A NEW ILLITE GEOTHERMOMETER

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ABSTRACT

Sericite, either as illite or illite/smectite, is ubiquitous in geothermal systems. Theoretical Ca- and Na-smectite contents of non-expanding geothermal sericites have been calculated from published electron microprobe analyses. Geothermal sericites can be modeled as solid solutions of muscovite and smectite. For those sericites that fit the model, the amount of smectite in solid solution is related to temperature by the expression:

$$T°C = 1000/(0.45 LogX_{smectite} + 2.38) - 273$$

The temperature dependence of illite interlayer chemistry suggests a related temperature dependence of the K, Na and Ca content of geothermal fluids. The original data used by Fournier and Truesdell (1973) to derive the empirical Na-K-Ca geothermometer for geothermal fluids can be modeled equally well by an equation incorporating the equilibrium constant for the reaction of smectite to illite:

$$T °C = 1.145*10^3/\{[0.35 LogNa + 0.175 LogCa - 0.75 LogK] + 1.51\} - 273$$

where the concentration units are molalities. This supports the hypothesis that illite and illite/smectite are important controls on the concentrations of Na, K and Ca in geothermal fluids.

INTRODUCTION

Fine grained white micas, including muscovite, illite and interstratified illite/smectite, and collectively termed sericite, are ubiquitous in geothermal systems (Browne, 1978). These minerals differ chemically primarily in the amount of K^+ in the interlayer site (Fig. 1). Interstratified illite/smectite contains <0.75 K^+ per $O_{10}(OH)_2$ (Srodon et al., 1986), illite contains 0.75 to 1.0, and muscovite (or its Fe-rich analog, phengite) contains 1.0 K^+ per $O_{10}(OH)_2$. The interlayer site can also contain minor amounts of Na^+ and Ca^{++}, and occasionally Mg^{++} and NH_4^+. Published studies of sericites from geothermal systems (McDowell and Elders, 1980, Ballantyne, 1981, Parry et al., 1984, Bishop and Bird, 1987) show that the interlayer site is incompletely filled in sericites formed at low temperatures, and becomes increasingly filled at higher temperatures.

The smectite general formula chosen for use in this study is:
$(0.5Ca,Na)_{0.35}(Al,Mg,Fe)_2[(Si,Al)_4O_{10}](OH)_2.n-H_2O$ (Deer et al., 1966). Exchangeable K^+ and Mg^{++} can also substitute for Ca^{++} and Na^+. The maximum interlayer site occupancy for a smectite is thus between 0.18 and 0.35 cations, compared to the maximum of 1.0 for an ideal muscovite.
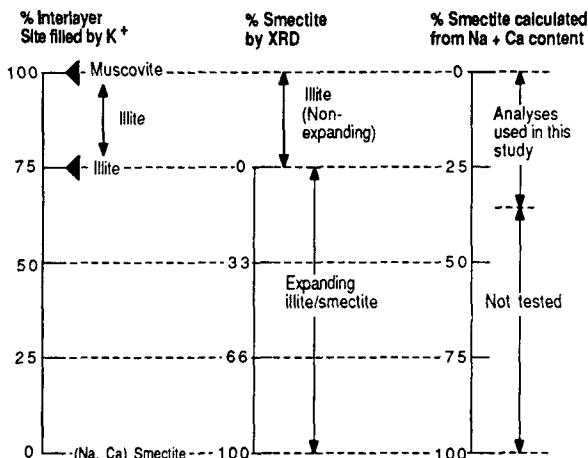

Figure 1. Comparison of models for illite and illite/smectite determined by XRD and from chemical analyses.

