CATION AND SILICA RELATIONSHIPS OF MICA WEATHERING TO VERMICULITE IN CALCAREOUS HARPS SOIL

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Abstract—A steady state reaction of apparent equilibrium of K mica $+ Ca^{2+} \rightleftarrows$ Ca vermiculite $+ K^+$ was indicated by prolonged dissolution extractions from Blount soil clay (from northern Indiana) abundant in dioctahedral mica and vermiculite, with log $K_{eq} = 2.92$ for the reaction when extrapolated to infinite time. From this and published free energies of formation of mica and kaolinite, a mineral phase stability diagram depicting the phase joins of Ca vermiculite, muscovite, and kaolinite was constructed with the solute activity functions pH–pK^+, 2pH–pCa^{2+}, and $pSi(OH)_4$. These solute functions for 14-day reactions of calcareous (and dolomitic), poorly drained Harps soil (from central Iowa) fell near the calcite–dolomite–CO_2-H_2O phase join, suggesting equilibrium. These functions for Harps soil and the control minerals muscovite, biotite, and (or) vermiculite plus calcite were plotted on the mica–vermiculite stability diagram for various CO_2 partial pressures. The points fell on the vermiculite-stable side of the mica–vermiculite plane at CO_2 partial pressures of 0.15 and 0.20 atm (similar to soil air that would exist under frozen soil during winter and early spring; 2pH–$pCa^{2+} \simeq 10.3$). They fell on the muscovite-stable side of the muscovite–vermiculite plane at CO_2 partial pressures of 0.0001 and 0.001 atm (similar to soil air under natural summer conditions; 2pH–pCa^{2+}, 13.6 and 12.6, respectively) *and therefore* K^+ (and $^{137}Cs^+$ in rainfall) would be expected to be fixed.

The 2pH-pMg^{2+} values determined for Harps soil at the various CO_2 partial pressures plotted either in the Mg montmorillonite stability field or on the Mg–montmorillonite-kaolinite phase join, in concordance with the abundance of montmorillonite and some kaolinite in the medium and fine clay fractions. The solute values for the nearby Clarion soil (upland, noncalcareous) plotted on the montmorillonite-kaolinite join, or with higher CO_2 partial pressure, in the kaolinite stability area. The Gibbs free energy of formation (ΔG_f^0) for a dioctahedral Ca vermiculite of -1303.7 kcal per O_{10} was determined from the K_{eq}. The solute functions for the Blount soil showed kaolinite to be the thermodynamically stable phase with respect to dioctahedral mica and (or) vermiculite. The 14-day solute values for the Harps and upland Clarion soils were also on the kaolinite stability side of the kaolinite–vermiculite join. The kinetics of kaolinite formation in the upper midwestern U.S.A. are apparently slow on a scale of $\sim 10^4$ years.

INTRODUCTION

The objective of this paper is to show, with the aid of mineral stability diagrams, the influence of varied CO_2 partial pressures and calcite upon the stability of mica, vermiculite, montmorillonite and kaolinite in Harps (calcareous) and Clarion soils and in artificial mixtures of micaceous minerals. The mica-kaolinite phase join, at elevated temperatures and pressures and in the presence of excess silica as quartz, was found to be controlled by the ratio of K^+ to H^+ existing in solution (Hemley, 1959). At 25°C and 1 atm, approximately the conditions existing at the earth's surface and in soils, the mica–kaolinite phase join was calculated from thermodynamics

to occur at a pH–pK^+ value between 6.5 (Garrels and Christ, 1965) and 5.5 (Hess, 1966).

Soil micas weather to the expansible layer silicate, vermiculite, through the replacement of interlayer K^+ by the hydrated cations, such as Ca^{2+} and Mg^{2+}, abundant in calcareous (dolomitic) soils. Poorly drained lowland Harps soil of the central Iowa contains vermiculite (Sawhney *et al.*, 1959), a mineral with the ability to fix K^+ and $^{137}Cs^+$, as well as mica, montmorillonite, and a little kaolinite.

MATERIALS

The Harps (classified as a Typic Calciaquoll; formerly, Harpster) and Clarion (a Typic Hapludoll) soils of the Clarion-Nicollet-Webster soil association located in Story County, Iowa (IA), were selected for study because of the known contrast in K^+ release and fixation properties. This soil association, less than 14 000 years of age, is located in silty Cary drift (Ruhe, 1969). Although carbonates have been leached from the A and B horizons of the Clarion soil, the Harps profile is calcareous (small snail shells) throughout.

