FREE ENERGY OF FORMATION OF BEIDELLITE FROM APPARENT SOLUBILITY MEASUREMENTS*

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Abstract—The structural formula for K and Mg saturated beidellite was calculated from the total elemental analysis of the $\langle 0.2\,\mu m$ clay fraction of the B_{2t} horizon of a Mexico soil. The free energies of formation (ΔG_f°) of K-beidellite and Mg-beidellite as determined from their apparent solubilities were -2491.3 and -2484.0 ± 3.2 kcal per mole, respectively. The free energies of formation correspond to a clay mineral structure calculated on the basis of a 24 oxygen cell.

INTRODUCTION

A close relationship is usually observed between naturally occurring mineral assemblages in a given environment, and those predicted from free energy data (Garrels, 1957). Reliable solubility data can be crucial to an understanding of the weathering reactions in soils and sediments. Helgeson *et al.* (1969) have pointed out that in most cases the mineral equilibria relations predicted from thermodynamic data were inadequate for critical comparison with those field observations reported in the literature. Although several studies have been made to calculate the free energy of formation (ΔG_f°) of clay minerals such as kaolinite (Kittrick, 1966, 1970; Huang and Keller, 1973), illite (Reesman and Keller, 1967, 1968), and montmorillonite (Huang and Keller, 1973; Kittrick, 1971a, 1971c) from their solubilities, no such data for beidellite are available. However, Helgeson (1969) has reported the (ΔG_f°) of idealized beidellite.

The purpose of this investigation was to calculate the formula of the expanding beidellite occurring in the Mexico soil and to determine the apparent solubility of the mineral in dilute aqueous systems. This information would be helpful for a better understanding of the weathering reaction, beidellite → kaolinite (Marshall *et al.*, 1973), occurring in the Mexico soil.

EXPERIMENTAL

The soil, from which the clay was obtained, belongs to the Mexico series of the fine montmorillonitic mesic family of the Aeric Udollic Albaqualfs. Soil samples were taken from the B_{2t} horizon at a depth of 20–22 in. The less than 0.2 μm clay was separated from the total clay fraction using a Sharples supercentrifuge and the procedure suggested by Jackson (1956). The dispersed clay was flocculated with $MgCl_2$ and stored for further use.

The X-ray diffractograms of oriented K and Mg saturated samples were made using the procedure described by Whittig (1965). The Greene–Kelly (1953) test was carried out on the colloidal clay fraction.

Equilibration of clay

A portion of the bulk clay sample was saturated with Mg and another with K, using 1 N $MgCl_2$ and 1 N KCl, respectively. The procedure followed was as that of Whittig (1965) for preparing samples for X-ray powder diffraction study. Portions of the saturated samples were washed several times and equilibrated with 0.01 N KCl or $MgCl_2$ solutions. Other portions of the K and Mg saturated samples were air dried after the removal of the free salt and subsequently equilibrated with deionized water and 10^{-4} N HCl. Air drying was used to reduce the amount of acetone remaining in the sample following the removal of free salt. It was not possible to centrifuge wash the saturated samples with the equilibrating solutions (deionized water and 10^{-4} N HCl) due to the dispersion of the colloidal clay or without changing the composition of the exchange surface.

Five per cent suspensions, 2.5 g clay/50 ml solution, were used in all equilibrations. The equilibrations were made in 100 ml polyethylene centrifuge tubes at room temperature with 8–10 hr of shaking daily. After 60 days, the samples were pressure filtered using stainless steel funnels with 0.05 μm filters. The filtrates were free of the Tyndall effect and apparently free of significant quantities of particulate matter (Hem *et al.*, 1973). The pH and Eh of the solutions were measured immediately after completion of filtration and the solutions then were acidified (to about 0.1 N HCl).

