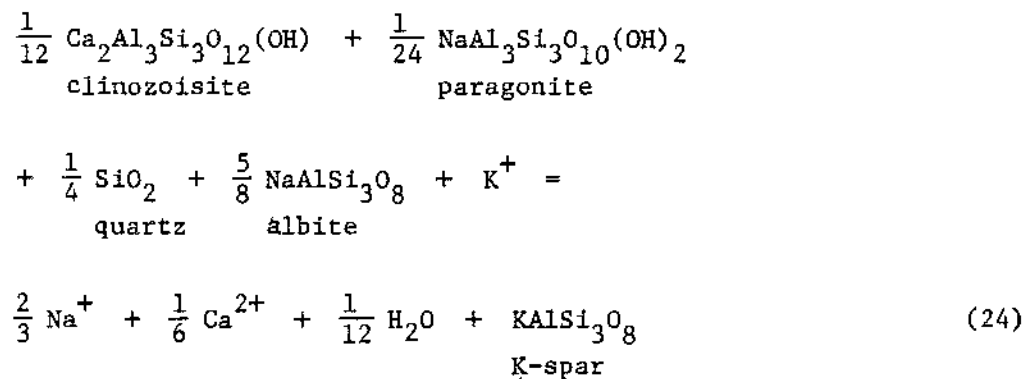
available.

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 ouf of 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 β is either 1 or slightly greater (4/3). An overall net irreversible

reaction for the Seikan tunnel ($\beta = 4/3$) is

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(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):

$$\underset{\text{albite}}{NaAlSi_3O_8} + K^+ \overset{K_1}{=} \underset{\text{K-spar}}{KAlSi_3O_8} + Na^+ \qquad (19)$$

Any of a variety of other reactions involving both stable and metastable

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

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

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

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

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

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

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

$$\frac{2}{3} Na^+ + \frac{1}{6} Ca^{2+} + \frac{1}{12} H_2O + KAlSi_3O_8 \qquad (24)$$
K-spar

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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.

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 50°. 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 50° 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 temperature is accompanied by an increase in the 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

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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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. $KAlSi_3O_8 + Na^+ \rightleftharpoons NaAlSi_3O_8 + K^+$, 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

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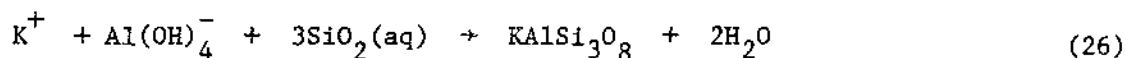
So that the net reaction becomes:

$$K^+ + NaAlSi_3O_8 \rightarrow KAlSi_3O_8 + 2H_2O \qquad (27)$$
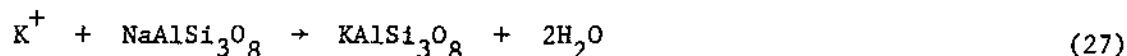
The net reaction proceeds until equilibrium Na/K values are attained. However, if reaction kinetics are sluggish, non-equilibrium Na/K values may be maintained for long times, especially in flowing systems. For example, if growth rates of K-spar in (26) are small relative to dissolution rates of albite 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 Holdrehon (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

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

Temperature, deg C	n	r	β	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 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 + Q z + K^+ = K-spar + $1/2Ca^{2+} + H_2O$	1.0	K	5.5	-14.9	4
6. $2/3$ anorth + $8/3$Am + 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.

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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 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

