

CLAY MINERAL STABILITY AS RELATED TO ACTIVITIES OF ALUMINIUM, SILICON, AND MAGNESIUM IN MATRIX SOLUTION OF MONTMORILLONITE-CONTAINING SOILS

R. M. WEAVER*, M. L. JACKSON and J. K. SYERST†

Department of Soil Science, University of Wisconsin, Madison, WI 53706

(Received 24 November 1975)

Abstract—The influence of geomorphological site characteristics on soil clay mineral stability of montmorillonite-containing horizons of a southern Wisconsin soil catena was interpreted in terms of the solute activity function values of $p\text{Si}(\text{OH})_4$, $\text{pH}-1/2p\text{Mg}^{2+}$ and $\text{pH}-1/3p\text{Al}^{3+}$ in suspensions of the separated clay fractions. Montmorillonite stability and/or formation vs that of kaolinite for the soil clays was evaluated by a plot of the solute activity functions on a three dimensional diagram derived for montmorillonite, kaolinite, and gibbsite at constant temperature (25°C) and constant pressure (one atm.). Although all the soil clays contained both montmorillonite and kaolinite, the position of the soil clay solute activity functions in the stability diagram clearly reflected the influence of the geomorphological-geochemical site conditions in which each soil horizon was developed, with corresponding differences in the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of the reactive fraction. Montmorillonite stability positions of the solute activity functions were induced by soils (clays with reactive fractions with $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios = 3-4) from calcareous or poorly drained horizons, while kaolinite stability positions of the functions were induced by soils (clays with reactive fractions of $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios = 2) from acid, freely drained horizons.

INTRODUCTION

Quantitative mineralogical analysis of the clay fractions and geomorphological-geochemical site characteristics were used to deduce montmorillonite stability or kaolinite stability in selected horizons in a southern Wisconsin soil catena (Weaver *et al.*, 1971). The matrix solution activities associated with each horizon were represented graphically in terms of the solution parameters $p\text{Si}(\text{OH})_4$ and $\text{pH}-1/2p\text{Mg}^{2+}$ in near neutral suspensions of clay exchange saturated with Mg^{2+} . Under these conditions clay mineral transformations could be interpreted in terms of solute activities of H^+ , Mg^{2+} , and $\text{Si}(\text{OH})_4$ while Al^{3+} is conserved in the solid phases.

Under soil acidity conditions of pH 5.0 or less, the activity of Al^{3+} becomes much greater, and is therefore important in clay mineral-solution interactions in acid soils and must be considered in the clay mineral stability diagrams along with those of $\text{Si}(\text{OH})_4$ and Mg^{2+} .

The purpose of this paper is to relate the solute activities in equilibrium with the clay fractions of a catena of soils ranging from geomorphological-geochemical conditions of montmorillonite stability to kaolinite stability to a three dimensional stability diagram with the solute functions, $p\text{Si}(\text{OH})_4$, $\text{pH}-1/2p\text{Mg}^{2+}$, and $\text{pH}-1/3p\text{Al}^{3+}$

MATERIALS

The montmorillonite-containing soil clays used were from selected horizons of the Dodge catena of southern Wisconsin (U. W. Arboretum, Madison), developed from montmorillonitic loessial materials overlying till. The mineralogy of the clay fractions of the soils (Weaver *et al.*, 1971) suggests that kaolinite was forming in the well-drained Dodge soil B2 horizon and the less well-drained Lamartine soil B2 horizon and that montmorillonite was stable in the Lamartine soil C2 horizon and the poorly-drained Pella soil B2g horizon. This was especially evident from the composition of the reactive fractions (0.5N NaOH extractable, Hashimoto and Jackson, 1960) of the soil clays. The B2 horizons from the acid, well-drained Dodge soil and less well-drained Lamartine soil contained reactive clay fractions of a kaolinitic or Al-chloritic composition ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios = 2). In contrast, the clays from the poorly drained Pella B2g and the dolomitic C2 horizon of the Lamartine soil contained reactive fractions or surfaces of montmorillonite composition ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio = 3-4).

Clay minerals used as controls included bentonite from Castle Rock, CO; bentonite from Upton, WY (courtesy American Colloid Co.); and bentonite from Colony, WY (Colony I, a fresh blue colored, unoxidized, unweathered sample and Colony II, an oxidized, buff sample from outcrop of the deposit courtesy of W. J. Lang, International Minerals and Chemical Corp.).

* Present address: Department of Agronomy, Cornell University, Ithaca, NY 14853, U.S.A.

† Present address: Department of Soil Science, Massey University, Palmerston North, New Zealand.