Total elemental analysis of clay

A portion of the bulk clay sample was treated with sodium dithionate (Whittig, 1965) to remove free Fe_2O_3 present. The clay was saturated with calcium using 1 N solutions of $CaCl_2$ and Ca $(OAC)_2$. The excess salt was removed by washing once with distilled water, twice with alcohol and several times with

about 95% acetone. After the first six washings, the sample was equilibrated for 24 hr before separating the wash liquid. The process was carried out for 15 days to insure that the sample was free of salt. The fusion of the Ca saturated clay was done following the semimicro analysis procedure suggested by Pruden and King (1969). The quantitative determinations were made following the analytical methods described below.

Cation exchange capacity

A portion of the Ca-clay prepared for total analysis was used for the determination of cation exchange capacity (C.E.C.). The exchange was carried out by repeated equilibration with 1 N $MgCl_2$ solution and the amount of Ca exchanged was determined.

Analytical methods

Sodium and potassium were determined by flame photometry. Calcium, magnesium, and iron were measured with a Jarrel Ash atomic absorption spectrophotometer, and aluminum by flame emission (Pickett and Koirtyohann, 1969) using a nitrous oxide flame. Silica was determined colorimetrically (Pruden and King, 1969). Eh was measured using a reference calomel electrode and a platinum electrode. An Orion Research Model 801 Digital pH/mV meter was employed for Eh measurement. The ferrous iron content of the clay mineral was determined following the procedures suggested by Pruden and King (1969).

Calculations

The extended form of the Debye-Huckel equation (1) was used to estimate activity coefficients (γ).

$$\text{Log} \frac{1}{\gamma} = (0.509\, Z^2 \sqrt{I})/(1 + ab\sqrt{I}). \qquad (1)$$

The ionic strength I was estimated from the total soluble salts. The product ab was assigned values of 1 for $Al(OH)_4^-$, $Al(OH)_2^+$, 2 for $Al(OH)^{2+}$, and 3 for Al^{3+}. The assigned values approximate the mean ab products for mono, di and trivalent ions. The values of ab used for Na^+, K^+, Ca^{2+} and Mg^{2+} were as given by Garrels and Christ (1965). Total aluminum in the extract was considered to be the sum of the concentration of the following aluminum species.

$$Al = \frac{(Al^{3+})}{\gamma^{+3}} + \frac{(Al(OH)^{2+})}{\gamma^{+2}} + \frac{(Al(OH)_2^+)}{\gamma^{+1}}$$
$$+ \frac{(Al(OH)_4^-)}{\gamma^{-1}}. \qquad (2)$$

Activities of various aluminum species were solved for by expressing various aluminum species in terms of Al^{3+} activity. The constants used to solve the equations were: $(Al(OH)^{2+})(H^+)/(Al^{3+}) = 1.05 \times 10^{-5}$ (Richburg and Adams, 1970), $(Al(OH)_2^+)(H^+)^2/(Al^{3+}) = 1.59 \times 10^{-10}$ (Raupach, 1963), and $(Al(OH)_4^-)(H^+)^4/(Al^{3+}) = 8.71 \times 10^{-23}$ (Truesdell and Jones, 1973).

It was assumed that apportioning the concentration of soluble Al to the monomeric species would provide an acceptable approximation of the activities of the dissolved species. Stability constants have not been derived for polymeric anionic complexes which some investigators (Plumb and Swaine, 1964; Marshall et al., 1973) have postulated may form in the alkaline range. Consideration of the cationic complex, $Al_6(OH)_{15}^{3+}$ (Richburg and Adams, 1970), did not change significantly the calculated activity of Al^{3+} in slightly alkaline soil extracts (Misra et al., 1974). Smith and Hem (1972) concluded that the concentration of measured Al in dilute solutions, resulting from the aging of aluminum hydroxide complexes, could be assigned to the four simple monomeric species by equilibrium calculations.