○ ANDESITES
▲ SERPENTINES
+ LIMESTONES AND DOLOMITES
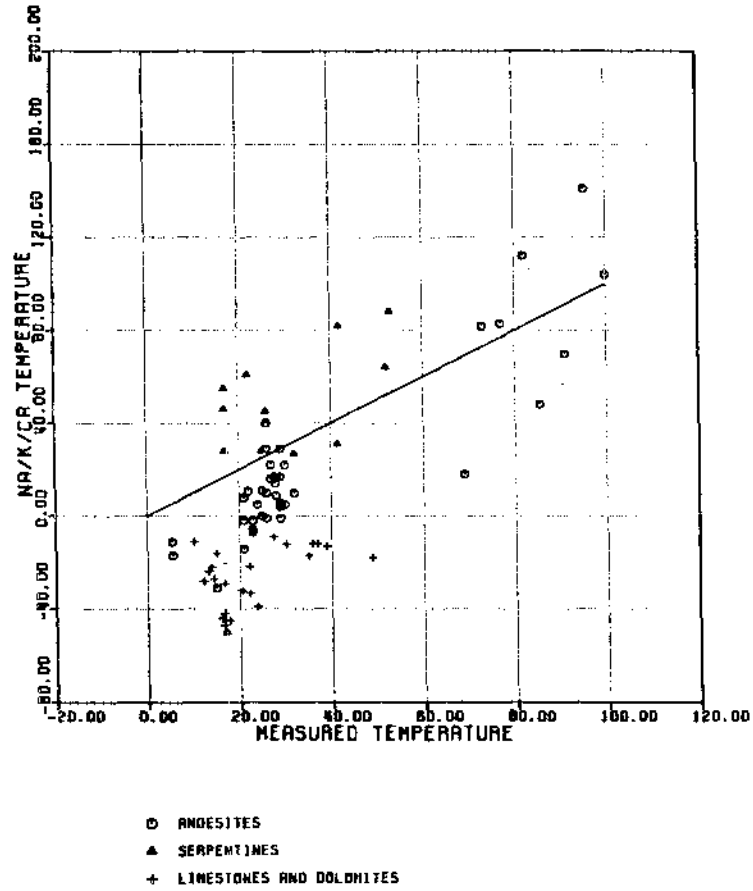
Figure 3. Na-K-Ca Geothermometer, CO_2 corrected: Comparison of predicted and discharge temperatures

○ ALBITE   NA-K-CA TEMP = 135
▲ ORTHOCLASE   QUARTZ TEMP = 145 (H)
+ MUSCOVITE   QUARTZ TEMP = 133 (F)
X KAOLINITE (H)   -NA-K-CA-MG   = 87
⊕ LAUMONTITE   CO2-NA-K-CA = 48
✦ ANALCIME   DISCH TEMP = 85.5
X CALCITE
Z QUARTZ
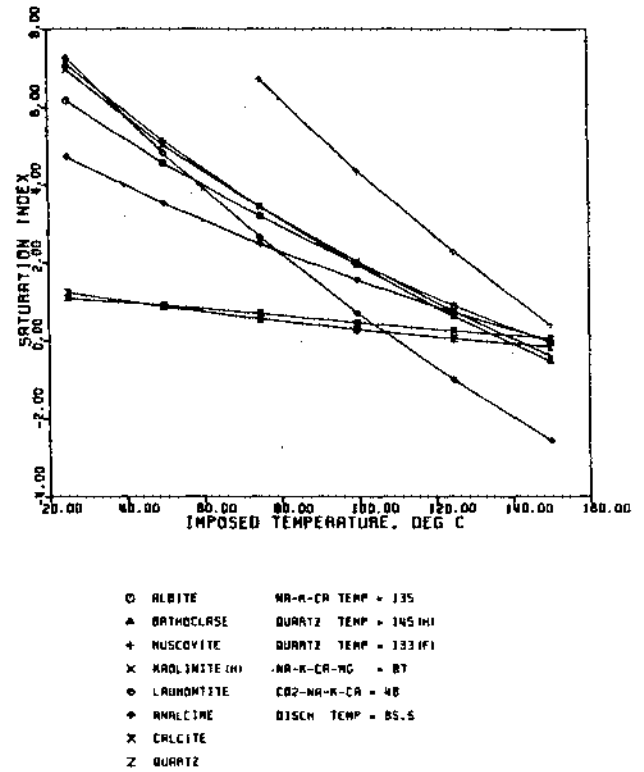
Figure 4. Temperature dependence of saturation indices: 85.5 ° water, Te Aroha, North Island, New Zealand (White et al., 1963). A 229 ft. well penetrates alluvium overlying andesite.
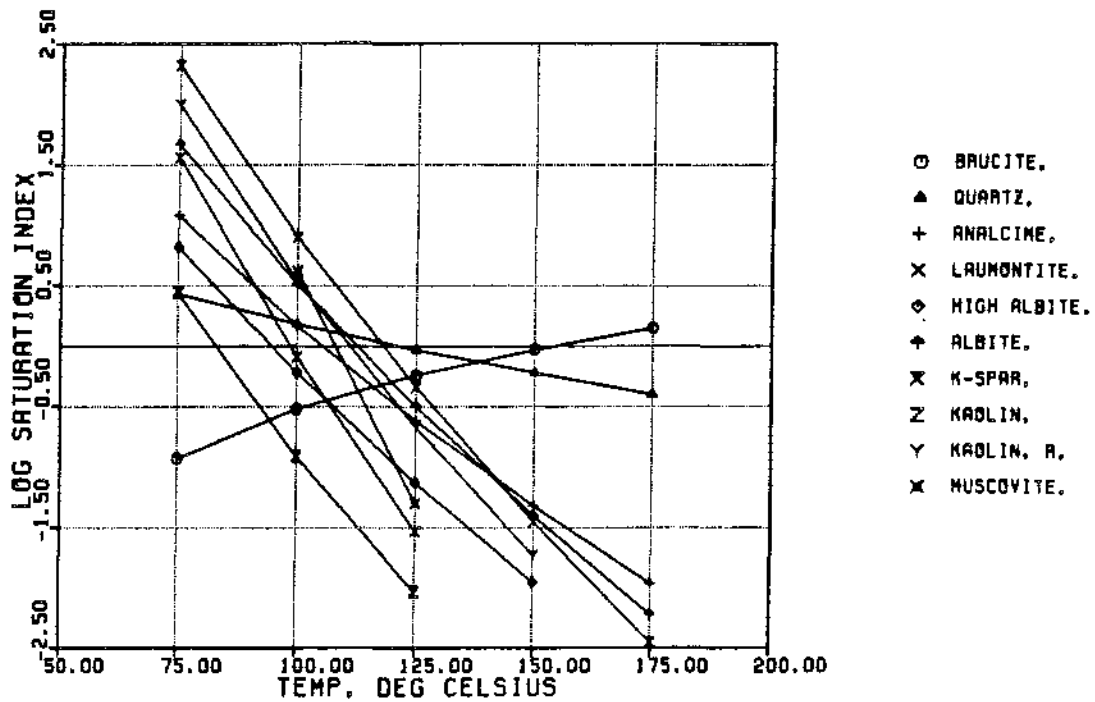
Figure 7. Temperature dependence of saturation indices; Geothermal waters of Taiwan, Lushan Spring