METHODS

Dissolution techniques

The dissolution experiments were carried out in 0.01 N Al^{3+} and 0.01 N Mg^{2+} solutions to provide a homogeneous cation saturation for all of the clays and so that structural species released would be displaced into a uniform solution phase. The clay dissolution with relatively high, constant activities of two cations that occur as structural and exchangeable species facilitated a test of the constancy of the solute activity product of each clay mineral. The pH of the equilibration solutions was adjusted to 3.5 so that the Al released would be predominantly the monomeric Al^{3+} species.

Duplicate samples of the soils and bentonites (weight taken to give 5 g of $<2 \mu\text{m}$ material on the 110°C basis) were distributed between 100-ml centrifuge tubes. After treatment with 1 N NaOAc of pH 5 to remove exchangeable cations and carbonates, and dispersion by an ultrasonic treatment, the $<2 \mu\text{m}$ fractions were separated by centrifugation and decantation (Jackson, 1969). The samples were then washed three times with 0.5 N MgCl_2 or 0.5 N AlCl_3 of pH 2.7 followed by washings with 0.01 N MgCl_2 (pH 3.5) or 0.01 N AlCl_3 (pH 3.5) until the pH of the supernatant solution approximated 3.5. The 5 g samples were suspended in 200 ml of either 0.01 N MgCl_2 (pH 3.5) or 0.01 N AlCl_3 (pH 3.5) in polyethylene bottles. The bottles were placed in a constant temperature ($25^\circ\text{C} \pm 1$) reciprocating shaker bath (pressure = 1 atm.). Aliquots of the suspensions (25 ml) were removed at various time intervals from 1 to 120 days. Following centrifugation, the pH of the supernatant solutions was determined with a Metrohm Compensator E388 pH meter; $\text{Si}(\text{OH})_4$ was determined colorimetrically by the blue, reduced molybdosilicic acid method (Weaver *et al.*, 1968); Al by the Ferron procedure (Rainwater and Thatcher, 1960); Fe by the Bathophenanthroline procedure (Smith *et al.*, 1952); and Mg by atomic absorption spectrophotometry, La being used as a releasing agent to prevent interference from Si and Al.

The activity coefficient (γ) for $\text{Si}(\text{OH})_4$ was assumed to be unity, and therefore the analytical concentrations of $\text{Si}(\text{OH})_4$ were taken to be equivalent to the activities of $\text{Si}(\text{OH})_4$. Activities of Mg^{2+} were calculated by multiplying the analytical concentration by the activity coefficient estimated from the ionic strength (μ) and the extended Debye-Hückel Law (Butler, 1964, p. 423):

$$-\log \gamma = 0.509z^2(\mu)^{1/2}/1 + 0.328 a(\mu)^{1/2} \quad (1)$$

where z is the charge on the ionic species and a is the value for the "effective" size of the hydrated ion. The activities of Al^{3+} and Fe^{3+} were calculated in a similar manner as for Mg^{2+} , but with consideration being given to the probable hydrolysis products. For Al^{3+} , the method of Hem and Roberson (1967) was used, while for Fe^{3+} , the method of Bohn (1967) was

used and both are given below:

$$[\text{Al}^{3+}] = \frac{[\text{Al}^{3+}]_T}{\frac{1}{\gamma_{\text{Al}^{3+}}} + \frac{10^{-4.70}}{(\text{H}^+) \gamma_{\text{Al}(\text{OH})_2^+}} \quad (2)$$

$$[\text{Fe}^{3+}] = \frac{[\text{Fe}^{3+}]_T}{\frac{1}{\gamma_{\text{Fe}^{3+}}} + \frac{10^{-2.40}}{(\text{H}^+) \gamma_{\text{Fe}(\text{OH})_2^+} + \frac{10^{-5.62}}{(\text{H}^+) \gamma_{\text{Fe}(\text{OH})_2^+}} \quad (3)$$

Values of a used in calculation of activity coefficients were 8 for $\text{Fe}(\text{OH})_2^+$; 7 for $\text{Fe}(\text{OH})_2^+$ and $\text{Al}(\text{OH})_2^+$; and 9 for Al^{3+} .

Steady state activities of $\text{Si}(\text{OH})_4$ and Mg^{2+} were estimated from plots of the activity at various times against the reciprocal of the square root of time and extrapolation to infinite time, as done by Kittrick (1966a).

Elemental and unit cell compositions of bentonites

The elemental compositions of the bentonite samples were determined by Na_2CO_3 and HF-HClO₄ dissolution procedures on the $<2 \mu\text{m}$ fractions following the removal of carbonates, free iron oxides, and amorphous materials by the procedures outlined by Jackson (1969). Unit cell formulas were calculated from the elemental compositions by the method given by Jackson (1969).

