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ESTIMATION OF THE THERMODYNAMIC PROPERTIES OF Na– Ca– AND Mg– BEIDELLITES

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ABSTRACT

The chemical composition of ground waters that were collected from granitic and basaltic terrains has been used to estimate the free energy of formation of sodium, calcium and magnesium beidellites. Their enthalpies, entropies and Maier-Kelley heat-capacity power functions have also been estimated. These thermodynamic properties have been combined with data for other phases to predict some mineral equilibria at 25°C and 200°C (1 bar total pressure). There is agreement between the predicted and observed assemblages under these conditions.

SOMMAIRE

La composition chimique d'échantillons d'eau prélevés dans des terrains aquifères granitiques et basaltiques a servi à déterminer l'énergie libre de formation des beidellites de sodium, de calcium et de magnésium. On a aussi évalué leur enthalpie, entropie et capacité calorifique de Maier-Kelley. Ces propriétés thermodynamiques, combinées aux données fournies par d'autres phases, permettent de prévoir certains équilibres minéraux à 25°C et 200°C (sous pression totale de 1 bar). Les assemblages observés dans ces conditions sont d'accord avec les prédictions.

(Traduit par la Rédaction)

INTRODUCTION

Clay minerals (subsequently referred to here as clay) are common alteration phases of aluminium silicates at the earth's surface, are often gangue constituents in ore deposits, and are ubiquitous in diagenetic and low-grade metamorphosed pelites. Even though they are common minerals, the stability of one clay over another, or even the presence and/or absence of clay in some environments, present problems to the geologist. If the thermodynamic properties of different clays were known their stability relations could be predicted, and processes such as the mineralogical transitions that occur in pelites during diagenesis and metamorphism could be elucidated. Unfortunately, calorimetric determination of thermochemical properties may often be impossible because large pure samples of a particular clay are difficult to obtain. Here an attempt has been made to obtain reliable thermodynamic data for some clay minerals by studying the composition of natural ground waters associated with these solids. Before proceeding with the calculations, some aspects of the interaction of ground waters with rocks are discussed.

Helgeson *et al.* (1969) calculate reaction paths that solutions follow when reacting with some minerals found in igneous rocks. A CO_2-charged dilute ground water, dissolving minerals from igneous rocks, generally equilibrates first with gibbsite, then with kaolinite and a clay mineral before equilibrating with feldspars. As illustrated in Figure 3 of Helgeson *et al.*, there may be conversion of one phase to a second (gibbsite to kaolinite or kaolinite to montmorillonite). If the conversion is rapid, the solution composition may be controlled by the reaction as is the case for the solution paths calculated by Helgeson *et al.* (their Fig. 3). In fact, Garrels (1967) demonstrates that the conversion of kaolinite to a calcium-bearing clay has significant effect on the concentrations of Ca^{2+}, SiO_2(aq) and pH in ground waters associated with igneous rocks. Garrels also demonstrates that the HCO_3^- content of a ground water is a good measure of the extent of reactions between a dilute CO_2-charged ground water and igneous rocks. He goes on to illustrate that those waters which have interacted only slightly with the rocks (low HCO_3^- content in the waters) are saturated with respect to kaolinite, but undersaturated in the calcium-bearing clay mineral. However, those which have reacted with the rocks to a significant extent (high HCO_3^- content in waters) approach equilibrium with kaolinite and the calcium-clay mineral. The method used by Garrels is applied here to demonstrate that ground waters collected from basaltic and granitic rocks approach equi-