Legend for Figure 7:
- O BRUCITE.
- ▲ QUARTZ.
- + ANALCIME.
- ✗ LAUMONTITE.
- ◇ HIGH ALBITE.
- ✦ ALBITE.
- ✗ K-SPAR.
- Z KAOLIN.
- Y KAOLIN, R.
- ✕ MUSCOVITE.

Legend for Figure 8:
- O 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
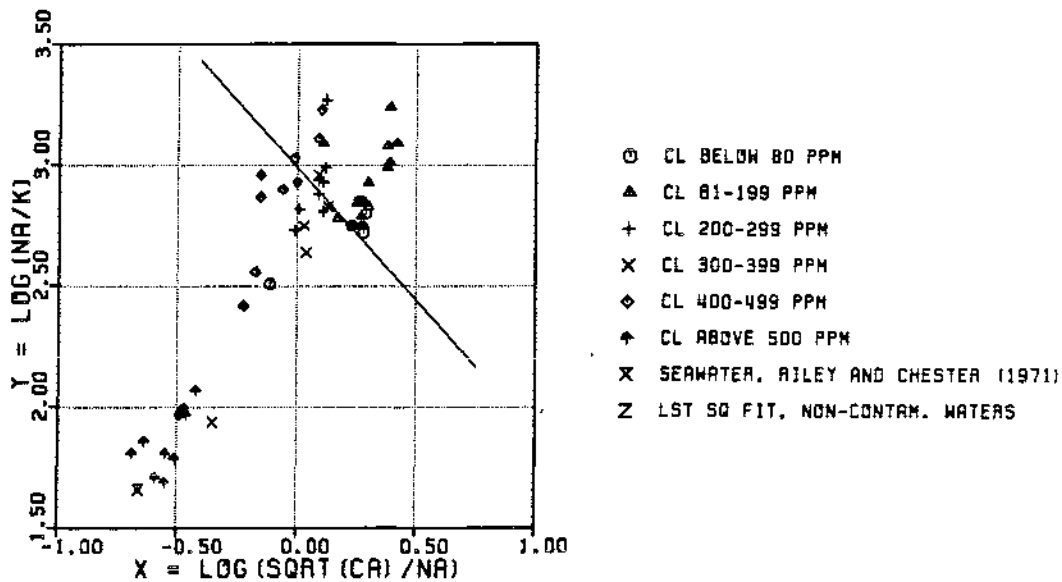
Figure 8. Tests of Equation 6; Seikan Tunnel Andesites, effects of mixing meteoric and seawater. Solid line represents least squares trend of uncontaminated meteoric waters alone.