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Samples (<2 mm in diameter) of the Harps B3 horizon (61 to 86 cm) and of the Clarion B2 horizon (48 to 64 cm) were used. The B horizon (30 to 71 cm), from the imperfectly drained Blount soil developed in shale-derived till of mid-Wisconsinan age, near Millersburg, Elkhart Co., Indiana (IN) was used because it was rich in mica and vermiculite.

As control minerals, biotite (Spruce Pine, NC) and muscovite (source unknown) were wet ground in a high speed rotary Sorvall Omnimixer and the fraction 2–50 μm dia. obtained by sieving and centrifugation. The 2–105 μm fraction of micaceous vermiculite from Transvaal, South Africa (Wards Scientific Establishment, Rochester, NY) was similarly prepared. Reagent grade $CaCO_3$ (calcite by X-ray powder diffraction, XRD) was used. Commercial mixtures containing 15% (0.15 atm) and 20% (0.20 atm) CO_2 and laboratory compressed air containing 0.1% (0.001 atm) of CO_2 were used.
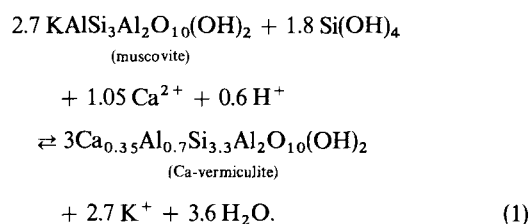
METHODS

The Blount sample was shaken with a soil:water ratio of 1:10. The solutes from Harps B3, Clarion B2, muscovite, biotite, vermiculite, and 1:1 mixtures of muscovite–vermiculite and biotite–vermiculite were obtained in solutions equilibrated with gas mixtures of varying CO_2 partial pressures, with 0.5 g samples of the soils and 0.25 g samples of the micaceous samples or mixtures, in 100 ml polyethylene tubes. The control micaceous minerals were washed five times with a 0.5 N $CaCl_2$ solution and subsequently washed free of salts with distilled water. A 100 mg sample of calcite (reagent grade $CaCO_3$) and 50 ml of distilled H_2O were added to each of the control micaceous systems. Five replicates of each sample combination were equilibrated with each of four gas mixtures having CO_2 partial pressures of 0.0001, 0.001, 0.15 and 0.20 atm, respectively, each gas being saturated with H_2O vapor. The gas mixture having a CO_2 partial pressure of 0.0001 atm was prepared by passage of compressed air through a $Ba(OH)_2$ trap. The suspensions were constantly agitated on a wrist-action shaker at 24 ± 1°C for 14 days, and centrifuged while tightly stoppered with plastic caps. The supernatant solutions were again aerated with the appropriate gas mixture for a few hours to insure the same CO_2 content as the initial equilibration. Subsequently, an aliquot was placed in a polyethylene

*The dioctahedral aluminous endmember of muscovite has been used in equation (1) for convenience, although small amounts of Fe^{3+} and Mg^{2+} may be present, unchanged in the layers of the vermiculite formed from mica in the Blount, Harps, and Clarion soils, while Si replaces Al as for phlogopite $\rightleftarrows$ saponite (Sridhar and Jackson, 1974). Layer charge change by protonation of apical oxygen (Raman and Jackson, 1966) or layer edges (Jackson, 1965) may also be involved. The Al for Si change back to mica may not be fully reversible at 25°C and 1 atm, but is at higher temperature and pressure under burial diagenesis (Weaver and Beck, 1971).
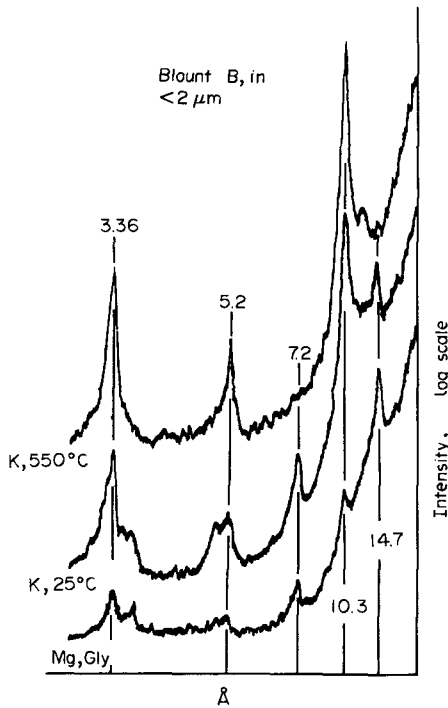
bottle containing a drop of concentrated HCl and used for K^+ determination. The pH of the remaining supernatant was determined with a Metrohm pH meter while the appropriate gas was bubbled through the solution. This portion of the supernatant solution was decanted into a polyethylene bottle containing one drop of concentrated HCl and used for the determination of Ca^{2+}, Mg^{2+} and $Si(OH)_4$. The concentrations of Ca^{2+} and K^+ were determined by flame emission spectrophotometry; of Mg^{2+} by atomic absorption spectrophotometry in the presence of Sr^{2+} (4000 ppm) which prevented interferences by other cations in solution. The concentration of $Si(OH)_4$ was determined colorimetrically by the molybdosilicate method of Boltz and Mellon (1947).