RESULTS AND DISCUSSION

Solute activities in matrix solutions

The steady state solute activities for matrix solutions in contact with soil clay fractions and montmorillonites suspended in 0.01 N Al^{3+} or 0.01 N Mg^{2+} of pH 3.5 are listed in Tables 1 and 2. The pH of the supernatant solutions showed a tendency to increase from the 1-day to 60-day values but was essentially constant between 60 days and the 120-day values shown. The Al^{3+} activities in the 0.01 N Mg^{2+} solutions rapidly reached a steady state, as the 120-day values in Table 2 did not differ significantly

Table 1. Steady state solute activities in supernatant solutions of soil clays and montmorillonites suspended in 0.01 N Al^{3+} ($p\text{Al}^{3+} = 2.9$)

Sample	pH	$p\text{Si}(\text{OH})_4$	$p\text{Mg}^{2+}$	$p\text{H}-1/2p\text{Mg}^{2+}$	$p\text{H}-1/3p\text{Al}^{3+}$
Soil clays					
Dodge B2	(3.45)* 3.71	3.65	4.52	1.45	2.74
Lamartine B2	(3.43) 3.74	3.68	4.58	1.45	2.77
Lamartine C2	(3.61) 3.82	3.47	3.88	1.88	2.86
Pella B2g	(3.48) 3.78	3.31	3.84	1.86	2.82
Montmorillonites					
Castle Rock	(3.50) 3.54	3.32	4.10	1.49	2.58
Upton	(3.61) 3.74	3.20	4.20	1.64	2.78
Colony I	(3.64) 3.67	3.55	4.12	1.61	2.71
Colony II	(3.57) 3.58	3.57	4.24	1.46	2.62

*pH at 1 day in parentheses; other values at 120 days.

Table 2. Steady state solute activities in supernatant solutions of soil clays and montmorillonites suspended in 0.01 N Mg^{2+} ($pMg^{2+} = 2.5$)

Sample	pH	$pSi(OH)_4$	pAl^{3+}	$pH-1/3pAl^{3+}$	$pH-1/2pMg^{2+}$
Soil clays					
Dodge B2	(3.81)*4.29	3.33	(5.19)*5.10	2.59	3.04
Lamartine B2	(3.89) 4.31	3.53	(5.05) 4.92	2.67	3.06
Lamartine C2	(4.00) 4.52	3.16	(5.08) 5.04	2.84	3.27
Pella B2g	(3.92) 4.28	3.02	(5.20) 5.10	2.58	3.03
Montmorillonites					
Castle Rock	(3.52) 4.00	2.89	(5.14) 5.10	2.30	2.75
Upton	(3.57) 4.12	2.97	(5.10) 5.04	2.44	2.87
Colony I	(3.42) 3.95	3.17	(5.13) 5.19	2.22	2.70
Colony II	(3.50) 3.95	3.10	(5.33) 5.28	2.19	2.70

*pH and pAl^{3+} at 1 day in parentheses; other values at 120 days.

from those after one day. The activities of $Si(OH)_4$ in both 0.01 N Al^{3+} and 0.01 N Mg^{2+} and those of Mg^{2+} in 0.01 N Al^{3+} initially increased rapidly and increased at a slower rate even up to 120 days of reaction time. To obtain steady state values for $pSi(OH)_4$ and pMg^{2+} , the activity functions at various reaction times were plotted against the reciprocal square root of time (assuming ion diffusion as the rate determining step) and extrapolated to infinite time. Some examples of such plots are given in Figs. 1 and 2.

The increases from 1 day to the steady state values at 120 days in pH values of the supernatant solutions of the clay suspensions in 0.01 N Mg^{2+} of pH 3.5 (Table 2) were greater than for those in 0.01 N Al^{3+} (Table 1). This larger pH increase in 0.01 N Mg^{2+} solutions is consistent with the release of greater amounts of $Si(OH)_4$ than in 0.01 N Al^{3+} . The latter is well illustrated in Fig. 1. The greater activity of $Si(OH)_4$ in 0.01 N Mg^{2+} than in 0.01 N Al^{3+} was also expected because (according to equation (4),

* In the development of the montmorillonite stability plane, the relatively low octahedral Fe(II) content of the montmorillonites was added to that of Fe(III).

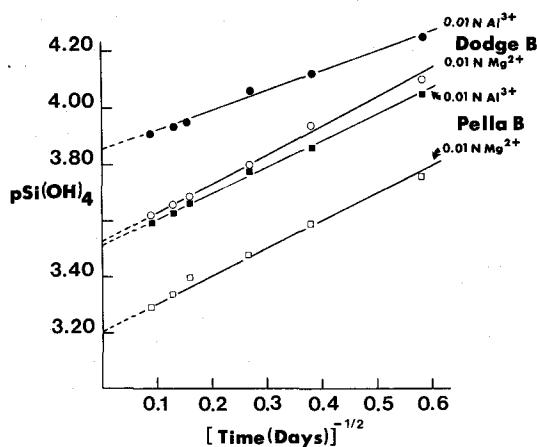


Fig. 1. $pSi(OH)_4$ in matrix solutions of soil clays suspended in 0.01 N Al^{3+} ($pAl^{3+} = 2.9$) and 0.01 N Mg^{2+} ($pMg^{2+} = 2.5$).