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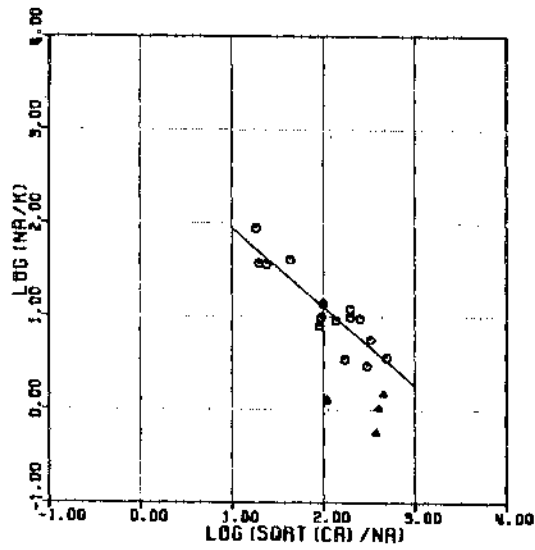
○ WHITE ET AL. 1963

▲ HELZ AND SILEX, 1974

LST. SQ. FIT. OMITTING HELZ DATA, SEE TEXT

○ 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 12: Estimation of beta and K^*, Limestones, 12 to 24^{0}C.
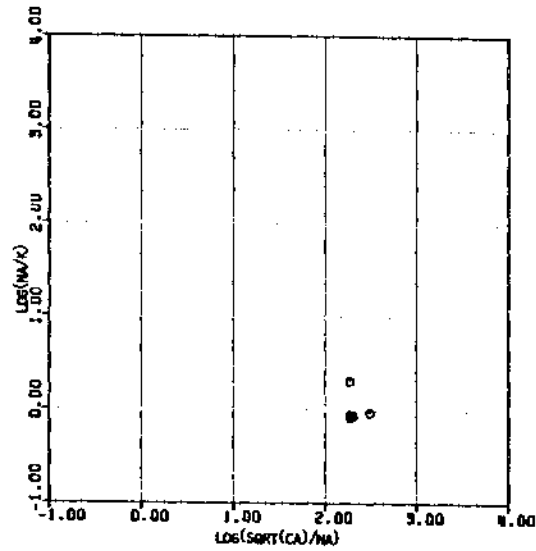
Figure 13: Estimation of beta and K^*, Limestones, 28 to 50^{0}C.