RESULTS AND DISCUSSION

Structural considerations

The results of the total chemical analysis of the calcium saturated clay are given in Table 1. The values in Table 1 are the averages of duplicate analyses. It may be seen that the cation exchange capacity of the clay (63.52 m-equiv./100 g) corresponded to 1.78% CaO, and the Ca-saturated clay contained 1.91% CaO. Thus a small portion of Ca which balances the frame work charge was not exchanged with Mg. The Na_2CO_3 fusion analysis of K-saturated clay showed 0.13% CaO, confirming the quantity of non-exchangeable charge balancing Ca as calculated from the analysis of the Ca-clay. The Si and Al content of the clay pretreated with NaOH, as suggested by Jackson (1956) to remove amorphous materials, did not differ significantly from the analytical values of the untreated clay. The percentages of SiO_2 and Al_2O_3 of the pretreated sample differed from the values given in Table 1 (untreated) by -0.57 and -0.32, respectively.

The structure of the clay mineral was calculated, from the results of chemical analysis, as was done

Table 1. Analysis of Ca-saturated beidellite

	Percentage (oven dry basis, 110 C)
SiO_2	50.62
Al_2O_3	22.48
Fe_2O_3	7.91
FeO	0.89
MgO	1.96
*CaO	1.91
Na_2O	0.50
K_2O	1.08
H_2O	12.71
Total	100.05

* CEC (Ca/Mg) = 63.52 m-equiv./100 g which corresponds to 1.78% CaO; 0.13% CaO was present as non exchangeable charge balancing calcium.
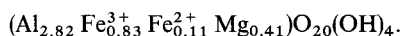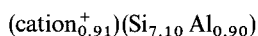
Table 2. Chemical composition* of the extracts after 60 days equilibration

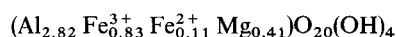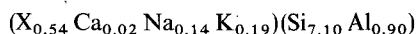| Sample	Treatment	pH	Na	K	Ca	Mg	$Si(OH)_4$	Al	Eh (mV)
					—Log Concentration (moles/l.)				
Mg-Beidellite	1	7.70	4.20	4.00	4.94	2.31	4.12	5.73	671
Mg-Beidellite	2	7.76	4.92	5.51	5.06	2.28	4.33	5.73	681
Mg-Beidellite	3	7.83	4.19	4.01	5.10	2.32	4.16	5.82	631
K-Beidellite	4	7.69	3.80	1.62	5.10	4.40	3.98	5.82	737
K-Beidellite	5	7.72	3.56	2.00	5.10	5.23	4.25	5.73	723
K-Beidellite	6	7.58	3.80	1.64	5.10	4.48	4.09	5.87	720

* All the values are averages of duplicate determination.
† Treatments 1 and 4 represent equilibration with 0.0001 N HCl, 3 and 6 with distilled water, 2 with 0.01 N $MgCl_2$ and 5 with 0.01 N KCl.

by Marshall (1949). The formula on the basis of 24 oxygen per unit cell would be:

$$(cation_{0.91}^+)(Si_{7.10} Al_{0.90})$$
$$(Al_{2.82} Fe_{0.83}^{3+} Fe_{0.11}^{2+} Mg_{0.41})O_{20}(OH)_4.$$

More specifically the formula may be written as:

$$(X_{0.54} Ca_{0.02} Na_{0.14} K_{0.19})(Si_{7.10} Al_{0.90})$$
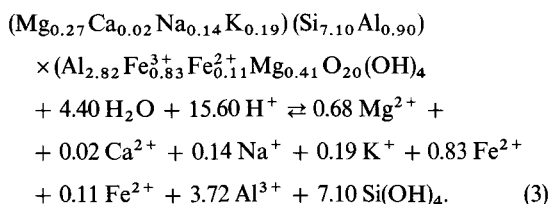$$(Al_{2.82} Fe_{0.83}^{3+} Fe_{0.11}^{2+} Mg_{0.41})O_{20}(OH)_4$$

where X is the exchangeable cations representing cation exchange capacity. For a Mg saturated clay, $X_{0.54} = Mg_{0.27}$ and for a K saturated clay $X_{0.54} = K_{0.54}$. The structural formula showed that the framework charge originated mainly from the tetrahedral layers and that the clay contained a small quantity of octahedral Fe as compared to nontronite. Hence, the formula corresponded to that of a beidellite in the montmorillonite–beidellite series.