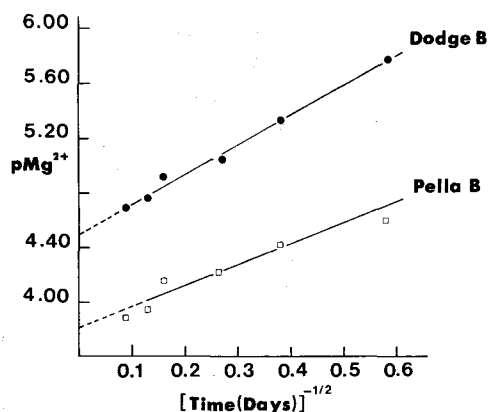


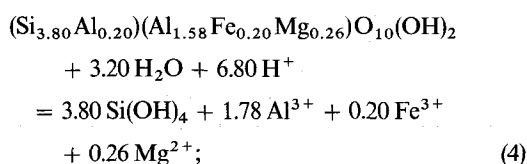
Fig. 2. pMg^{2+} in matrix solutions of soil clays suspended in 0.01 N Al^{3+} ($pAl^{3+} = 2.9$).

below) Al^{3+} should be more effective in suppressing the dissolution of structural constituents of montmorillonite by the common ion effect than would Mg^{2+} .

The Fe concentrations in the supernatant portions of the suspensions in 0.01 N Al^{3+} or 0.01 N Mg^{2+} were found to be in the order of 2.0×10^{-6} M or less. With the aliquot size available for analysis, this concentration was only slightly above the lower limit of the analytical range of the method used and therefore the values have not been tabulated. However, some approximation to the apparent solubility of Fe^{3+} in these soil clays and montmorillonites can be made. Calculated activities of Fe^{3+} (equation (3)) for an Fe^{3+} concentration of 2.0×10^{-6} M show for the pH range of 3.5–4.0, that these soil clays and montmorillonites have $pH-1/3pFe^{3+}$ values slightly in excess of 1.0 which corresponds to values obtained for acid soils (Bohn, 1967) considered to contain an amorphous $Fe(OH)_3$ compound.

Interpretation of soil clay solute activities

Clay minerals as control. To facilitate comparison of the observed soil clay solute activity functions to those expected for the clay minerals—montmorillonite, kaolinite, and gibbsite, the solute activity functions were plotted in a three dimensional diagram (Fig. 3). The stability plane for montmorillonite in Fig. 3 was calculated from the solute activity data (Tables 1 and 2) and formula (Table 3) of the Colony I montmorillonite.* Calculations showed that this montmorillonite gave a stability plane that was intermediate in relation to the other three montmorillonites. The development of the stability plane for the Colony I montmorillonite was carried out by first writing a balanced dissolution equation,



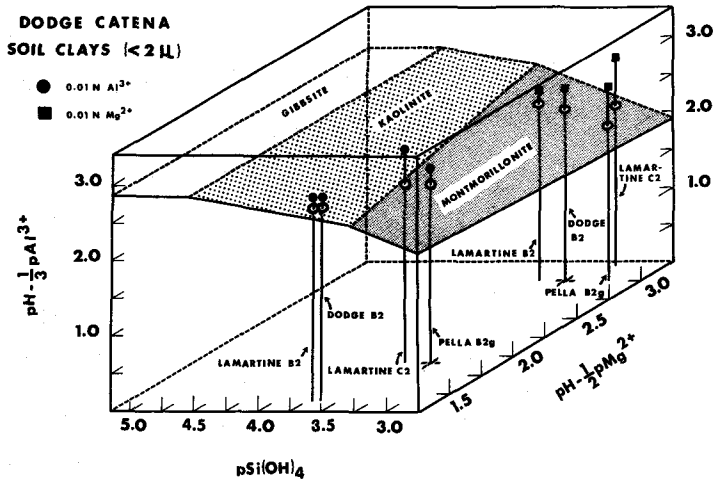


Fig. 3. Solute activity functions of $pSi(OH)_4$, $pH - 1/2pMg^{2+}$, and $pH - 1/3pAl^{3+}$ in matrix solutions of soil clays suspended in 0.01 N Mg^{2+} or 0.01 N Al^{3+} (initially pH 3.5) plotted in mineral stability diagram for montmorillonite, kaolinite and gibbsite in aqueous system at 25°C and one atmosphere.