The percentage of smectite interstratified with illite in illite/smectite is normally determined by X-ray diffraction (XRD), not by chemical analysis. The amount of expansion of glycolated samples relative to non-glycolated equivalents is converted to percent smectite. Numerous studies of expanding illite/smectite have shown decreasing expandability with increasing temperature. The temperature dependence of non-expanding sericites has been modeled assuming solid solution between muscovite $(KAl_2[AlSi_3O_{10}](OH,F)_2)$, paragonite $(NaAl_2[AlSi_3O_{10}](OH,F)_2)$, and pyrophyllite $(Al_2[Si_4O_{10}](OH,F)_2)$ to account for the K, Na and incomplete site occupancy $(1-(K+Na+Ca))$, respectively (Bird and Norton, 1981, Capuano and Cole, 1982, Parry et al., 1984, Bishop and Bird, 1987). While this method has shown correlations between temperature and the

activities of these solid solution components, it does not account for Ca, and it cannot readily be extended to interlayered illite/smectites formed at lower temperatures. In this paper we describe an alternative hypothesis, that illite is actually a muscovite-smectite solid solution. We then use this data to establish a relationship between temperature and sericite chemistry. Finally, we discuss a possible relationship between illite/smectite and the Na-K-Ca geothermometer of Fournier and Truesdell (1973).

SMECTITE SOLID SOLUTION IN NON-EXPANDING ILLITE

Geothermal sericites range from illite/ smectite to muscovite (or phengite), and from <0.75 to 1.0 K^+ per $O_{10}(OH)_2$ (McDowell and Elders, 1980, Ballantyne, 1981, Parry et al., 1984, Bishop and Bird, 1987). Table 1 shows sericite analyses calculated as muscovite, Ca-, and Na-smectite components. Averages of analyses for each depth are listed because individual grain analyses are reported only for Roosevelt Hot Springs samples (Ballantyne, 1981). Small differences in analysed Ca and Na content make large differences in calculated smectite content. A step of 0.01 cations per $O_{10}(OH)_2$ represents 6% Ca-smectite, 3% Na-smectite, but only 1% muscovite or paragonite.

The sum of the smectite and muscovite components for the majority of samples in Table 1 is surprisingly close to 100%, given the uncertainties in the method of calculation described above. Totals close to 100% in Table 1 support the hypothesis that most sericites can be considered as muscovite either interstratified or in solid solution with Ca- and Na-smectite. High temperature samples from the Salton Sea have totals much higher than would be expected if Na were present as smectite. These four samples are better described as muscovite in solid solution with paragonite. One Coso sample with an exceptionally high Ca content may be intergrown with another Ca-bearing mineral (Table 1), and a total of 100% is assumed for this sample.

Some samples from each system, particularly low temperature samples, have unaccounted-for vacancies in the interlayer site. We suspect that this is due to cations that were not determined, such as NH_4^+ and Sr^{++}, or to inaccuracies inherent in methods of chemical analysis and structural formula computation. Some volatilization of K and Na can occur under the microprobe beam. In addition, a small amount of K^+ can be present as K-smectite. K-smectite is not detectable by XRD analysis because it does not swell (Drever, 1982), and analytical techniques yield only total K. We assume that all K^+ is present as muscovite.

Table 1. Calculated smectite and muscovite components in geothermal sericites.

Depth (m)	T °C	Interlayer Cations K[1]	Ca[1]	Na[1]	% K-Musc	% Ca-Smect	% Na-Smect	% Total
Coso well 16-8[2]								
	190	0.630	0.145	0.017	63	83[5]	5	152[5]
	215	0.755	0.025	0.006	76	14	2	92
	236	0.831	0.013	0.016	83	7	5	95
	250	0.861	0.004	0.035	86	2	10	98
Salton Sea well Elmore #1[3]								
439	190	0.56	0.03	0.06	56	17	17	90
622	251	0.65	0.03	0.05	65	17	14	96
675	264	0.68	0.01	0.04	68	6	11	85
845	295	0.83	0.01	0.08	83	6	23[6]	112[7]
924	306	0.90	0.00	0.08	90	0	23[6]	113[7]
991	315	0.91	0.01	0.09	91	6	26[6]	122[7]
1064	322	0.93	0.00	0.07	93	0	20[6]	113[7]
Roosevelt Hot Springs well 14-2[4]								
503	215	0.675	0.004	0.014	68	3	4	75
518	215	0.795	0.009	0.020	80	6	6	91
610	220	0.760	0.007	0.018	76	3	6	85
854	230	0.805	0.010	0.025	81	6	7	93
869	230	0.870	0.007	0.020	87	3	6	96
896[8]	250	0.860	0.010	0.015	86	6	4	96
1341	250	0.740	0.020	0.015	74	11	4	90
1524	255	0.900	0.010	0.015	90	6	4	100