The X-ray diffractograms of the Mg-saturated and Mg-saturated plus ethylene glycol solvated oriented clays showed characteristic 14Å and 17Å peaks of montmorillonite, respectively. No characteristic peaks for other clay minerals were found. The basal spacings of the clay when subjected to the Greene-Kelly (1953) test were in accordance with the criterion given for beidellite. The test proposes to distinguish montmorillonite from beidellite with the lattice spacing of montmorillonite collapsing irreversibly when the mineral is saturated with small ions like Li and dehydrated by moderate heating (200°C). The Li saturated sample gave a basal spacing of 14.9 Å which collapsed on heating and reconstituted to a spacing of 17 Å on ethylene glycol solvation: hence the expan-

sion behavior of the clay was as described for beidellite.

Dissolution of beidellite

The dissolution reaction of the Mg-saturated beidellite at 25°C, and 1 atmosphere is shown below:

$$(Mg_{0.27} Ca_{0.02} Na_{0.14} K_{0.19}) (Si_{7.10} Al_{0.90})$$
$$\times (Al_{2.82} Fe_{0.83}^{3+} Fe_{0.11}^{2+} Mg_{0.41} O_{20}(OH)_4$$
$$+ 4.40 H_2O + 15.60 H^+ \rightleftarrows 0.68 Mg^{2+} +$$
$$+ 0.02 Ca^{2+} + 0.14 Na^+ + 0.19 K^+ + 0.83 Fe^{2+}$$
$$+ 0.11 Fe^{2+} + 3.72 Al^{3+} + 7.10 Si(OH)_4. \qquad (3)$$

The pK value for the above reaction (r) can be written as follows:

$$pK_{(r)_3} = 0.68 \, pMg^{2+} + 0.02 \, pCa^{2+} + 0.14 \, pNa^+$$
$$+ 0.19 \, pK^+ + 0.83 \, pFe^{3+} + 0.11 \, pFe^{2+}$$
$$+ 3.72 \, pAl^{3+} + 7.10 \, pSi(OH)_4$$
$$- 15.60 \, pH^+. \qquad (4)$$

The composition of the equilibrated solution (Table 2) was used to calculate the apparent pK value. The solubility data represent only one of several data points required for graphical interpretation of the progress to equilibrium conditions and the pK value (Kittrick, 1966; 1971a). A single 60 day equilibration period was used due to a constraint of time and in consideration of the results obtained when soil samples dominated by the beidellite clay were equilibrated for periods of 2–120 days (Misra *et al.*, 1975). The composition of the solution for the 60–120 day

Table 3. Negative log activity of various ions in the extract

Sample* Number	pH	pAl^{3+}	$pAl(OH)^{2+}$	$pAl(OH)_2^+$	$pAl(OH)_4^-$	pNa	pK	pCa	pMg	pFe^{3+}	pFe^{2+}	$pSi(OH)_4$
1	7.70	14.60	12.82	8.93	5.77	4.25	4.06	5.13	2.50	18.20	16.56	4.12
2	7.76	14.80	12.94	9.01	5.77	4.96	5.56	5.24	2.47	18.38	16.91	4.33
3	7.83	15.20	13.27	9.26	5.86	4.24	4.06	5.30	2.51	18.59	16.27	4.16
4	7.69	14.60	12.87	9.00	5.88	3.86	1.69	5.36	4.62	18.17	17.63	3.98
5	7.72	14.60	12.85	8.95	5.77	3.61	2.05	5.28	5.39	18.26	17.50	4.25
6	7.58	14.20	12.59	8.83	5.93	3.86	1.71	5.34	4.70	17.84	17.03	4.09

* Corresponds to treatments described in Table 2.

periods were similar, thus it was concluded that a 60 day equilibration of the clay separate would provide compositional data that would be a reasonable reflection of the solubility of the clay mineral.