RESULTS AND DISCUSSION

Development of mineral stability diagram

The K^+ release-fixation and transformation of muscovite to vermiculite in the soils may be represented*:

$$2.7\ KAlSi_3Al_2O_{10}(OH)_2 + 1.8\ Si(OH)_4$$
$$\text{(muscovite)}$$

$$+\ 1.05\ Ca^{2+} + 0.6\ H^+$$

$$\rightleftarrows 3Ca_{0.35}Al_{0.7}Si_{3.3}Al_2O_{10}(OH)_2$$
$$\text{(Ca-vermiculite)}$$

$$+\ 2.7\ K^+ + 3.6\ H_2O. \tag{1}$$

In the presence of free carbonates such as calcite, the CO_2 partial pressure controls the range of pH and the pH is sufficiently high that aluminum may be considered to remain in the layers of the neoformed solid phases (Feth et al., 1964; Weaver et al., 1971). The equilibrium constant (K_{eq}) for equation (1), with the activities of H_2O and of the solid phases being taken as unity, is:

$$K_{eq} = \frac{(K^+)^{2.7}}{(H^+)^{0.6}[Si(OH)_4]^{1.8}(Ca^{2+})^{1.05}} \tag{2}$$

and

$$\log K_{eq} = 2.7 \log \frac{(K^+)}{(H^+)}$$
$$- 1.05 \log \frac{(Ca^{2+})}{(H^+)^2} - 1.8 \log[Si(OH)_4]. \tag{3}$$

The log Q values for solute activities were determined for the Blount soil, the clay fraction of which is dominated by dioctahedral mica and vermiculite (Fig. 1), in water at time intervals from 3 to 100 days (Table 1). The plot of log Q against the reciprocal square root of time was extrapolated to infinite time

Fig. 1. X-ray diffractograms of <2 μm size fraction of the Blount soil B horizon. K, 550°C = K-saturated sample heated at 550°C (the presence of the strong (002) near 5 Å is characteristic of dioctahedral vermiculite and mica); K, 25°C = K-saturated sample dried at 25°C; Mg–gly = Mg-saturated sample, glycerol solvated.
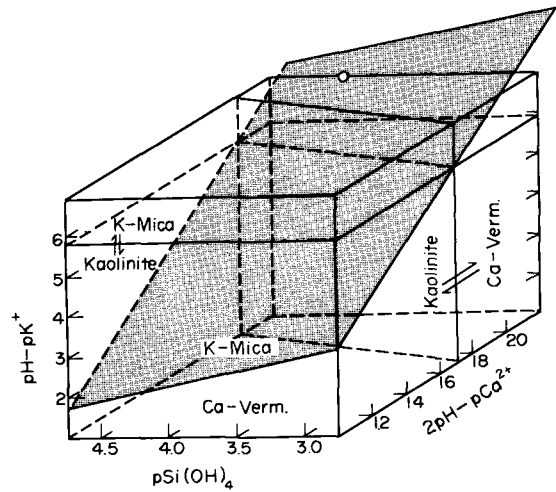

Fig. 2. Mineral stability diagram for muscovite, Ca vermiculite, and kaolinite at 1 atm and 25°C. The shaded plane represents the mica–vermiculite system in the absence of kaolinite, in the range of pSi(OH)$_4$ from the kaolinite/gibbsite join (Garrels and Christ, 1965) to the solubility of amorphous silica.

to obtain a log K_{eq} = 2.92 for substitution in equation (3), giving:

$$2.92 = 2.7\,(\text{pH}-p\text{K}^+) - 1.05\,(2\text{pH}-p\text{Ca}^{2+})$$
$$+ 1.8\,p\text{Si(OH)}_4. \quad (4)$$

This clay is virtually free of montmorillonite but contains small amounts of kaolinite and chlorite, the effects of which are to provide common ion and common solute sources (as discussed for kaolinite, Kit-

Table 1. Solute activity functions in a suspension* of Blount B horizon soil (30–71 cm), abundant in dioctahedral mica and vermiculite