$$K_{mont} = \frac{[Si(OH)_4]^{3.80} [Al^{3+}]^{1.78} [Fe^{3+}]^{0.20} [Mg^{2+}]^{0.26}}{(H^+)^{6.80}} \tag{5}$$

and

$$\begin{aligned} \log K_{mont} = & 5.34 (pH - 1/3 pAl^{3+}) \\ & + 0.60 (pH - 1/3 pFe^{3+}) \\ & + 0.52 (pH - 1/2 pMg^{2+}) \\ & + 0.36 pH - 3.80 pSi(OH)_4. \end{aligned} \tag{6}$$

Rearranged in terms of $pH - 1/3 pAl^{3+}$, the montmorillonite equilibrium expression is,

$$\begin{aligned} pH - 1/3 pAl^{3+} = & 0.19 \log K_{mont} + 0.71 pSi(OH)_4 \\ & - 0.11 (pH - 1/3 pFe^{3+}) \\ & - 0.10 (pH - 1/2 pMg^{2+}) \\ & - 0.07 pH. \end{aligned} \tag{7}$$

Table 3. Unit cell formulas* of montmorillonites of bentonites (<2 μm)

Castle Rock, CO	
$X_{0.49}$	$(Si_{3.68}Al_{0.32})(Al_{1.52}Fe^{3+}_{0.12}Fe^{2+}_{0.03}Mg_{0.46})_0(OH)_2$
Upton, WY	
$X_{0.36}$	$(Si_{3.93}Al_{0.07})(Al_{1.55}Fe^{3+}_{0.18}Fe^{2+}_{0.03}Mg_{0.24})_0(OH)_2$
Colony I, WY (blue)	
$X_{0.36}$	$(Si_{3.80}Al_{0.20})(Al_{1.58}Fe^{3+}_{0.17}Fe^{2+}_{0.03}Mg_{0.26})_0(OH)_2$
Colony II, WY (buff)	
$X_{0.44}$	$(Si_{3.81}Al_{0.19})(Al_{1.52}Fe^{3+}_{0.19}Fe^{2+}_{0.03}Mg_{0.29})_0(OH)_2$

*The formulas shown are for 10-oxygen half unit cells, since most of the past thermodynamic calculations for montmorillonites have been reported in terms of half unit cells. The values of X are based on the CaEC.

A value of $\log K_{mont}$ was determined by substitution of the steady state or extrapolated solute activities (Tables 1 and 2) into equation (6). For the Colony I montmorillonite, a $\log K$ value of 3.2 (Table 4) was determined by equilibration in 0.01 N Mg^{2+} and a value of 3.7 by equilibration in 0.01 N Al^{3+} . The difference, though large, is within experimental variability mainly arising from the pH measurements, since H^+ activity is multiplied by 6.8 in the dissolution equation (equations (4) and (5)). The montmorillonite stability plane in Fig. 3 is that for the $\log K$ value of 3.2 (Table 4).

Only the structural cation species of the montmorillonite have been considered in equation (4). The exchangeable cations of the montmorillonite are reflected in the term, 0.07 pH, in equation (7), which is a small component compared to the overall pH functionality, 6.80 pH, in the dissolution (equation 4). The montmorillonite plane (Fig. 3) corresponds to pH 4.0, applicable to acid soils such as the Dodge B2 and Lamartine B2 in which H^+ and Al^{3+} are present in appreciable amounts. The activity of Fe^{3+} (discussed above) in the development of the montmorillonite stability plane was taken to be controlled by amorphous $Fe(OH)_3$ ($pH - 1/3pFe^{3+} = 1.0$, Bohn, 1967).

Table 4. Equilibrium constants (K) for montmorillonites suspended in 0.01 N Al^{3+} and 0.01 N Mg^{2+} of pH 3.5

Sample	log K	
	In Al^{3+}	In Mg^{2+}
Castle Rock	5.2 ± 0.4	6.6 ± 0.4
Upton	3.7 ± 0.5	3.5 ± 0.5
Colony I	3.7 ± 0.5	3.2 ± 0.5
Colony II	3.2 ± 0.5	2.7 ± 0.5

Table 5. Standard free energy of formation (ΔG_f°) values* used in the development of the stability diagrams

Species	ΔG_f°	Reference
Kcal/Formula wt.		
H ₂ O	-56.7	Rossini <i>et al.</i> (1952)
H ⁺	0.0	Latimer (1952)
Mg ²⁺	-109.0	Rossini <i>et al.</i> (1952)
Al ³⁺	-119.5	Tardy and Garrels (1974)
Fe ³⁺	-2.52	Garrels and Christ (1965)
Si(OH) ₄	-312.5	Tardy and Garrels (1974)
Gibbsite Al(OH) ₃ [†]	-278.7	Kittrick (1966a)
Gibbsite, micro-crystalline Al(OH) ₃	-276.8	Hem and Roberson (1967)
Kaolinite, relatively crystalline Al ₂ Si ₂ O ₅ (OH) ₄	-911.1	Kittrick (1966b)
Kaolinite, relatively soluble Al ₂ Si ₂ O ₅ (OH) ₄	-908.6	Kittrick (1966b)

*25°C, one atmosphere.