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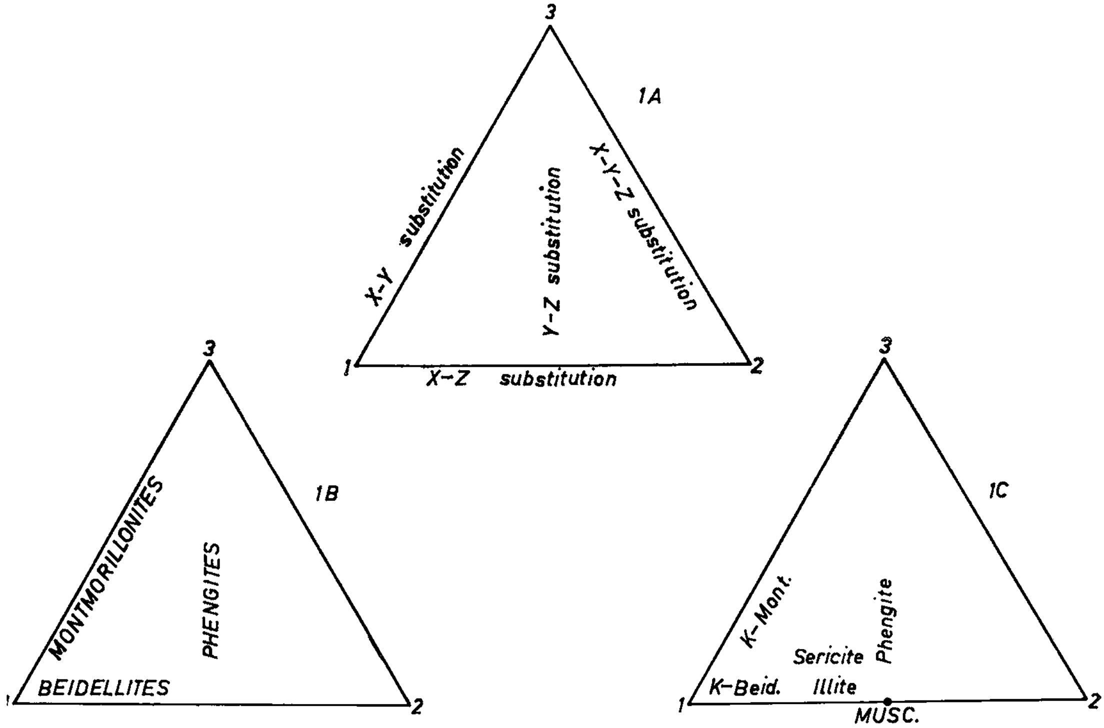

FIG. 1. Some of the common chemical variations in clays and micas. Figure 1A demonstrates types of substitutions for which electrical balance is maintained. The names associated with some of the substitutions are given in Figure 1B. Figure 1C represents the mineral solid solutions in the system K_2O-MgO-Al_2O_3-SiO_2-H_2O. Component 1 $= 0Al_4SiO_8O_{20}(OH)_4$; component 2 $= X_{4\text{-}2}\ Al_4(Si_4Al_4)O_{20}(OH)_4$; component 3 $= X_{2\text{-}1}(Y_2Al_2)Si_8O_{20}(OH)_4$;

librium with respect to kaolinite and other clays. From the composition of the aqueous solutions equilibrated with kaolinite and clay, free energies of formation of sodium, magnesium and calcium clays are calculated.

The thermodynamic properties of all aqueous species are taken from Helgeson (1969), as are the properties of kaolinite, gibbsite, and sodium and potassium feldspar. The thermodynamic properties of muscovite and pyrophyllite have been evaluated from calorimetric measurements and hydrothermal experimental data. The data for these two phases have also been tested for internal consistency with respect to the thermodynamic properties of the minerals and aqueous species obtained from Helgeson (1969).

NOMENCLATURE USED FOR CLAYS

The nomenclature employed is intended to connote chemical variations in the clay minerals. As a result, the end-member components proposed may have no naturally occurring equivalents, but are particularly useful to characterize the chemistry of the clays. One component used here is $0Al_4Si_8O_{20}(OH)_4$ (pyrophyllite component). There is no cation in the 12-fold coordination site (denoted by 0). The second component is $X_{4\text{-}2}Al_4(Si_4Al_4)O_{20}(OH)_4$ where X represents 4 monovalent cations or 2 divalent cations in the 12-fold coordination site. It is referred to as the mica component. If $X = Ca$ (2 ions), then the mineral corresponding to this component is margarite. If $X = K$ (4 ions), then the sum of ½ mole of the pyprophyllite component plus ½ mole of the mica component yields $K_2Al_4(Si_6Al_2)O_{20}(OH)_4$, muscovite. The third component is $X_{2\text{-}1}(Y_2Al_2)Si_8O_{20}(OH)_4$ and is referred to as the phengite component. X represents ions in the 12-fold coordination site (2 ions if cation is monovalent, one ion if cation is divalent). Y represents divalent cations substituting in two octahedral sites.