Figure 14: Estimation of beta and K^*, Serpentines, 17 to 52^{0}C.
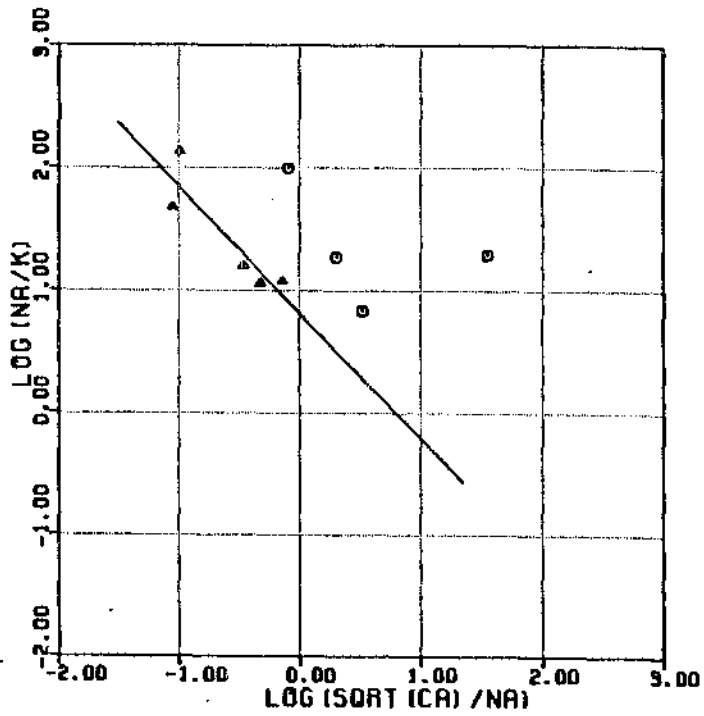
Figure 17. Estimation of beta and K* using raw, total metal concentrations in equation 6. Andesites, 77 to 100°C. Solid line is least squares fit to data for which pH is above 5.
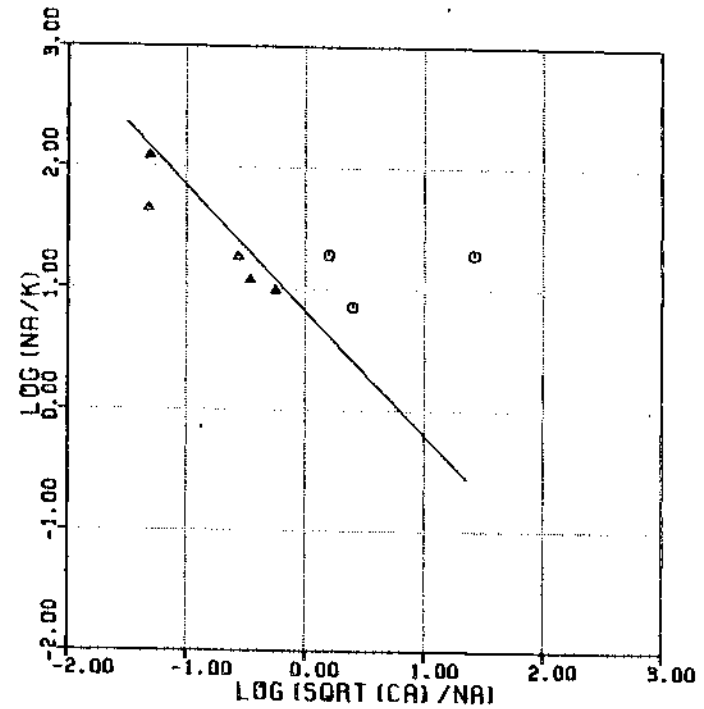
Figure 18. Estimation of beta and K* using computed free ion activities in equation 6. Andesites, 77 to 100°C. Solid line is least squares fit to data for which pH is above 5.
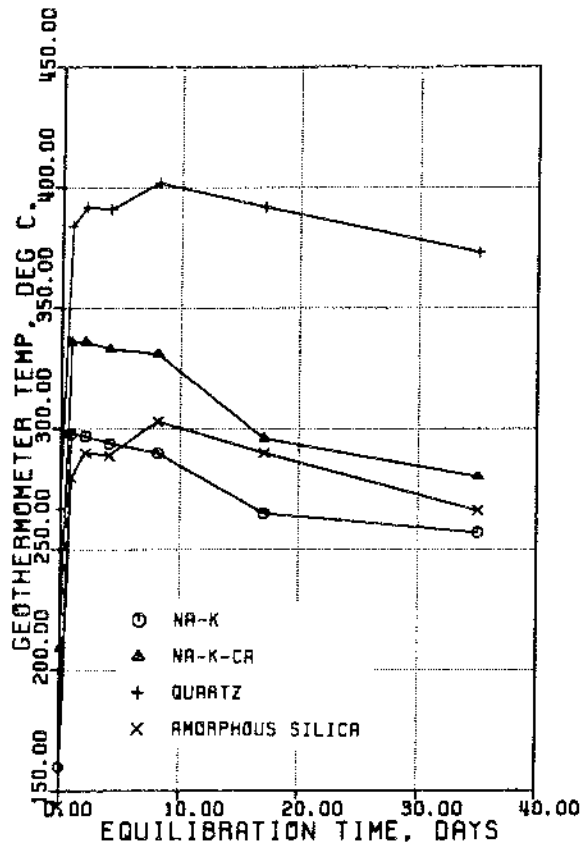
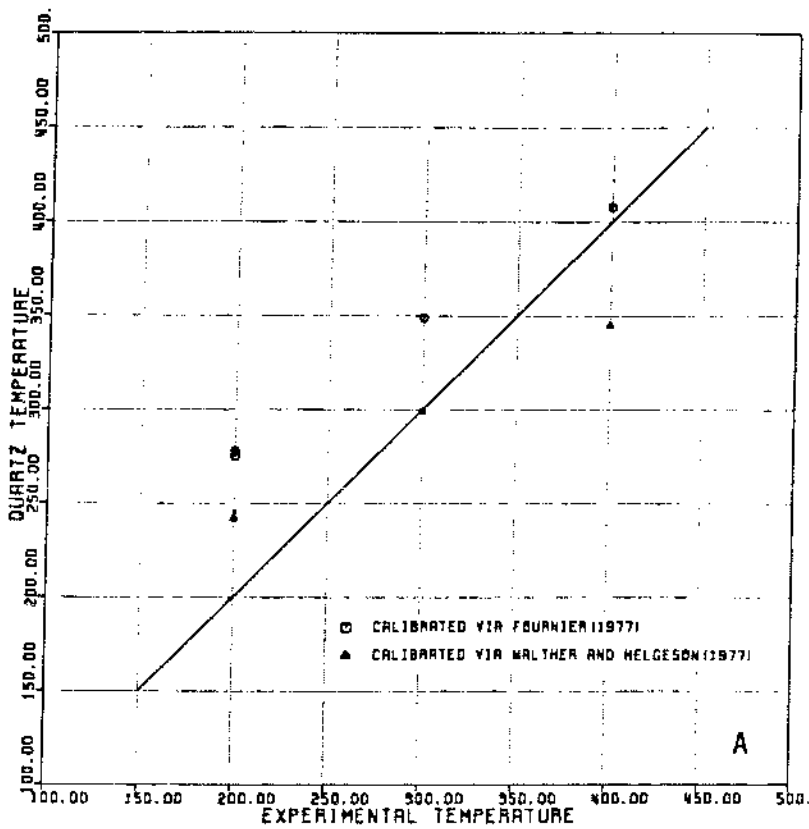Figure 20. Evolution of geothermometer temperatures. Basalt (Data from Guillemette, Stanford University, 1982)
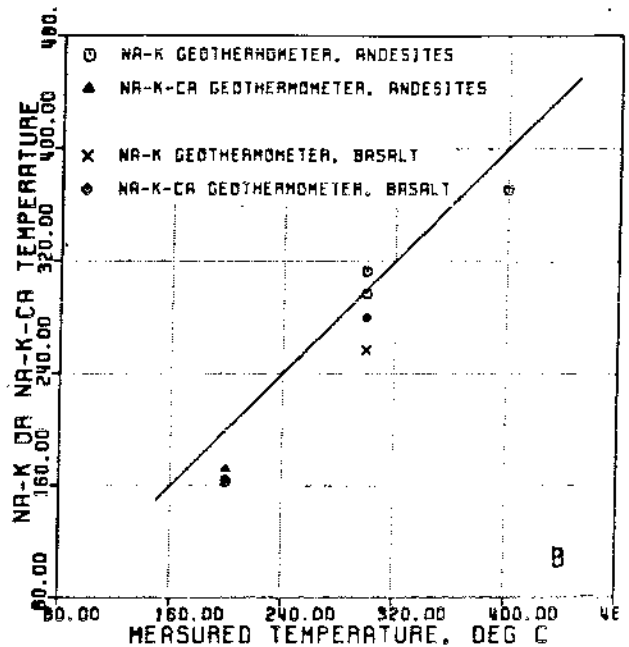
Figure 21. Comparison of Geothermometric and experimental temperatures for experimental water-rock systems.
A. Quartz temperatures
B. Aa-K and Na-K-Ca temperatures