[†]The ΔG_f° values for gibbsite and kaolinite, originally reported on the basis of ΔG_f° Al³⁺ = -115.0 Kcal/mole and ΔG_f° Si(OH)₄ = -313.0 Kcal/mole have been recalculated using the more recent values of -119.5 Kcal for Al³⁺ and -312.5 Kcal for Si(OH)₄.

Although not necessary for the construction of the montmorillonite stability plane, standard free energy of formation (ΔG_f°) values were calculated from the log K values and the data in Tables 3 and 5, and for reference have been tabulated in Table 6. Inasmuch as only the structural cations were considered, the values in Table 6 are generally lower than those previously reported (Weaver *et al.*, 1971) in which exchangeable cations, in addition to structural constituents, were considered. The similarity of the log K values in either 0.01 N Mg²⁺ or 0.01 N Al³⁺ suggests that the solubilities of montmorillonites are independent of the nature of the exchangeable cations as also suggested by Kittrick (1971) and supports the assumption that the structural cations are the more important in regard to montmorillonite stability. The latter was also evident from the fact that there was generally good agreement (Table 6) between the experimentally determined ΔG_f° values and those estimated by the scheme of Tardy and Garrels (1974) that requires only a knowledge of the structural composition of the montmorillonites.

The montmorillonite stability plane is intercepted on the right of the three dimensional diagram (Fig. 3) by amorphous silica ($p\text{Si(OH)}_4 = 2.72$) as before (Weaver *et al.*, 1971) and discussed by Kittrick (1969). Stability planes for kaolinite ($\text{pH}-1/3\text{pAl}^{3+} = -0.17 \text{pK}_{\text{kaol}} + 0.33 \text{pSi(OH)}_4$) and gibbsite ($\text{pH}-1/3\text{pAl}^{3+} = -1/3 \text{pK}_{\text{gib}}$) were also plotted in Fig. 3. The values of pK for kaolinite and gibbsite were taken as -7.82 and -8.70, respectively and represent median values of those reported in the literature (Table 5).

The solute activity functions of $\text{pH}-1/3\text{pAl}^{3+}$ for the soil clay fractions suspended in 0.01 N Al³⁺ were sufficiently high for either kaolinite or montmorillonite formation or stability (Fig. 3). The solute activity functions, $\text{pH}-1/2\text{pMg}^{2+}$ and pSi(OH)_4 , for the

Pella B2g and Lamartine C2 clay fractions are in the montmorillonite stability range, while those for the Lamartine B2 and Dodge B2 are in the kaolinite stability range. These relationships are consistent with the respective geomorphological environments of the soil horizons, which are also reflected in the composition of the field-formed reactive fractions of these soil clays (Weaver *et al.*, 1971). The SiO₂/Al₂O₃ molar ratios of the reactive fractions from the Dodge and Lamartine B2 horizons were near 2.0 (suggesting a kaolinitic or Al-chloritic composition), while those from the Lamartine C2 and Pella B2g ranged from 3 to 4 (i.e. of montmorillonitic or beidellitic composition). The composition of the reactive fraction can probably be considered to represent a partial equilibrium state (Helegeson, 1968) in the montmorillonite \rightleftharpoons kaolinite transformation.

The solute activity functions of the soil clays suspended in 0.01 N Mg²⁺ (initially pH 3.5) plotted in the montmorillonite stability range for all of the horizons (upper right in Fig. 3). The effects of the kaolinite-forming site conditions on the reactive clay composition in the Dodge B2 and Lamartine B2 horizons were evidently in part overridden by the increased Mg²⁺ activity supplied in the experiment, even though the final acidity was approximately pH 4. Analogous montmorillonite stability was noted earlier in the acid, poorly drained Henry soil of Kentucky (Weaver *et al.*, 1968). It is important to note, however, that the geomorphological-geochemical site conditions are still reflected in the solute activity values. That is, the values for the acid, well drained horizons plotted closer to the kaolinite stability area largely as a result of decreased Si(OH)₄ activities.

Table 6. Standard free energy of formation (ΔG_f°)* values of montmorillonites

Sample	ΔG_f°		Estimated (Tardy and Garrels, 1974)
	Experimental [†]		
	In Al ³⁺	In Mg ²⁺	
Kcal/formula wt.			
Castle Rock	-1259.0 ± 0.6	-1257.1 ± 0.6	-1254.9
Upton	-1232.4 ± 0.7	-1232.7 ± 0.7	-1235.4
Colony I	-1242.5 ± 0.7	-1243.2 ± 0.7	-1242.1
Colony II	-1239.0 ± 0.7	-1239.7 ± 0.7	-1240.6

*25°C, one atmosphere.