When X equals 12-fold coordination sites, Y equals octahedral sites, and Z equals tetrahedral sites, then the possible substitutions that may occur with charge balance being maintained are illustrated in Figure 1A. The names of mineral groups (solid solutions) associated with some of the substitutions are given in Figure 1B. If $X =$ K, $Y =$ Mg, and there is only Al-Si substitution in Z, the names of the solid-solution groups in this system are as illustrated in Figure 1C. According to the nomenclature used here the 'montmorillonites' of Garrels (1967) and Helgeson (1969) are beidellites, and are referred to as such hereafter.

DEMONSTRATION OF SOLUTION-SOLID EQUILIBRIUM BETWEEN K-MICA AND KAOLINITE

White *et al.* (1963) have tabulated analyses that were chosen as typical of solutions derived from acid and basic igneous rocks. For the reaction:

$$2KAl_3Si_3O_{10}(OH)_2 + 2H^+ + 3H_2O = 3Al_2Si_2O_5(OH)_4 + 2K^+ \qquad (1)$$

the equilibrium constant is given by

$$\log K = \log([K^+]^2/([H^+]^2([H_2O]^3)) \qquad (2)$$

if the activities of the solids equal 1.0. The square brackets denote activities and K the equilibrium constant.

Log K for reaction (1) is calculated to be 3.8 at 25°C and 4.1 at 15°C [using the data from Helgeson (1969) and ΔG°_f (25°C, muscovite)= –1332420 cal/mole]. The activities of the ions in the solutions (from White *et al.* 1963) are calculated using the Debye-Huckel theory. These activities are then used to calculate the value of the right side of equation (2) for each water. The value is referred to as the log saturation quotient and each is plotted on Figure 2. As seen in Figure 2, equilibrium with kaolinite and K-mica is approached in waters that have interacted significantly with the igneous rocks ($HCO_3^- > 100$ ppm).

The log saturation quotients for kaolinite equilibrated with the Na, Mg and Ca beidellites are calculated in the same manner as above. If a constant value for the log saturation quotient is defined by waters which have interacted significantly with the igneous rocks, it is assumed that the log saturation quotient represents the logarithm of the equilibrium constant for the reaction between kaolinite and the specified beidellite.

The equilibrium constant, combined with the free energy of formation of kaolinite and the activities of the appropriate aqueous species, permits calculation of the free energy of the beidellite.

STABILITY OF Na-BEIDELLITE

For the reaction:

$$3Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + H^+ + 11.5H_2O = 3.5Al_2Si_2O_5(OH)_4 + Na^+ + 4H_4SiO_4 \qquad (3)$$

$$\log K = \log \left| \frac{[Na^+]\,[H_4SiO_4]^4}{[H^+]\,[H_2O]^{11.5}} \right| \qquad (4)$$

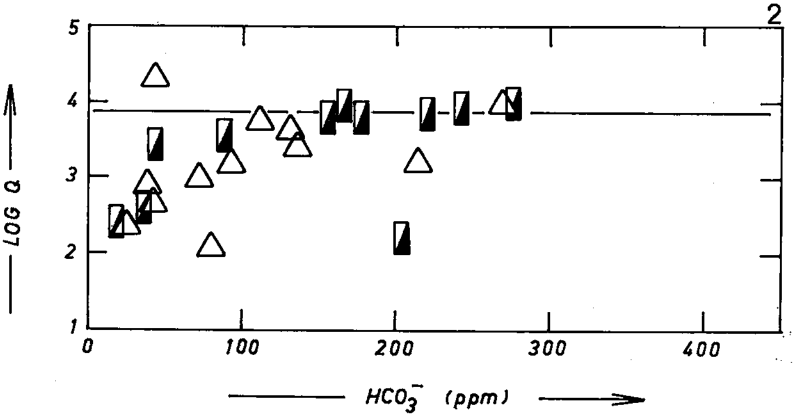

FIG. 2. Changes in the log solubility quotient (Log Q) for reaction 1 (text) as a function of HCO_3^- concentration of ground waters collected from igneous rock terrain (triangles: waters from acidic igneous rocks; rectangles: from basic igneous rocks). The solid curve is the logarithm of the equilibrium constant for reaction 1. Waters plotting above the curve are saturated in K-mica, those plotting below the curve are saturated in kaolinite, and those close to the curve are equilibrated with respect to both solids.

when the activities of the solids are taken as 1.0.

