

MICA-DERIVED VERMICULITES AS UNSTABLE INTERMEDIATES*

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Abstract—Stability determinations were made by solubility methods on two trioctahedral mica-derived vermiculites. The phlogopite-derived vermiculite was found to be unstable under acid solution conditions, where stabilities of montmorillonite, kaolinite and gibbsite had previously been determined. An attempt was next made to locate a possible montmorillonite-vermiculite-amorphous silica triple point. This triple point involved conditions of alkaline pH, high pH_4SiO_4 and high Mg^{2+} . These are conditions where phlogopite and biotite-derived vermiculites are most likely to control equilibria if they are stable minerals. The montmorillonite-vermiculite-amorphous silica samples went to the montmorillonite-magnesium-amorphous silica triple point, leaving no stability area whatsoever for the vermiculites. These large particle-size, trioctahedral, mica-derived vermiculites appear to be unstable under all conditions of room T and P .

Arguments are presented indicating that micas are unstable in almost all weathering environments. A hypothesis is proposed that mica-derived vermiculites result from the unique way in which unstable micas degrade in these environments. It is proposed that vermiculite derives from a series of reactions whose relative rates often result in an abundance of vermiculite. These relative reaction rates are slow for mica dissolution, rapid for K removal and other reactions pursuant to vermiculite formation, and slow for vermiculite dissolution. In chemical terms, mica-derived vermiculites may be considered fast-forming unstable intermediates.

INTRODUCTION

THE MAJOR clay minerals of soils and sediments compete for a relatively small group of elements during their formation. In theory at least, each clay mineral forms only under solution conditions where it is the least soluble of the clay minerals competing for that group of elements. Thus, because of the stability of other minerals, the stability field of a particular mineral represents a much more restricted chemical environment than does a solution saturated with respect to that mineral alone. The objective of this investigation was to provide some initial stability information for vermiculite. It was anticipated that this information would help define the stability fields of vermiculite and of other clay minerals, and thereby contribute to a better understanding of the formation and weathering of clay minerals in soils and sediments.

Vermiculite is a 2:1 layer silicate with a negative charge of about 0.6 to 0.9 per formula unit. Operationally, the term 'vermiculite' is usually applied to a 2:1 layer silicate that has a dehydrated c -repeat distance of about 10 Å, that expands to about 14 Å when solvated with a polar liquid, provided the exchange sites are saturated with one of the more highly hydrated cations. This behavior is exhibited by materials that are not necessarily identical in their other properties. Vermiculites used in this investigation are those most readily obtained in relatively pure form; i.e. they were large particle size, trioctahedral mica-derived vermiculites, with mica impurities artificially converted to vermiculite in the laboratory. It is from similar materials that most of the properties of vermiculites are inferred.

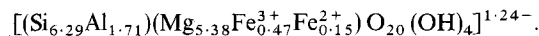
MATERIALS AND METHODS

The vermiculite derived from phlogopite was from Palabora, South Africa, obtained from C. H. Kingsland, Lahabralite Co. The vermiculite derived from biotite was from Libby, Montana, obtained from J. D. Hayes, Zonolite Co. Both vermiculites were wet ballmilled to pass a 300 mesh sieve ($< 50 \mu\text{m}$). Both vermiculites contained considerable micaceous impurities which were converted to vermiculite by repeatedly

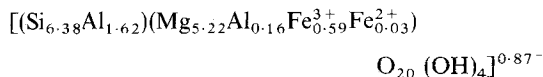
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extracting the K with hot 1 N NaCl. Samples were then Mg-saturated by 4 centrifuge washes with 1.0 M MgCl₂, followed by four water washes. The NaCl-treated Palabora sample contained no detectable K, with the calculated (Jackson, 1956) unit cell formula,



X-ray diffraction analysis indicated no detectable impurities (Fig. 1). The NaCl-treated Libby sample contained 0.34 per cent K corresponding to 5.8 per cent biotite, with the calculated vermiculite unit cell formula,



X-ray diffraction analysis indicated a small interstratified biotite impurity remaining (Fig. 1). X-ray traces of the vermiculites did not appear to change during the course of the experiments.