[1]Calculated on the basis of 22 negative charges, equivalent to $O_{10}(OH)_2$. Smectite is considered to contain $(0.5Ca, Na)_{0.35}$ per unit formula. Averages of analyses for each depth are listed. [2]Bishop and Bird (1987). [3]McDowell and Elders (1980). [4]Ballantyne (1981). Temperatures are estimated to nearest 5°C from static log (Glenn and Hulen, 1979). [5]The anomalously high Ca content of this sample is believed to be due to an intergrown Ca-rich mineral. A total of 100% is assumed in later calculations, and a Ca-smectite content of 32% used. [6]The Na in these samples is believed to be in paragonite, not smectite. [7]Totals with Na as paragonite instead of smectite would be (from top to bottom) 97, 98, 106 and 100%, respectively. [8]One anomalously Na-rich analysis was omitted from the average.

A few samples may contain Mg-smectite. The three shallow samples from Roosevelt Hot Springs, 503m, 518m and 610m, have octahedral site occupancies of 2.07, 2.01 and 2.04 respectively, while all other samples from the same well contain less than the ideal 2.00 cations in the octahedral site (Ballantyne, 1981). If the excess (>2.00) site occupancy is calculated as Mg-smectite, Mg-smectite contents of 39%, 6% and 22%, respectively, are obtained for the three samples. These amounts are more than enough to account for the low totals (Table 1) of 75%, 92% and 85%, respectively. Two Coso samples with

octahedral site occupancies >2.00 correspond to downhole measured temperatures of 190° and 236°C. Octahedral site occupancies of 2.018 and 2.005 for these samples (Bishop and Bird, 1987), can be converted as above to 10% and 3% Mg-smectite, respectively. No estimates of octahedral site occupancy can be made for the Salton Sea samples because structural formulas were calculated assuming the ideal 2.00, with all Mg in the octahedral site (McDowell and Elders, 1980).

A comparison of chemically-calculated and XRD-determined smectite contents can be made for the one expandable Salton Sea sample, from 439 m depth. The XRD data shows 10-12% expandable layers (McDowell and Elders, 1980). The smectite content calculated from chemical analyses is 34% (Table 1). According to our model, non-expandable illite containing 0.75 K^+ per $O_{10}(OH)_2$ can contain up to 25% non-expandable smectite. Thus a chemically-calculated smectite content of 34% is equivalent to [1.33(34-25) = 12]% expandable smectite. The conversion factor of 1.33 is required to convert chemically-calculated % smectite to % expandable smectite (see Fig. 1). Thus, for this Salton Sea sample, the two methods give identical results.

TEMPERATURE DEPENDENCE OF INTERLAYER SITE CHEMISTRY

Figure 2 shows the relationship of calculated smectite content to the sum of muscovite and paragonite components. The closer to the line on the figure that a sample lies, the more fully its interlayer site occupancy is accounted for.
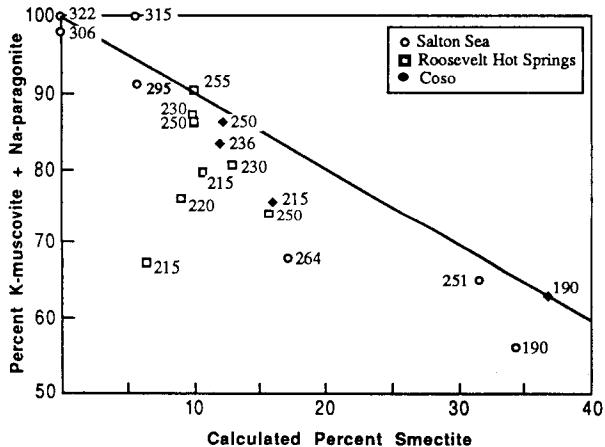

Figure 2. Components accounting for interlayer cations in geothermal sericites, calculated from microprobe analyses. The diagonal line represents interlayer site occupancy fully accounted for by the four components, equivalent to 100% totals in Table 1. Points are labelled with measured downhole temperatures in °C. Data are from Table 1.