The log saturation quotient for reaction 3 equivalent to right-hand side of equation (4) is calculated for the waters listed in tables 1 and 2 of White *et al.* (1963). The calculated value for each water is plotted against the HCO_3^- content of the solution in Figure 3. The triangles represent waters derived from acidic igneous rocks (Table 1 of White *et al.* 1963), and the rectangles represent waters from basic igneous rocks (Table 2 of White *et al.*). The rectangles plotted at values of HCO_3^- greater than 100 ppm define a constant log saturation quotient. The dash-dot curve is a best fit to these rectangles. The data from the acid igneous rocks do not display the same consistency. However, data plotting at HCO_3^- values greater than 100 ppm do define a mean log saturation quotient in accord with the value defined by the rectangles.

The solid curve (above the dash-dot curve) in Figure 3 represents the equilibrium constant estimated by Helgeson (1969). The equilibrium constant (from Helgeson 1969) at 10°C is identical to the value given by the dash-dot curve. There is agreement between the equilibrium constant for reaction 3 quoted by Helgeson

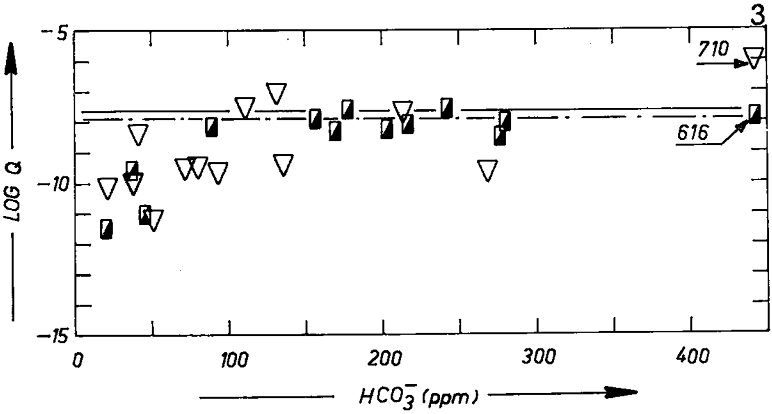

FIG. 3. Variations in the log saturation quotient (Log Q) of reaction 3 with respect to HCO_3^- in the ground waters (symbols are as in Fig. 2). The dot-dash curve is the best fit to the rectangles. Waters plotting significantly below the curve are equilibrated with respect to kaolinite, those above with respect to the beidellite.

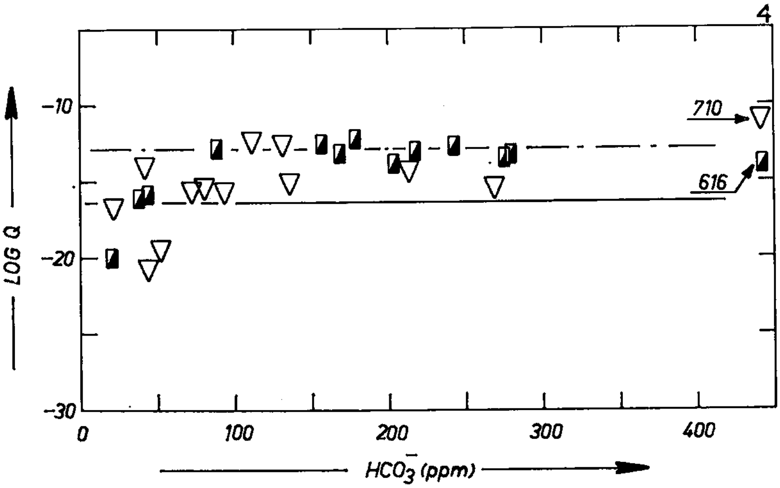

FIG. 4. Variations in the log saturation quotient (Log Q) of reaction 6 (M=Ca^{2+}) with respect to HCO_3^- (symbols are as in Fig. 2 and the dot-dash curve has the same significance as in Fig. 3). The solid curve is the log equilibrium value from Helgeson (1969).