The concentrations of ions (Table 2) converted to activities are given in Table 3. The concentration of iron in the extracts was below the analytical range of the method used in its determination (0.1 ppm; Olson, 1965). The Fe^{3+} and Fe^{2+} activities in the extract were calculated from the pH and Eh measurements assuming that amorphous $Fe(OH)_3$ controlled the activity of iron. Truesdell and Jones (1973) recalculated the ΔG_f° of montmorillonite given by Kittrick (1971a,c) assuming hydrogen montmorillonite was dissolved in equilibrium with amorphous $Fe(OH)_3$ rather than hematite. The constants chosen for computation of iron were $(Fe^{3+})(OH^-)^3/(Fe(OH)_3) =$ $10^{-37.1}$ (Langmuir, 1964) and $(Fe^{3+})(e^-)/Fe^{2+} =$ $10^{-13.013}$. (Truesdell and Jones, 1973). The computed activity of Fe^{2+} is subject to the uncertainty of the reliability of measured Eh potentials of dilute systems (Stumm and Morgan, 1970). It was assumed that the error in the apparent pK value due to the uncertainty of the Fe^{2+} activity defined by a questionable Eh potential would not be any greater than the error associated with simply ignoring the component as a minor constituent or attempting to relate the $Fe^{3+}/$ Fe^{2+} couple to other possible redox processes such as the $H_2O/O_{2(g)}$ couple which would have required the system be in equilibrium with an assumed partial pressure of oxygen.

The apparent pK values for the dissolution of Mg-beidellite are recorded in Table 4. The apparent pK = -14.61 ± 0.51 given for the dissolution in 0.1 N $MgCl_2$, the more positive value for the three equilibration conditions, was taken for computation of the apparent ΔG_f° of the mineral. The uncertainty factor of the apparent pK is related to the random errors in the analyses of the solutions only which were estimated to be ± 0.013 (pK$^+$, pNa$^+$ and pMg^{2+}), 0.021 (pCa^{2+} and pH$_4$SiO$_4$), ± 0.03 pH$^+$ and ± 0.04 pAl^{3+}. The standard free energy of the reaction would be,

$$\Delta G_f^\circ = 1.364 \times pK$$
$$= 1.364 \times -14.61 \pm 0.51$$
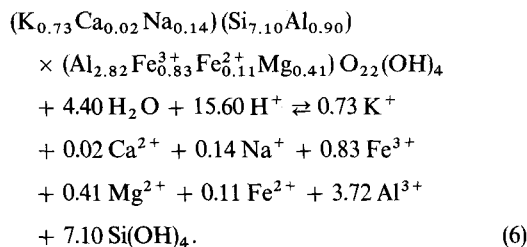$$= -19.93 \pm 0.69 \, kcal. \quad (5)$$

Using the standard free energies of formation of ions (taken from Robie and Waldbaun, 1968) the ΔG_f° of Mg-beidellite is computed from the $\Delta G_{(r3)}^\circ$. The com-

puted ΔG_f° for Mg-beidellite was -2484.0 ± 3.2 kcal/mole. The ΔG_f° for $Si(OH)_4$ chosen (-312.56 kcal/mole) was calculated from the solubility of quartz = 6 ppm SiO_2 (Iler, 1955) and the ΔG_f° of SiO_2 and H_2O (Robie and Waldbaum, 1969).

The dissolution reaction of K-beidellite may be written as follows:

$$(K_{0.73}Ca_{0.02}Na_{0.14})(Si_{7.10}Al_{0.90})$$
$$\times (Al_{2.82}Fe_{0.83}^{3+}Fe_{0.11}^{2+}Mg_{0.41})O_{22}(OH)_4$$
$$+ 4.40 \, H_2O + 15.60 \, H^+ \rightleftarrows 0.73 \, K^+$$
$$+ 0.02 \, Ca^{2+} + 0.14 \, Na^+ + 0.83 \, Fe^{3+}$$
$$+ 0.41 \, Mg^{2+} + 0.11 \, Fe^{2+} + 3.72 \, Al^{3+}$$
$$+ 7.10 \, Si(OH)_4. \quad (6)$$

The apparent pK value for reaction (6), (Table 4), and the ΔG_f° for K-beidellite were calculated in similar manner as Mg-beidellite. The ΔG_f° for K-beidellite obtained was -2491.3 ± 3.2 kcal/mole.