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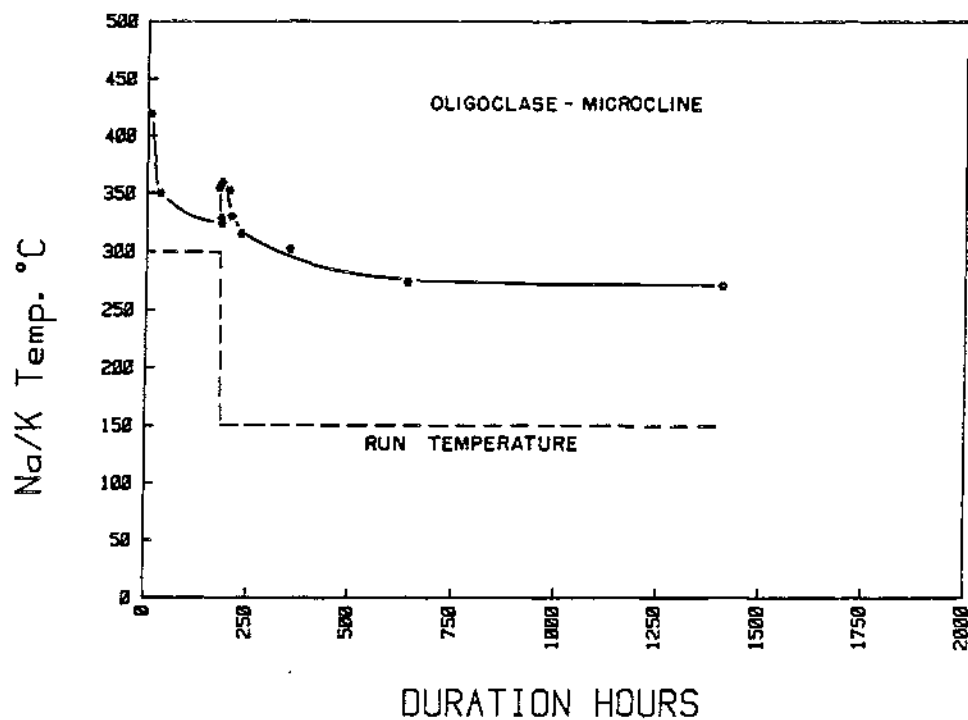
Figure 24. Na/K temperature -experimental duration curve for agitated feldspar experiment at 300° and 150°C, and 200 bars.
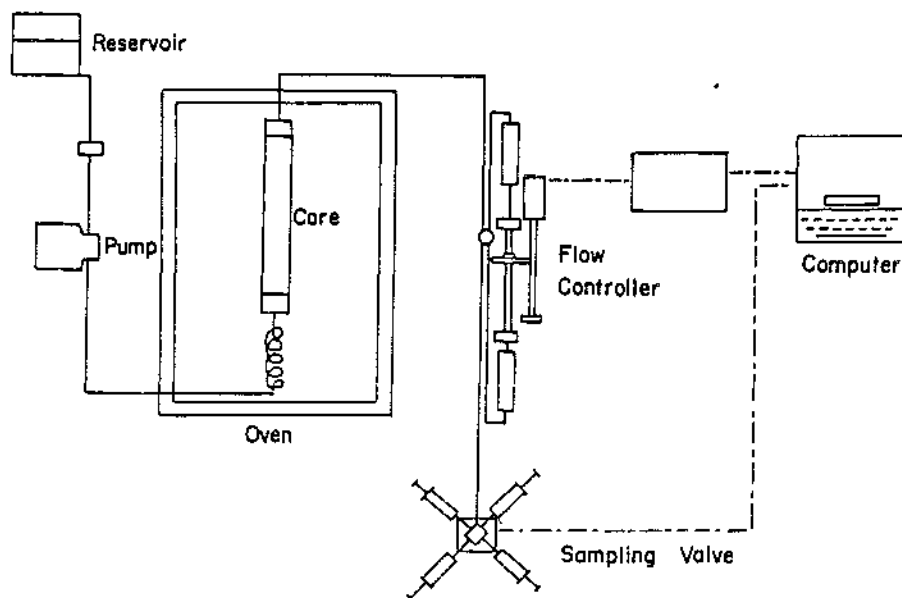