TABLE 1. THERMODYNAMIC DATA FOR BEIDELLITES

Mineral	ΔG°_f Cal/mole	ΔH°_f Cal/mole	S° Cal/deg. mole	Cp Power Fn. Coefficients* A	B*x10^3	C*x10^{-5}
$Na_{.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2$	-1277760	-1368170	58.34	81.09	34.61	-24.62
$Ca_{.167}Al_{2.33}Si_{3.67}O_{10}(OH)_2$	-1278470	-1368485	56.93	81.72	34.34	-24.88
$Mg_{.167}Al_{2.33}Si_{3.67}O_{10}(OH)_2$	-1274505	-1364735	56.41	81.48	34.45	-24.87

*Cp Power Function Coefficients for pyrophyllite from Helgeson *et al.*, personal comm.

(1969) and the value estimated here.

The free energy of formation of Na-beidellite (25°C, 1 bar total pressure) is calculated from

$$\Delta G^\circ_B = RT\ln K \qquad (5)$$

where K is the equilibrium constant and has a value defined by the dash-dot curve of Figure 3. R is the gas constant, T the temperature (°K). The calculated free energy of formation is given in Table 1.

THE STABILITIES OF CALCIUM- AND MAGNESIUM-BEIDELLITE

For the reaction:

$$6M_{0.167}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 2H^+ + 23H_2O$$
$$= 7Al_2Si_2O_5\,(OH)_4 + Ca^{2+} + 8H_4SiO_4 \qquad (6)$$

$$\log K = \frac{[M^{2+}]\,[H_4SiO_4]^8}{[H^+]^2\,[H_2O]^{23}} \qquad (7)$$

where M is Ca^{2+} or Mg^{2+} and the activities of the solids are taken as unity. As for the Na-beidellite–kaolinite reaction, solubility quotients are calculated for the waters given in Tables 1 and 2 of White *et al.* The logarithm of the solubility quotients relating to Ca-beidellite and Mg-beidellite are plotted on Figures 4 and 5, respectively. In each Figure a constant solubility quotient is defined by the rectangles plotting at $HCO_3^- > 100$ ppm. The triangles in each Figure do not display as consistent a value, but those triangles plotting at $HCO_3^- > 100$ ppm do approach the value defined by the rectangles. The dash-dot curves in Figures 4 and 5 are the best fit to the rectangles. The solid lines drawn below the dash-dot curves (Figs. 4 and 5) are the equilibrium values estimated by Helgeson (1969). The dash-dot curve, if taken as the equilibrium value, necessitates that Ca- and Mg-beidellites are much less stable than estimated by Helgeson. The free energy of formation of Ca and Mg-beidellites are calculated using equation 5 and assuming that the dash-dot curves of Figures 4 and 5 represent the equilibrium values for the respective reactions. The free energy is given in Table 1.

INTERPRETATION OF THE THERMOCHEMICAL DATA

There can be significant cation exchange in the beidellites and many of the clays may be of the mixed-layer type.

The actual compositions of the clays and whether the clays were mixed layers, are un-

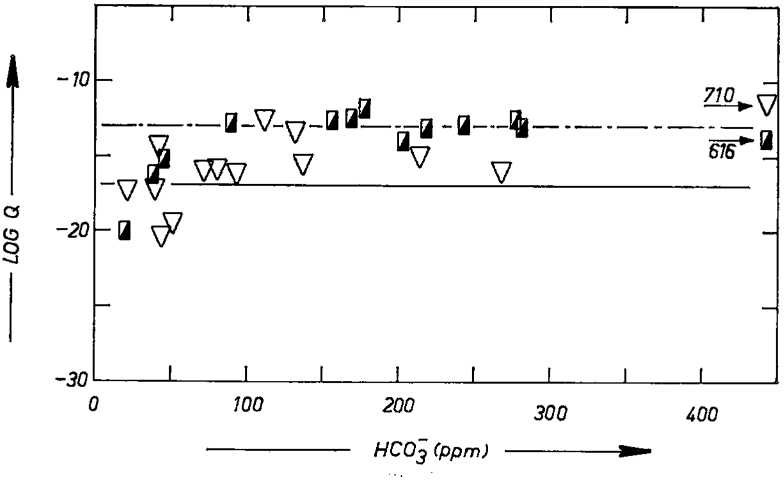

FIG. 5. The same as Figure 4 except that $M = Mg^{2+}$.