Days $t^{-\frac{1}{2}}$	3 0.58	9 0.33	20 0.22	48 0.15	100 0.10	∞ 0†
pH	5.35	5.03	5.00	5.01	5.03	—
pSi(OH)$_4$	3.95	3.87	3.72	3.67	3.64	·
pCa^{2+}	4.41	4.37	4.17	4.24	4.30	·
2pH–pCa^{2+}	6.29	5.69	5.83	5.78	5.76	—
pK$^+$	4.35	4.21	4.07	4.12	4.10	—
pH–pK$^+$	1.00	0.82	0.93	0.89	0.93	—
log Q	3.21	3.18	3.09	2.94	3.02	2.92

* 10 g of soil to 100 ml of H$_2$O, agitated gently at 25°C; at CO$_2$ partial pressure (<0.1 atm) of air and total cations $<10^{-3}$ M, at which ion pairing (Nakayama, 1968) would be expected to be insignificant.
† Extrapolated.

trick, 1966). Kaolinite dissolution provides a source of Si(OH)$_4$ in solution (and aluminum hydroxide coatings, Weaver et al., 1971, equation 14) as do silica relics that may be present in the soil. The activity functions of the mica–vermiculite systems, 2pH–pCa^{2+} and pH–pK$^+$ (equation 4), approach equilibrium with the existing activity of Si(OH)$_4$, according to equation (2). At the same time, the adsorption capacity of chlorite for Si(OH)$_4$ (Weaver et al., 1971) has been satisfied (Table 1) by the soil sources of silica.

The mica–vermiculite join based on equation (4), shaded in Fig. 2, covers the observed range of pSi(OH)$_4$ (3.6 to 4.7, Tables 1 and 3) in the various systems studied (Table 2). The geochemical reaction muscovite ⇌ dioctahedral vermiculite, between two meta-stable phases, is apparently rapid enough to reach a steady state that approximates thermo-dynamic equilibrium, while the low kaolinite contents reflect slow kinetics. These relationships will be discussed in a section below.

Plot of solute activities on activity diagrams

Since over 100 days were required for the mica ⇌ vermiculite reaction to approach equilibrium, only the kinetics of that reaction can be interpreted for the 14-day solute activities from the soils and control minerals with varying CO$_2$ partial pressures (Table 2). The carbonates had apparently come to equilibrium with each CO$_2$ partial pressure, since the Harps B3 points fall, within experimental error, on the calcite dolomite join (Fig. 3). The determined solute concentrations were converted to activities through activity coefficients calculated by the expanded Debye-Huckel law (Butler, 1964), with the radii of the hydrated cations reported by Grim (1968). In saturated

Table 2. The pH and K^+, Mg^{2+}, Ca^{2+} and $Si(OH)_4$ concentrations in aqueous solution from suspensions of soil materials and control micaceous minerals plus calcite after 14 days, as affected by the CO_2 content of the equilibrium gas phase

Sample	pH	$K^+ \times 10^5$ M	$K^+ \times 10^5$ a	$Ca^{2+} \times 10^5$ M	$Ca^{2+} \times 10^5$ a	$Mg^{2+} \times 10^5$ M	$Mg^{2+} \times 10^5$ a	$Si(OH)_4$ $M \times 10^5$
				0.0001 atm CO_2				
Harps B3	8.61	3.58	3.40	32.5	27.3	27.9	23.4	23
Clarion B2*	7.98	3.33	3.33	7.5	6.95	n.d.†	n.d.†	8.5
				0.001 atm CO_2				
Harps B3	8.02	3.02	2.83	77.5	64.4	27.8	22.2	6.98
Clarion B2*	6.60	3.58	3.43	27.5	23.6	28.9	24.9	19.0
Muscovite	7.97	1.23	1.17	60.0	50.4	1.25	1.05	4.08
Biotite	8.09	2.69	2.55	57.5	47.7	6.45	5.41	1.93
Vermiculite	8.00	4.86	4.56	85.5	69.3	5.93	4.74	7.70
Muscovite + verm.‡	8.00	3.27	3.17	37.5	32.3	2.47	2.12	3.81
Biotite + verm.‖	8.07	5.12	4.86	42.5	36.1	2.47	2.12	4.97
				0.15 atm CO_2				
Harps B3	6.52	3.07	2.76	346	235	67.9	46.85	10.8
Muscovite	6.50	1.92	1.70	384	265	1.19	0.82	4.56
Biotite	6.46	3.41	3.06	353	247	3.53	2.47	3.04
Vermiculite	6.51	7.30	6.57	340	235	11.1	7.76	9.29
Muscovite + verm.‡	6.48	4.60	4.14	340	238	8.49	6.01	6.60
Biotite + verm.‖	6.47	6.00	5.40	340	238	8.80	6.16	7.45
				0.20 atm CO_2				
Harps B3	6.36	1.61	1.40	630	397	60.8	38.4	11.4
Clarion B2*	5.06	2.25	2.18	10.0	8.90	9.80	8.82	10.5

* Non-calcareous and no calcite added.   † n.d. = not determined.   ‡ Muscovite + vermiculite. ‖ Biotite + vermiculite.