[†]The calculation of the ΔG_f° values from the experimental log K values is illustrated for the Colony I montmorillonite. The Gibbs free energy change (ΔG_r°) for the dissolution of the Colony I montmorillonite (equation 4) is given by

$$\Delta G_r^\circ = -1.364 \log K \quad 25^\circ\text{C}, 1 \text{ atm.} \quad (8)$$

For the Colony I montmorillonite, in 0.01 N Mg²⁺, log K = 3.2 (Table 3) and

$$\Delta G_r^\circ = -4.37 \text{ Kcal} \quad (9)$$

ΔG_r° in equation (9) is also given by

$$\Delta G_r^\circ = \Sigma \Delta G_f^\circ(\text{products}) - \Sigma \Delta G_f^\circ(\text{reactants}) \quad (10)$$

which for the Colony I montmorillonite is

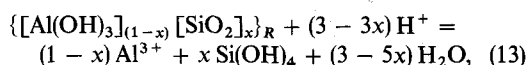
$$\Delta G_r^\circ = [3.80\Delta G_f^\circ\text{Si(OH)}_4 + 1.78\Delta G_f^\circ\text{Al}^{3+} + 0.20\Delta G_f^\circ\text{Fe}^{3+} + 0.26\Delta G_f^\circ\text{Mg}^{2+}] - [\Delta G_f^\circ\text{Col.I} + 3.20\Delta G_f^\circ\text{H}_2\text{O}] \quad (11)$$

Rearrangement and substitution of known ΔG_f° values (Table 4) into equation

(11) gives

$$\Delta G_f^\circ\text{Col.I} = -1247.6 - \Delta G_r^\circ = -1243.2 \text{ Kcal/formula weight} \quad (12)$$

Non-crystalline reactive component as control. Although all of the soils contained kaolinite and montmorillonite, they differed considerably in their reactive fraction composition which in turn appeared to correspond to their position in the phase stability diagram (Fig. 3) and reflected the influence of the geomorphological-geochemical site conditions in which each soil horizon was developed. This suggests that the reactive fraction may have more immediate control on the solute activities than the crystalline clay minerals that are present in the soils. From kinetic considerations the latter would seem highly plausible as precipitation and dissolution reactions of the non-crystalline reactive components should occur more rapidly than those of crystalline clay minerals. Recently, Weaver (1975) found that the solute activities of some gibbsitic-kaolinitic Brazilian soil clays were more related to dissolution of a surface-reactive non-crystalline aluminosilicate than to that of gibbsite and kaolinite. The latter conclusion was based on the work of Paces (1973) who showed that the activities of Al^{3+} and $\text{Si}(\text{OH})_4$ in ground waters of the Sierra Nevada were controlled by the chemical equilibrium with respect to a non-crystalline aluminosilicate weathering product. The applicability of this interpretation to the present kaolinitic-montmorillonitic soil clays can be determined by considering that the dissolution of the reactive fraction (R) occurs by the following reaction as suggested by Paces (1973),



where x is the mole fraction of silica in the reactive component. The equilibrium condition for the reaction is,

$$\text{Log } K_R = (1 - x)\text{log}(\text{Al}^{3+}) + x\text{log}(\text{Si}(\text{OH})_4) - (3 - 3x)\text{log}(\text{H}^+). \quad (14)$$

Values for $\text{log } K_R$ were calculated by substituting the steady state activities of H^+ , Al^{3+} , and $\text{Si}(\text{OH})_4$ (Tables 1 and 2) into equation (14), along with values of x which were calculated from previous data (Weaver *et al.*, 1971). If the reactive fraction controls the solute activity functions, then $\text{log } K_R$ should be a linear function of x , which is indeed the case as shown in Fig. 4. This complements and extends the information obtained in the previous section where the solute activity functions were plotted in the phase stability diagram (Fig. 3). That is the position of the reactive fraction-controlled solute activity functions in the phase stability diagram (Fig. 3) enables a prediction of the ultimately stable clay mineral.

CONCLUSIONS

The results show that dissolution studies of soil clay fractions under controlled conditions, in conjunction with phase stability diagrams based on control clay minerals, can be extremely useful for interpre-

DODGE CATENA SOIL CLAYS

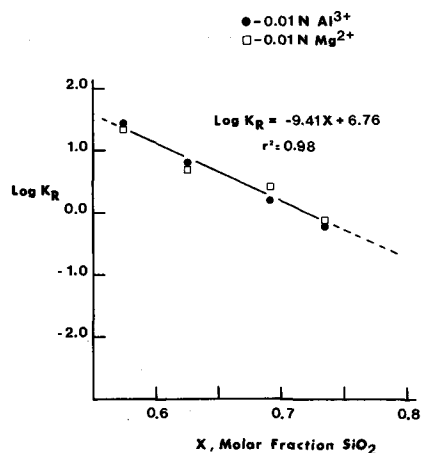


Fig. 4. The relationship of $\text{log } K_R$ to X , the molar fraction of silica in the reactive component, for soil clays suspended in 0.01 N Mg^{2+} or 0.01 N Al^{3+}

tation of clay mineral stability in soils with fairly distinct geomorphological-geochemical site characteristics.