known. Because of these ambiguities it has been assumed that the activity of each end-member component has a constant value for its activity. The value may not be 1.0, but as long as it is close to constant, it can be incorporated into the equilibrium constant (K) so that K actually applies to a beidellite of some intermediate composition. This compositional restriction is of little significance compared to the error associated with the saturation quotient that was obtained from the rectangles ($HCO_3^- > 100$ ppm) of Figures 3, 4 and 5.

Entropies and Heat-Capacity Power Functions of Beidellites

There are no measurements of the entropies of beidellites. Their entropies can be estimated by summing the entropies of the constituent oxides, or using the algorithm given by Fyfe *et al.* (1958). The entropies estimated here are based on a correspondence of structure between pyrophyllite and beidellites. Beginning with the composition of pyrophyllite, appropriate oxides are added to or subtracted from pyrophyllite to obtain the desired beidellite composition. The entropies of these oxides are also added to or subtracted from that of pyrophyllite.

If the heat capacity power functions of beidellites are taken as $Cp = A+BT+C/T^2$, the coefficients in the power functions can be estimated in the same way as the entropies.

As an example, the entropy is estimated for Na-beidellite.

SPECIES	ENTROPY
$Al_2Si_4O_{10}(OH)_2$	56.6
$+ \frac{1}{6} Na_2O$	+ 3.0
$+ \frac{1}{6} Al_2O_3$	+ 2.03
$- \frac{1}{3} SiO_2$	− 3.29
Na-beidellite	58.34

The properties of the other beidellites are calculated similarly and listed in Table 1. From