The labels on data points in Fig. 2 are measured downhole temperatures. The distribution of the temperatures relative to compositions suggests an equilibrium reaction between muscovite and smectite. If such an equilibrium occurs, then a relationship of the type:

$$\Delta G°_{f(reaction)} = -2.303RTlog K$$

is expected, where K is the equilibrium constant, and a plot of smectite activity vs 1/T should be linear. Only samples close to the line on Fig. 2 (those with totals >90% in Table 1) are used in determining temperature dependence (Fig. 3). In addition, the Salton Sea sample from 622 m is excluded because the associated temperature is much higher than for other samples in this range of smectite content. With smectite activity approximated by mole fraction, X, the data in Fig. 3 are linearly distributed, with a correlation coefficient of 0.86. The regression equation for this line is given by the equivalent expressions:

$$1000/T = 0.45log\ X_{smectite} + 2.38 \qquad (1)$$

and:

$$T\ (°C) = 1000/(0.45*log\ X_{smectite} + 2.38) -273 \qquad (2)$$

where T is in degrees Kelvin.
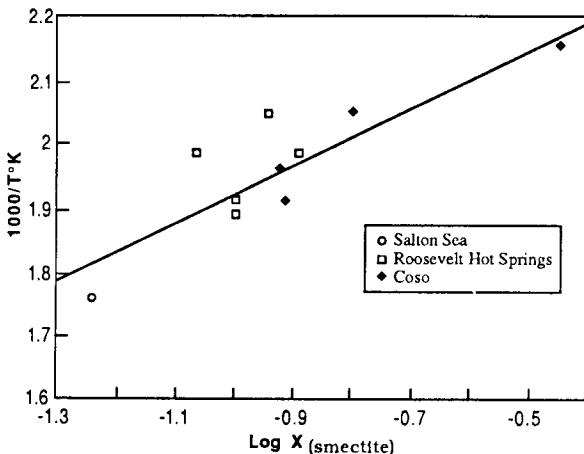
Figure 3. Relationship of temperature (°K) to calculated smectite content of sericite (NOT XRD-determined expandability). Data are from Table 1.

Table 2 compares downhole measured temperatures to the temperatures calculated using the illite geothermometer, for all samples. Two methods are used to calculate $X_{smectite}$. The first converts Ca and Na content to smectite. The second assumes that all interlayer sites not filled by K (and Na in paragonite) are filled by smectite. The lower temperature samples from Coso and Roosevelt Hot Springs give a much closer fit to measured temperatures using this second method. One reason is that cations other than Na and Ca may occur in smectite interlayer sites, as discussed above, and therefore a smectite component calculated using only Ca and Na data would be too low.

Table 2. Comparison of measured temperatures with those predicted from the illite geothermometer.

Depth (m)	Meas[1] Temp °C	Smect[2] Temp °C	Vac[3] Temp °C
Coso well 16-8[4]			
	190	185	185
	215	222	202
	236	236	219
	250	235	228
Salton Sea well Elmore #1[5]			
439	190	188	178
622	251	191	187
675	264	218	191
845	295	276	251
924	306	346	346
991	315	276	NA
1064	322	NA	NA
Roosevelt Hot Springs well 14-2[6]			
503	215	263	190
518	215	238	210
610	220	253	203
854	230	232	212
869	230	253	232
896	250	245	228
1341	250	222	199
1524	255	245	245

[1]Measured downhole temperature. [2]Temperature predicted from calculated Ca- and Na-smectite content. [3]Temperature predicted assuming all interlayer site vacancies are due to smectite. [4]Bishop and Bird (1987). [5]McDowell and Elders (1980). [6]Ballantyne (1981). Temperatures estimated to nearest 5°C from static log (Glenn and Hulen, 1979).

The high smectite contents of the Salton Sea samples from depths of 622 and 675 m, relative to the Roosevelt Hot Springs and Coso samples may be due to differences in the fluid chemistries between the systems. The rate of illitization in hydrothermal experiments is slowed by the presence of Ca, Mg and Na (Eberl and Hower, 1976; Roberson and Lahann, 1981). The K/Ca ratio in Salton Sea fluids (Helgeson, 1968) is 2 to 3 orders of magnitude lower than in fluids from Coso (Bishop, 1985) or Roosevelt Hot Springs (Capuano and Cole 1982). K/Na and K/Mg are of similar orders of magnitude in all three systems.