Total chemical analysis of the vermiculites (with Ba as the exchangeable ion) for Mg, Al, Si, Fe, K and Ba was done with the X-ray spectrograph. Standard rock and mineral samples were used as references. The proportion of Fe²⁺ and Fe³⁺ was determined with ortho-

phenanthroline (Roth *et al.*, 1968). Composition of the Palabora vermiculite was similar but not identical to that determined previously by wet chemical methods on a separate NaCl-treated batch (Kittrick, 1969a).

Vermiculite samples were suspended in solutions whose compositions are described in detail later. After suitable equilibration times, aliquots of these solutions were removed from the supernatant liquid after centrifuging to the absence of suspended material in a Tyndall beam. Al was determined colorimetrically with aluminon (Hsu, 1963), and Si with molybdate and aminonaphthol sulfonic acid (APHA, 1960). Na and K were determined with a flame photometer and Mg with an atomic absorption spectrophotometer. The pH measurements were made with a Corning Model 12 unit calibrated to within 0.01 pH units of two or sometimes three buffers. Precision of the analyses for pAl, pSi and pH was approximately ±0.02.

The Al³⁺ component of total Al was calculated from the first hydrolysis constant where necessary (Schofield and Taylor, 1954). Ion activities were calculated from the extended form of the Debye-Hückel equation (Klotz, 1964). Room temperature during analysis periods was between 23 and 25°C. The samples were agitated almost continuously on a shaker. X-ray diffraction analysis at high sensitivity before and after equilibration did not reveal the formation of any new phases, although solution analyses indicated precipitation must be occurring in some cases, as described later.

For equilibration under low pH conditions, four 1.0 g samples of Palabora vermiculite were given three washes with 0.010 N HCl, suspended in 200 ml of 0.0010 N HCl and then acidified to approximately pH 3 with HCl. In addition to the vermiculite, sample three contained 1.0 g of kaolinite (No. 3 Colloidal, Hammil and Gillespie, Inc., from England) and sample 4 contained 5.0 g of gibbsite (synthetic C-730, from Aluminum Co. of America).

For equilibration under high pH conditions, samples contained a mixture of 5.0 g vermiculite, 5.0 g montmorillonite (Belle Fourche, South Dakota, from A. G. Clem, American Colloid Co., <150 mesh), 5.0 g hematite (Mapico Red 347, from Columbia Carbon Co.), and 5 g amorphous SiO₂ (the amorphous SiO₂ was precipitated from 500 ml of solution containing 47.3 g Na₂SiO₃·9H₂O, by decreasing the pH with HCl. The precipitate was centrifuge-washed with water, twice with the solution in which the vermiculite samples were equilibrated and then divided). To ensure removal of possible carbonates, soluble hydroxides and other soluble substances, the vermiculite-montmorillonite-amorphous silica mixtures were given pH 4.0 HOAc treatments until the pH of the solution rose

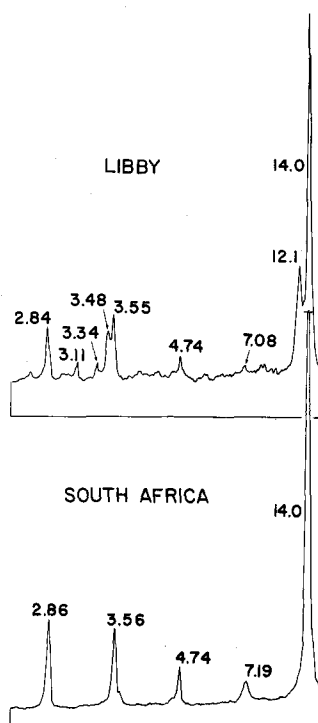


Fig. 1. Oriented X-ray diffraction patterns of <50 μm Palabora South Africa and Libby vermiculites after K-removal by hot 1 N NaCl extractions. Glycerated samples, CuKα, Ni filter, 1° 2θ/min.

no higher than pH 6.0 after overnight contact. They were then given three centrifuge washes with a solution $1 \times 10^{-2.0}$ M in Mg and $1 \times 10^{-2.52}$ M in Si, pH 7.90. Finally, the samples were equilibrated in 30 ml of this same solution.