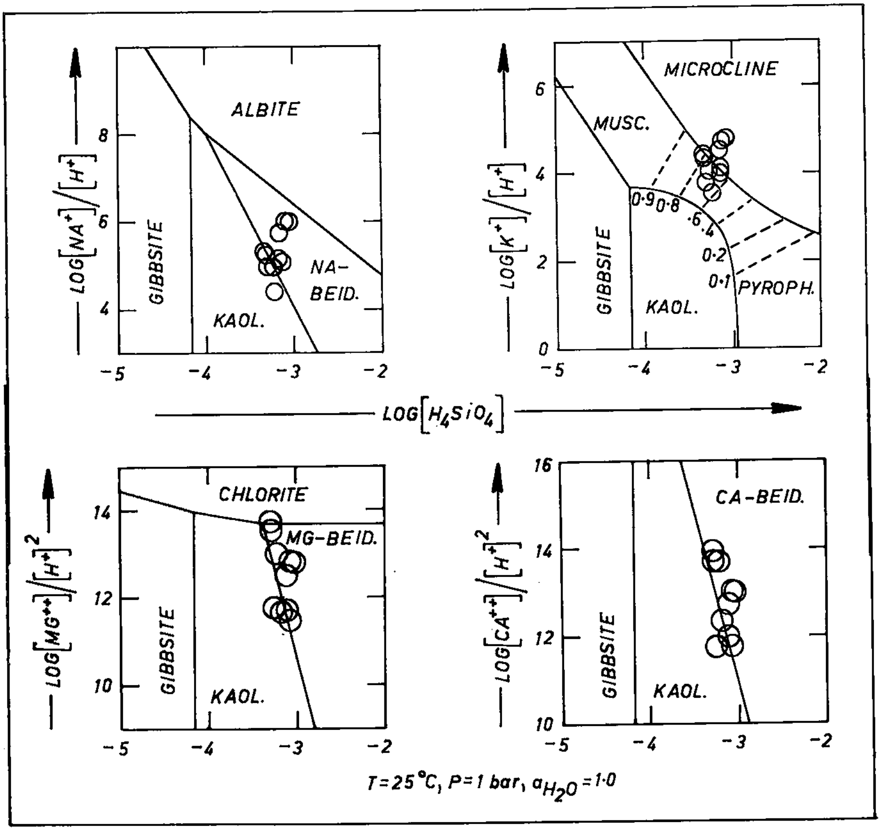

Fig. 6. Illustrates clay and other silicate equilibrium assemblages at 25°C and 1 bar. The circles are the dilute inflow waters to Saline Valley (Hardie 1968). The dashed curves numbered 0.1 to 0.9 represent illites of composition $K_nAl_2(Si_{4-n}Al_n)O_{10}(OH)_2$ (where n has the value denoted on the dashed curves).

the free energies of formation and the estimated entropies of formation the enthalpies of formation of the beidellites are calculated and also listed in Table 1.

Application of Data to Geologic Environments

Ground-water–clay equilibration

Hardie (1968) has published analyses of dilute spring and ground waters that feed into the Saline Valley closed basin. Within the basin exists a salt lake and playa region where evaporite minerals form. Around the margins of the playa are muds composed of quartz, plagioclase, 14Å chlorite, 10Å mica, and clay minerals. Associated with these minerals are dilute inflow waters of the basin. Using data presented here for beidellites and muscovite and data from Helgeson (1969) for other species, activity diagrams have been constructed which illustrate the stability fields of the clays relative to some other common minerals (Fig. 6). The dilute inflow waters to the basin (Table 2 of Hardie 1968) have been treated, using the Debye-Huckel theory, to obtain activities of the ions in the solutions. The waters plot on the beidellite-kaolinite boundaries and in the illite solid-solution field (Fig. 6). The water compositions seem to be controlled by the clay minerals.

Stable assemblages in a hydrothermal Environment

Figure 7 illustrates some equilibrium mineral assemblages stable at 200°C, in equilibrium with quartz, if the thermodynamic data of Helgeson (1969) are used for the minerals plotted in the diagram. The diagram suggests that chlorite+K-mica is not stable at this temperature, but this is a most common assemblage in hydrothermally altered rocks. If the data for Mg-beidellite and muscovite presented here are used in conjunction with the other data from Helgeson, chlorite+K-mica is a stable assemblage (Fig. 7b).

Conclusions

The thermodynamic properties of beidellites are estimated from the composition of ground waters emanating from igneous acidic and basic rocks. These estimates are in accord with mineral assemblages observed in the field, and hence seem more reliable than previous estimates.

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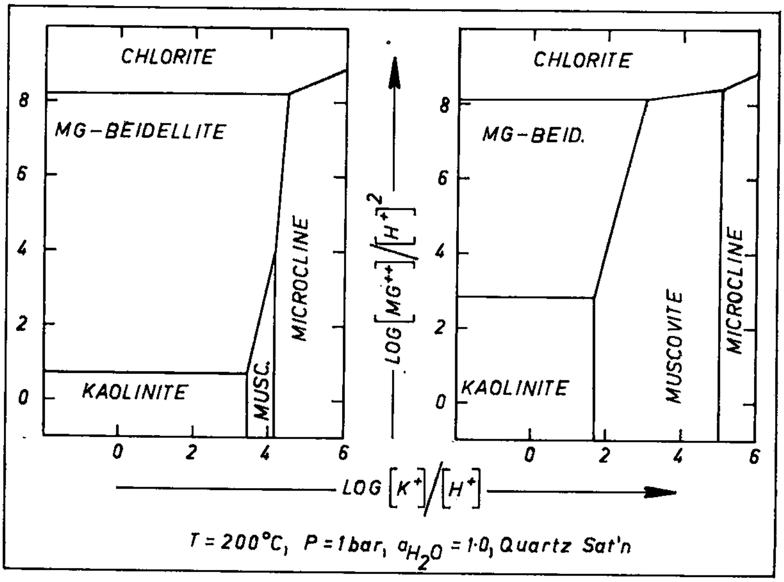

Fig. 7. (Left): predicted equilibrium assemblages at 200°C, 1 bar at quartz saturation and activity of water equalling unity, computed entirely from the data of Helgeson (1969); (right): predicted assemblages for the same conditions except that the thermodynamic properties of Mg-beidellite and

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