$CaCO_3$ solutions at equilibrium with CO_2 gas compositions over the range from 0.54 to 20.3% (Nakayama, 1968), approximately 90% of the total Ca exists in the Ca^{2+} form. The remaining 10% exists as ion-pairs predominantly in the form of $CaHCO_3^+$ and $CaCO_3^0$. Ion-pairs of Ca^{2+} and Mg^{2+} were not considered here because the calculated pCa^{2+} or pMg^{2+} values, within a few percent of values corrected for ion-pair formation, involved a magnitude of error comparable to the uncertainties of the pH values, particularly when doubled in the function $2pH–pCa^{2+}$.

Harps B3: The 14-day solute activity functions (Table 3) for the Harps B3 horizon and control mineral systems, plotted on isoplethic sections of the mineral activity diagram (Fig. 2), were in the musco-

Table 3. Solute activity functions of solutions in contact with soil materials and control micaceous minerals plus calcite as affected by the CO_2 partial pressure of the equilibrium gas phase

Sample	pH	$pSi(OH)_4$	$pH–pK^+$	$2pH–pCa^{2+}$	$2pH–pMg^{2+}$	Ionic strength
		0.0001 atm CO_2				
Harps B3	8.61	3.64	4.14	13.66	13.59	0.0018
Clarion B2*	7.98	4.07	3.50	11.79	n.d.†	0.0003
		0.001 atm CO_2				
Harps B3	8.02	4.16	3.47	12.85	12.39	0.0032
Clarion B2*	6.60	3.72	2.14	9.57	9.60	0.0013
Muscovite	7.97	4.39	3.04	12.64	10.96	0.0018
Biotite	8.09	4.72	3.50	12.86	11.91	0.0019
Vermiculite	8.00	4.21	3.65	12.84	11.68	0.0028
Muscovite + Verm.‡	8.00	4.42	3.50	12.51	11.34	0.0012
Biotite + Verm.‖	8.07	4.30	3.76	12.70	11.47	0.0014
		0.15 atm CO_2				
Harps B3	6.52	3.97	1.96	10.41	9.71	0.0124
Muscovite	6.50	4.34	1.73	10.42	7.91	0.0116
Biotite	6.46	4.52	1.95	10.31	8.31	0.0107
Vermiculite	6.51	4.04	2.33	10.39	8.90	0.0106
Muscovite + Verm.‡	6.48	4.18	2.10	10.34	8.74	0.0103
Biotite + Verm.‖	6.47	4.13	2.20	10.31	8.72	0.0105
		0.20 atm CO_2				
Harps B3	6.36	3.94	1.51	10.32	9.30	0.0207
Clarion B2*	5.06	3.98	0.40	6.07	6.07	0.0006

* Non-calcareous and no calcite added. † n.d. = not determined.
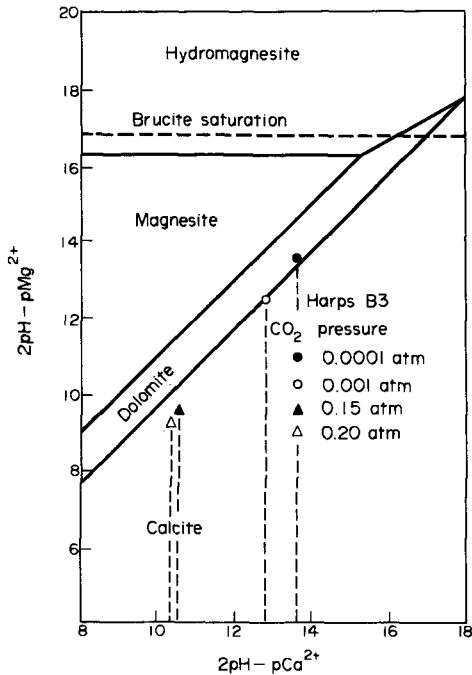‡ Muscovite plus vermiculite. ‖ Biotite plus vermiculite.