The beidellite dissolution reaction, involving aluminum species other than Al^{3+} can be written and pK for the reaction calculated from the data in Table 3.

The potassium saturated beidellite differed from its magnesium saturated counterpart by 7.3 kcal. No data on ΔG_f° of beidellite of the composition used in the present study is available in the literature with which the data can be compared. However, considering idealized beidellite structure with 0.66 charge on 24 oxygen unit cell, Helgeson (1969) has reported ΔG_f° values of -2550.7 and -2559.2 kcal/mole, Mg-beidellite and K-beidellite, respectively. The difference between the two beidellites is 8.5 kcal. The differences in the ΔG_f° values of beidellites found in the present study and that reported by Helgeson may be attributed to the differences in the elemental substitution in the lattice structure and the charge balancing cations. For other 2:1 type minerals such as Na-rich Wyoming bentonite and Ca-rich Arizona montmorillonite, the ΔG_f° calculated from their solubilities were -2496.4 and -2504.2 kcal/mole based on 24 oxygen cell, respectively (Huang and Keller, 1973). Although, these minerals do not fall in the beidellite group, their ΔG_f° values are closer to our findings.

Ionic relations

The average of the ion activity products calculated on the basis of the dissolution of kaolinite, pK = $2p$Al^{3+} + $2p$H$_4$SiO$_4$ − 6pH, was -8.6. This would indicate that the solutions were saturated with respect to a relative soluble kaolinite (Kittrick, 1966). The ratio of Si/Al in solution was about 55, differing from the ratio of the beidellite by a factor of 25. The incongruent solution could have resulted from the precipitation of kaolinite during the initial phase of dissolution (Kittrick, 1970) when the solution was undersaturated relative to beidellite, or from the presence of an undetected (by X-ray powder diffraction and electronmicrographs) quantity of poorly crystal-

Table 4. pK values for the dissolution reaction of beidellite

Equilibrating solution	Mg-Beidellite	K-Beidellite
Dilute acid	-16.42	-16.57
Dilute salt	-14.61	-14.52
Distilled water	-15.67	-15.83
Random error (analytical) ± 0.51		± 0.51

line kaolinite in the sample. The implied conditions would not invalidate the applicability of the solution data to the dissolution of beidellite but they would place additional constraints on the system; namely, that the kaolinite content of the original sample be of an insignificant quantity relative to the chemical composition of the beidellite, and that the equilibrium conditions would require that the mineral phase not only be in equilibrium with a saturated solution of their common ions but that the mineral components be in their most stable or crystalline form. It is evident from the ionic relations of the solutions that at least one of the criteria of equilibrium was not met. In consideration of this fact and the physical nature of the clay sample, the $<0.02\,\mu m$ fraction which would contain the most finely divided crystalline and possibly some poorly crystalline beidellite with enhanced solubilities, the solubility data presented must be considered as representative of a metastable state in the progress of the system to a thermodynamic equilibrium.

The equilibrium composition of the solution would necessitate at least that the ion activity product, $2pAl^{3+} + 2pH_4SiO_4 - 6pH$ be no more negative than -6.6, the value for crystalline kaolinite (Kittrick, 1966). Apportioning the required change in the ion product to the activities of Al^{3+} and H_4SiO_4 with the assumption that the pH of the system after 60 days would closely approximate the equilibrium pH (Kittrick, 1971b), the recalculated ΔG_f° values for Mg-beidellite and K-beidellite were -2488.1 and -2496.3 ± 3.2 kcal/mole. The activities used in the calculations were those of samples number 2 and 5, $0.01\,N$ $MgCl_2$ and $0.01\,N$ KCl equilibrated solutions. Each magnitude of error associated with the assumptions made in estimating pFe^{3+} and pFe^{2+} would modify the ΔG_f° values by 1.1 and 0.14 kcal/mole, respectively.

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