Analytical and/or mathematical limitations may also cause uncertainties in temperatures calculated from compositions. Smectite contents of 5, 4, 3, 2 and 1% respectively correspond to temperatures of 284°, 298°, 317°, 346° and 403°C. Because of the detection limits for Ca and Na it seems that 300°C is a practical limit above which the

interlayer site can be considered completely filled, i.e. that illite becomes muscovite. The lower temperature limit for the geothermometer is about 200°C. "Pure" non-expanding illite containing 0.75 K^+ per $O_{10}(OH)_2$ (Srodon et al., 1986) corresponds to 25% calculated smectite, and has a calculated geothermometer temperature of 202°C.

We have limited our discussion to non-expanding illites because of lack of good analytical data on expandable illite/smectite from geothermal systems. Extrapolation of the geothermometer into the expandable range (Fig. 4), shows that 100% smectite yields a temperature of 147°C. Smectite persists in many geothermal systems to higher temperatures than this, and mixed-layer illite/smectite can occur at lower temperatures (Hulen and Nielson, 1986). Figure 4 also compares XRD data for samples from two Salton Sea wells (Moore and Adams, 1988) to the predicted geothermometer. Temperatures shown were obtained from fluid inclusions in anhydrite from the same or adjacent samples. The smectite content estimated by XRD is increased by 25% non-expandable smectite as discussed above. The predicted temperatures are better for those samples having intermediate expandabilities than those at either end of the range. This relationship suggests that expanding interstratified illite/smectite may behave differently from non-expanding illite.
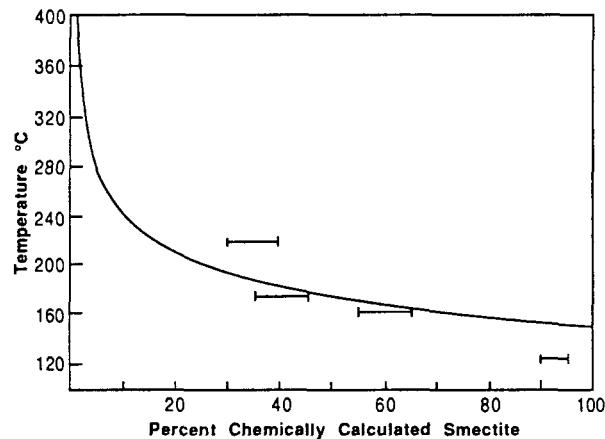

Figure 4. Geothermometer curve extrapolated to 100% smectite. Shown for comparison are expandable illite/smectites from two Salton Sea wells (Moore and Adams, 1988, this volume). An assumed 25% non-expandable smectite is added to XRD-determined expandabilities. Temperatures are from fluid inclusions.

For comparison with the temperature dependence of smectite content (Fig. 3), the relationship between temperature and the mole fraction of muscovite + paragonite is shown in Fig. 5. All samples in Table 1 are included

in Fig. 5. Sericites from the saline Salton Sea system appear to behave differently from the dilute system samples.
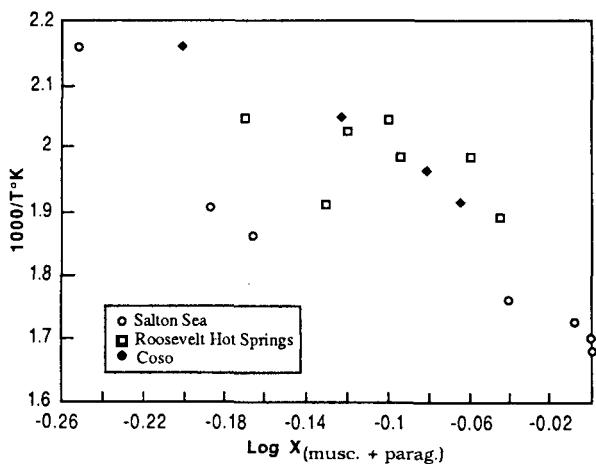

Figure 5. Relationship of temperature (°K) to calculated muscovite plus paragonite content of sericite. Data are from Table 1.