Fig. 3. Plots of solute activities for Harps soil determined at various CO_2 partial pressures on the carbonate mineral stability diagram of Helgeson et al. (1969). Partial pressure of CO_2 varies functionally with values of $2pH-pCa^{2+}$.

vite stability field (Fig. 4) at the higher $2pH-pCa^{2+}$ values (lower CO_2 partial pressures). They plotted in the vermiculite stability field (Fig. 5) at the lower values (higher partial pressure of CO_2). When the CO_2 pressure was changed, a rapid kinetic change-over (<14 days) occurred between which of the two phases was indicated to be metastable. A rapid, non-equilibrium reaction has been suggested for the trioctahedral mica $\rightleftarrows$ vermiculite system (Kittrick, 1973).

The Harps B3 data plotted in the montmorillonite stability field at a CO_2 partial pressure of 0.0001 atm and within the limits of the montmorillonite–kaolinite phase join at higher CO_2 partial pressures (Fig. 6). The 14-day pH and concentrations of Mg^{2+} thus appear favorable for formation or preservation of montmorillonite (43% of the clay, perhaps from Cretaceous sources).

Clarion B2: The Clarion B2 horizon had $2pH-pCa^{2+}$ values (Table 3) that are much lower than the other samples, because of the absence of calcite. Plots of the solute activity data for the Clarion B2 determined at a CO_2 partial pressure of 0.001 atm, representative of the natural conditions existing in a well-drained soil within two weeks after a rain, was located within the limits of the montmorillonite–kaolinite phase join (Fig. 5), suggesting kaolinite coexistence (and formation) could occur in equilibrium with montmorillonite, as in a Wisconsin acid upland site (Weaver et al., 1971). At a higher CO_2 partial pressure, the function plotted in the kaolinite stability area (Fig. 6).

Stability diagram relationships

The mineral stability relationships in the soil were examined by use of the ΔG_f^0 values for kaolinite, K mica, and Ca vermiculite (Table 4), calculated by standard methods as illustrated by equations (5)–(10) (Table 4, footnote). The $\Delta G_{f,\text{verm}}^0$ of -1303.7 kcal/O_{10} compares well (within 1.45 kcal) to the calculated value of -1305.15 derived from generalized silicate data (Tardy and Garrels, 1974) when traditional values for the free energy of formation for Al^{3+} and H_2O are used (as done throughout this paper).

Use of the -3.5 kcal/Al correction (Tardy and Garrels, 1974) changes the ΔG_f^0 of mica (-1330.1, Barany, Table 4) by -10.5 to -1340.6 kcal; the same
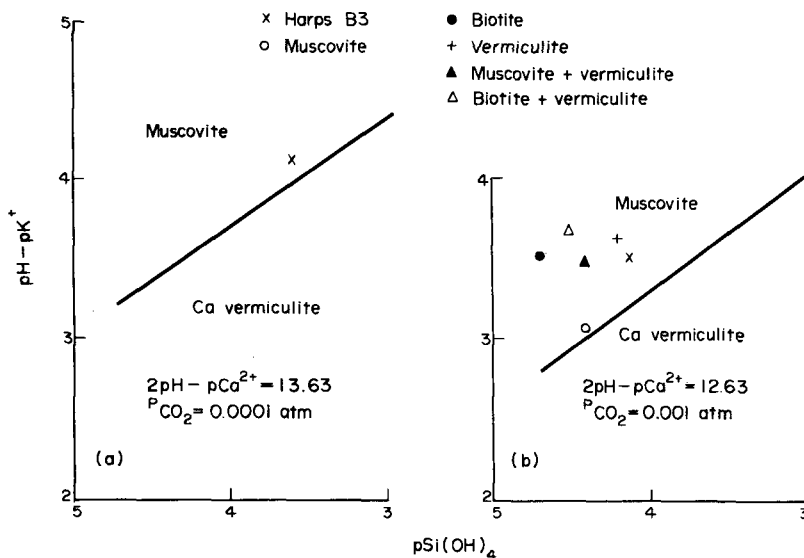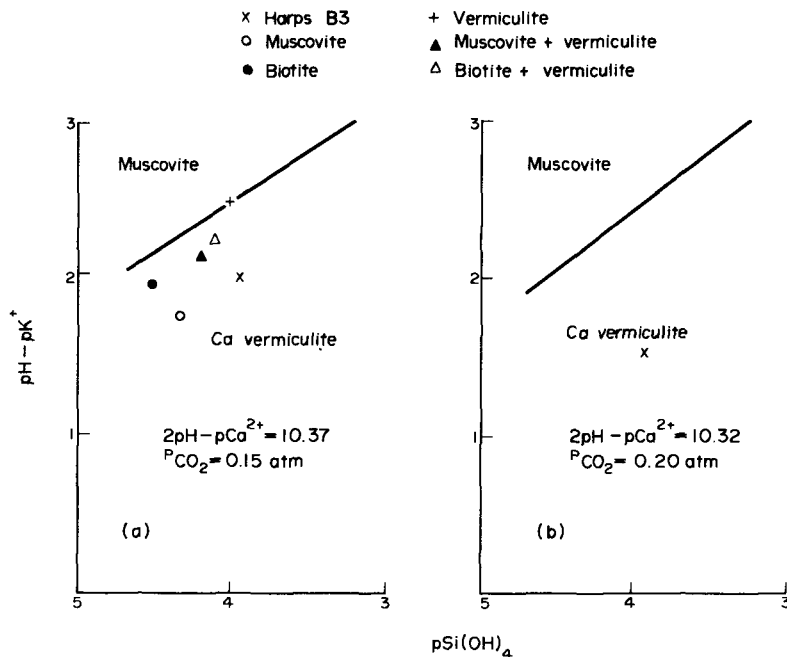