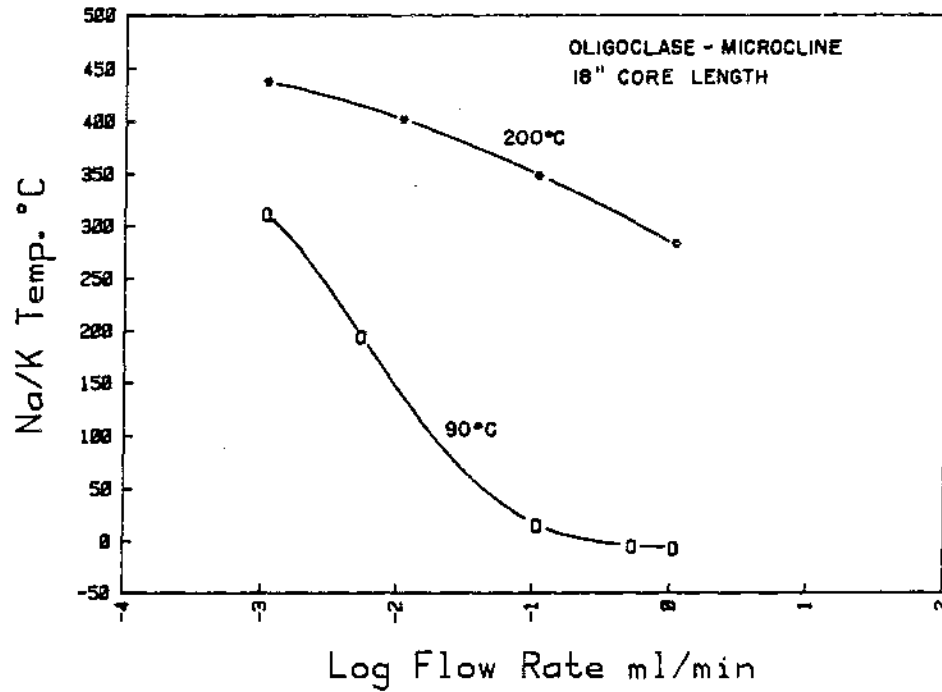Figure 25. Schematic diagram of experimental flow through apparatus.