ILLITE/SMECTITE AND THE NA-K-CA GEOTHERMOMETER

Because illite and interstratified illite/smectite are so common in geothermal systems, these minerals are expected to exert some control on fluid chemistry. The relationship between Na, K and Ca in geothermal fluids should therefore be consistent with equilibria involving illite/smectite. Possible reactions include:

$Ca_{smectite}$ + $Na_{smectite}$ + $1.0K^+$ = $K_{muscovite}$
$+0.175Ca^{++}$ + $0.35Na^+$ (3)
for non-expanding illite, and:
$Ca_{smectite}$ + $Na_{smectite}$ + $0.75K^+$ = K_{illite}
$+0.175Ca^{++}$ + $0.35Na^+$ (4)
for expanding illite/smectite.
The equilibrium constants for these reactions are:
K = $(Ca^{++})^{0.175}(Na^+)^{0.35}$ / $(K^+)^{1.0}$ (5)
and:
K = $(Ca^{++})^{0.175}(Na^+)^{0.35}$ / $(K^+)^{0.75}$ (6)
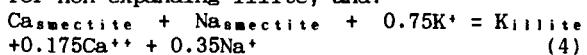
A test for such a relationship can be made using the data that Fournier and Truesdell (1973) used to derive the empirical Na-K-Ca geothermometer. Only those samples with measured temperatures ≥ 100°C are used in this figure. Figure 6 shows the data plotted in logarithmic form according to Eqn. 6. The correlation coefficient, r, for a regression of this data is 0.95. Similar regressions can be calculated using the logarithmic form of Eqn. 5 (r=0.92), and the empirical geothermometer (r=0.96) as the dependent variables. In the case of the empirical geothermometer, the expression used is: $Log(Na/K)$ + $(1/3)Log((Ca)^{0.5}/Na)$. Nearly identical correlation coefficients of 0.96 and 0.95 are obtained for the empirical geothermometer and for the equilibrium constant expression for illite/smectite. This

suggests that the relationship of Na, K and Ca in geothermal fluids is controlled by reactions involving illite/smectite.
An alternative expression for the Na-K-Ca geothermometer, based on illite/smectite equilibrium, is given by:
T °C = $1.145*10^3/\{[0.35LogNa+0.175LogCa-0.75LogK]+1.51\}$ - 273.
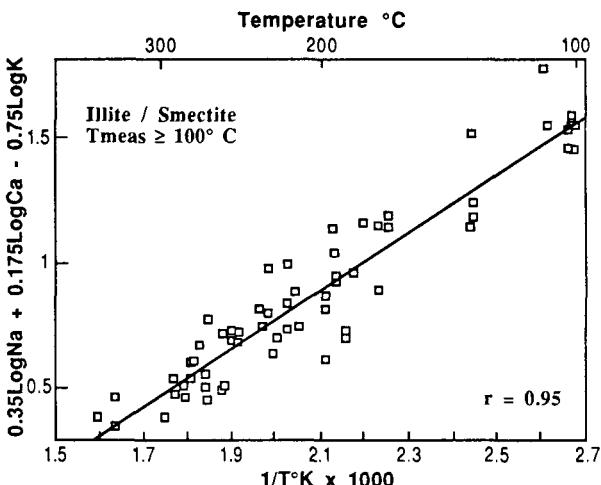

Figure 6. Fit of fluid chemistry to the equilibrium constant expression for illite/smectite equilibrium, Eqn. 6. Data are those with measured temperatures ≥ 100°C, from Fournier and Truesdell (1973).

CONCLUSIONS

The data discussed above challenge the conventional belief that illite does not contain smectite. The calculated smectite content of illite appears to be a reasonable predictor of temperature, at least for the published data available. More studies are necessary to test the geothermometer derived here.

Aqueous concentrations of Na, K and Ca are consistent with equilibria involving illite/smectite. Testing of the illite/smectite equilibrium form of the equation for the Na-K-Ca geothermometer is recommended.

Because of the exchangeability of interlayer cations in smectite and the general non-reversibilty of the smectite to illite reaction, use of the illite geothermometer derived here may be restricted to systems in which the associated aqueous chemistry conforms to the Na-K-Ca geothermometer. Thus illites in sedimentary basin systems, and in waning or fossil hydrothermal systems subjected to subsequent, non-illitizing fluids, may not fit the model described here.

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