Fig. 4. Plots of solute activities for Harps soil and mixtures of micaceous minerals and calcite used as controls, on isoplethic sections of the muscovite–vermiculite phase join of Fig. 2 at CO_2 partial pressures of 0.0001 and 0.001 atm.

Fig. 5. Plots of solute activities for Harps soil and mixtures of micaceous minerals and calcite used as controls, on isoplethic sections of the muscovite–vermiculite phase join of Fig. 2 at a CO_2 partial pressures of 0.15 and 0.20 atm.

done for our Ca vermiculite ΔG_f^0 changes the value by -9.45 and the calculated value by the same amount. Substitution of a few tenths mole of Fe for Al in the Ca vermiculite formula lowers the end-member dioctahedral mica/vermiculite model ΔG_f^0
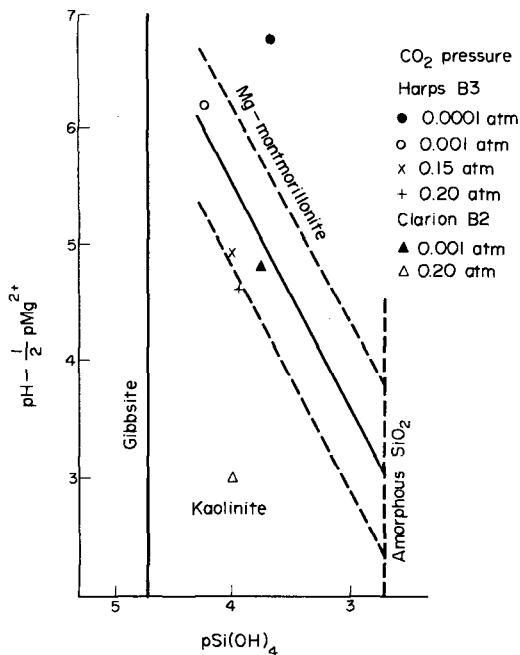

Fig. 6. Plots of solute activities for Harps and Clarion B horizons on a montmorillonite–kaolinite mineral stability diagram by Weaver *et al.* (1971). Expressing the ordinate function as $2pH–pMg^{2+}$ would double the numbers without altering the relationships.

value by a few tens of kcal. Endmember Al systems have been used earlier as thermodynamic models (Hemley, 1959; Kittrick, 1969).

The equilibrium diagram (Fig. 2) indicates that kaolinite, K mica, and Ca vermiculite would theoretically co-exist in thermodynamic equilibrium with solute activities given by the intersection of the three equilibrium planes which corresponds to:

$$8.67 = 0.7(2pH - pCa^{2+}) - 1.2\,pSi(OH)_4;$$
$$pH - pK^+ = 5.90. \quad (11)$$

The observed solute activity functions of the Blount soil (Table 1), are too low for such coexistence. The $2pH - pCa^{2+}$ values for the Harps and Clarion soils (Table 3) are too low for vermiculite stability with reference to kaolinite (Fig. 2).