Figure 28. Calculated Na/K temperature as a function of log flow rate for 18"long feldspar experiments at 90 and 200°C.
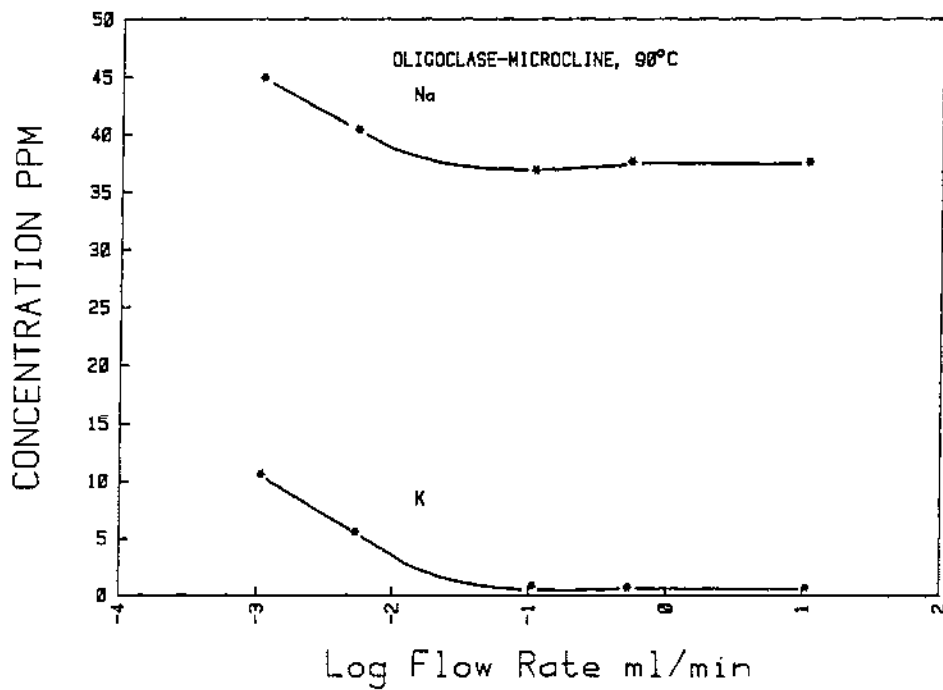

Figure 29. Concentrations of Na and K as a function of log flow rate for 18" long, 90°C experiment.

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.

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

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

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 A1b 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 A1b.

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 A1b. 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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