The results also show that the composition of the non-crystalline, reactive component associated with clay mineral surfaces may be more important with respect to control of solute activities than the crystalline clay minerals. However, in the present study, solute activity control by a reactive component does not lead to results inconsistent with those expected from the geomorphological-geochemical site conditions in which the soils were developed. This is because the compositions of the reactive component are also determined by the latter conditions.

Acknowledgements—This work was supported by the College of Agricultural and Life Sciences under project 1123 and the National Science Foundation, grants GP4144 and GA1108-Jackson.

REFERENCES

- Bohn, H. L. (1967) The $(\text{Fe}(\text{OH})_3)$ ion product in suspensions of acid soils: *Soil Sci. Soc. Am. Proc.* **31**, 641–644.
- Butler, J. N. (1964) *Ionic Equilibrium*. Addison-Wesley Inc., Reading, Mass.
- Garrels, R. M. and Christ, C. L. (1965) *Solutions, Minerals and Equilibria*. Harper & Row, New York.
- Hashimoto, I. and Jackson, M. L. (1960) Rapid dissolution of allophane and kaolinite-halloysite after dehydration: *Clays & Clay Minerals* **6**, 144–153.
- Helgeson, H. C. (1968) Evaluation of irreversible reactions in geochemical processes involving minerals and aqueous solutions—I: Thermodynamic relations: *Geochim. Cosmochim. Acta* **32**, 853–877.
- Hem, J. D. and Roberson, C. E. (1967) Form and stability of aluminum hydroxide complexes in dilute solution: *U.S. Geol. Water-Supply Paper* 1827-A.

- Jackson, M. L. (1969) *Soil Chemical Analysis—Advanced Course*, 3rd Edition, 8th Printing, 1973: Published by the author, Department of Soil Sci., University of Wisconsin, Madison, Wisc. 53706.
- Kittrick, J. A., (1966a) The free energy of formation of gibbsite and $\text{Al}(\text{OH})_4^-$ from solubility measurements: *Soil Sci. Soc. Am. Proc.* **30**, 595–598.
- Kittrick, J. A. (1966b) Free energy of formation of kaolinite from solubility measurements: *Am. Miner.* **51**, 1457–1466.
- Kittrick, J. A. (1969) Soil minerals in the Al_2O_3 – SiO_2 – H_2O system and a theory of their formation: *Clays & Clay Minerals* **17**, 157–167.
- Kittrick, J. A. (1971) Stability of montmorillonites—I: Belle Fourche and Clay Spur Montmorillonites: *Soil Sci. Soc. Am. Proc.* **35**, 140–145.
- Latimer, W. M. (1952) *Oxidation Potentials* 2nd Edition. Prentice-Hall, Inc., Englewood Cliffs, N.J.
- Paces, T. (1973) Steady-state kinetics and equilibrium between ground water and granitic rock: *Geochim. Cosmochim. Acta* **37**, 2641–2663.
- Rainwater, F. H. and Thatcher, L. L. (1960) Methods for collection and analysis of water samples: *Geol. Survey Water-Supply Paper* 1454.
- Rossini, F. D., Wagman, D. D., Evans, W. H., Levine S. and Jaffe, I. (1952) Selected values of thermodynamic properties: *Nat. Bur. Standards Circ.* 500. U.S. Dept. of Commerce.
- Smith, G. Frederick, McCurdy, Jr., W. H. and Diehl, H. (1952) The colorimetric determination of iron in raw and treated municipal water supplies by use of 4:7-diphenyl-1:10-phenanthroline: *Analyst* **77**, 418–422.
- Tardy, Yves and Garrels, R. M. (1974) A method of estimating the Gibbs energies of formation of layer silicates: *Geochim. Cosmochim. Acta* **38**, 1101–1116.
- Weaver, R. M., Syers, J. K. and Jackson, M. L. (1968) Determination of silica in citrate-bicarbonate-dithionite extracts of soils: *Soil Sci. Soc. Am. Proc.* **32**, 497–501.
- Weaver, R. M., Jackson, M. L. and Syers, J. K. (1971) Magnesium and silicon activities in matrix solutions of montmorillonite-containing soils in relation to clay mineral stability: *Soil Sci. Soc. Am. Proc.* **35**, 823–830.
- Weaver, R. M. (1975) Gibbsite-kaolinite stability in some Brazilian Oxisols: *Agronomy Abstracts for 1975 Am. Soc. Agron. Annual Meetings*, Am. Soc. Agron., Madison, Wisc., p. 176; full paper being submitted to *Soil Sci. Soc. Am. Proc.*