Interpretations

The 14-day solute activity functions for Harps B3 horizon at high CO_2 pressures (Fig. 5) would favor vermiculite formation from micas as Ca^{2+} from calcite replaced interlayer K^+; the situation simulates that during wet and frozen seasons when high soil CO_2 partial pressures would occur (Kristensen, 1964). The 14-day solute activity data for lower partial pressures of CO_2 (Fig. 4), expected during the summer season, suggest a rapid change to conditions favoring uptake of K^+ and other fixing cations such as Rb^+ and $^{137}Cs^+$ in rainfall (equation 1) by micaceous vermiculite wedges peripheral to mica cores (Jackson, 1963; Newman and Brown, 1969), where "clean" (uncoated) freshly opened mica occurs. Leaching of K^+

Table 4. Standard free energy of formation values (ΔG_f^0) used in development of the stability diagrams

Species	ΔG_f^0 (kcal)	Reference
H_2O	−56.7	Rossini et al. (1952)
H^+	0.0	Latimer (1952)
K^+	−67.5	Rossini et al. (1952)
Ca^{2+}	−132.2	Rossini et al. (1952)
$Si(OH)_4$	−313.0	Kittrick (1969)
Kaolinite $Al_2Si_2O_5(OH)_4$	−903.8	Kittrick (1966)
Muscovite $KAlSi_3Al_2O_{10}(OH)_2$	−1330.1	Barany (1964)
Ca–vermiculite $Ca_{0.35}Si_{3.3}Al_{2.7}O_{10}(OH)_2$	−1303.7*	This paper
Mg–montmorillonite $Mg_{0.20}(Si_{3.81}Al_{1.71}Fe^{3+}_{0.22}Mg_{0.29})O_{10}(OH)_2$	−1255.8 ± 0.6†	Weaver et al. (1971)

* The log K_{eq} value (equation 4) was used to calculate a ΔG_f^0 value for the Ca–vermiculite. The Gibbs free energy change (ΔG_r^0) for the reaction in equation (1) is given by

$$\Delta G_r^0 = -RT \ln K_{eq} \tag{5}$$

which at 25°C and one atmosphere may be written

$$\Delta G_r^0 = -1.364 \log K_{eq} \tag{6}$$

Substitution of log K_{eq} = 2.92 into equation (6) gives:

$$\Delta G_r^0 = -3.99 \text{ kcal} \tag{7}$$

ΔG_r^0 in equation (7) is also the difference between the standard free energy of formation of the products and the reactants:

$$\Delta G_r^0 = -\Delta G_f^0 (\text{products}) - \Delta G_f^0 (\text{reactants}) \tag{8}$$

$$\Delta G_r^0 = [3 \Delta G_{f,\text{Verm}}^0 + 2.7 \Delta G_{f,K}^0 + 3.6 \Delta G_{f,H_2O}^0] - [2.7 \Delta G_{f,\text{Muscovite}}^0 + 1.05 \Delta G_{f,Ca^2}^0 + 1.8 \Delta G_{f,Si(OH)_4}^0] \tag{9}$$

The ΔG_f^0 value for Ca vermiculite is calculated by substitution in equation (9) of the known ΔG_f^0 values (Table 4) to give

$$\Delta G_f^0 \text{ Verm} = -1303.7 \text{ kcal/10 oxygen unit cell.} \tag{10}$$

This value is of course approximate in as much as it involves the use of ΔG_f^0 end-member of muscovite. However, the real composition of the muscovite and vermiculite in Blount is reflected in the position of the join in Fig. 2.
† A ΔG_f^0 of −1234.2 kcal was determined by Kittrick (1971) for Belle Fourche, SD montmorillonite having the composition $M^+_{0.28}(Si_{3.935}Al_{1.58}Fe^{3+}_{0.225}Mg^{2+}_{0.28})O_{10}(OH)_2$, with the free energy of exchangeable cations omitted. The Weaver et al. (1971) montmorillonite ΔG_f^0 value in Table 4, when calculated in a similar manner, gives virtually the same $\Delta G_f^0 = -1234.4$ kcal.

in winter and fixation of K^+ in summer correlates well with the K^+ deficiency and the K^+/Ca^{2+} relationships of plants growing on Harps soil (Allaway and Pierre, 1939). The rapidity of change in the solute functions with respect to the mica–vermiculite join in the stability diagram illustrates the importance of reaction kinetics.

The fact that young Harps and Clarion soils have abundant dioctahedral mica and vermiculite, but have accumulated little kaolinite in ∼1.4 × 10^4 years, is proof that the rate at which equilibrium is attained (kaolinite forms from the 2:1 phyllosilicates) is apparently slow on this time scale. Some portion of the time was required to remove carbonates from the parent glacial material of the Clarion A and B horizons. Carbonates of Ca^{2+} and Mg^{2+}, as found in the Harps soil, act as buffers against kaolinization (Fig. 6); a HCO_3^- concentration of 100 ppm (1.6 × 10^{-3} M) has been found to inhibit kaolinization and to promote montmorillonite neoformation (Garrels, 1967).

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