RESULTS

Acid pH

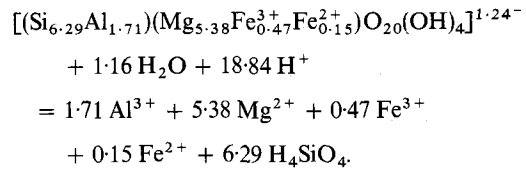
If vermiculite is stable under soil solution conditions similar (not necessarily identical) to those of montmorillonite, kaolinite and gibbsite, a reasonable approach would be to equilibrate vermiculite under the acid solution conditions already used for stability determinations on these minerals. Under acid conditions, the pH_4SiO_4 of the four Palabora vermiculite samples decreased with time (Table 1) until most of them became supersaturated with respect to amorphous silica ($\text{pH}_4\text{SiO}_4 < 2.72$). The $\text{pH}-1/3\text{pAl}^{3+}$ of the samples increased with time, approaching or exceeding 2.66 (Table 1), which is the $\text{pH}-1/3\text{pAl}^{3+}$ of gibbsite. These compositions are also supersaturated with respect to kaolinite and montmorillonite. Most of the preceding changes took place in the first 2 months, with the samples remaining supersaturated for over 2 yr. Apparently under the low pH conditions of this experiment, vermiculite dissolves faster than more stable minerals can precipitate.

The worldwide abundance of vermiculite suggests a rather large stability area in terms of solution composition, yet it is evident that the phlogopite-derived vermiculite is unstable relative to gibbsite, kaolinite and montmorillonite under conditions that previously permitted stability determinations on these minerals. To confirm the surprising contrast between vermiculite abundance and stability and to delimit a vermiculite stability area even if it were very small, a search was made for conditions of maximum vermiculite stability.

Alkaline pH

Strategy for equilibrating vermiculite. In order to determine the solution conditions under which vermi-

culite is most likely to be stable, consider the dissolution of Palabora vermiculite



$$\begin{aligned} \text{Then } \text{pK} &= 1.71 \text{pAl}^{3+} + 5.38 \text{pMg}^{2+} \\ &+ 0.47 \text{pFe}^{3+} + 0.15 \text{pFe}^{2+} \\ &+ 6.29 \text{pH}_4\text{SiO}_4 \\ &- 18.84 \text{pH} \end{aligned}$$

where K is the equilibrium constant, and the activity of vermiculite and water are assumed to be unity. By appropriate grouping of terms and division to reduce the coefficient of $\text{pH}-1/3\text{pAl}^{3+}$ to unity, we have

$$\begin{aligned} \text{pH}-1/3 \text{pAl}^{3+} &= 1.23 \text{pH}_4\text{SiO}_4 - [2.10 \\ &(\text{pH}-1/2 \text{pMg}^{2+}) \\ &+ 0.27 (\text{pH}-1/3 \text{pFe}^{3+}) \\ &+ 0.04 (\text{pH}-1/2 \text{pFe}^{2+}) \\ &+ 0.25 \text{pH} - 0.19 \text{pK}]. \end{aligned} \quad (1)$$

On $\text{pH}-1/3\text{pAl}^{3+}$ vs pH_4SiO_4 coordinates, this equation represents a straight line of slope 1.23 and an intercept of minus the quantity inside the brackets.

Selecting $\text{pH}-1/3\text{pAl}^{3+}$ as the variable controlling the relative stability of Al-containing clay minerals (Kittrick, 1969b), it can be shown from (1) that the level of $\text{pH}-1/3\text{pAl}^{3+}$ supported by Palabora vermiculite will be lowest (the vermiculite will be least soluble) when pH_4SiO_4 is low and pH is high. When the pH is high, $\text{pH}-1/2\text{pMg}^{2+}$, $\text{pH}-1/3\text{pFe}^{3+}$ and $\text{pH}-1/2\text{pFe}^{2+}$ are also high, which also makes the vermiculite more stable. There are no experimental difficulties in equilibrating vermiculite in low pH_4SiO_4 solutions (up to slight supersaturation with respect to

Table 1. Composition of the solution in contact with Palabora vermiculite samples after 918 days equilibration. Initial solution was pH 3.0 HCl

Sample	Composition	pMg ²⁺	pH	pAl ³⁺	pH-1/3pAl ³⁺	pH ₄ SiO ₄
1	Vermiculite	2.92	4.05	4.58	2.52	2.52
2	Vermiculite	2.92	4.05	4.64	2.50	2.51
3	Vermiculite-kaolinite	2.93	4.08	4.78	2.49	2.51
4	Vermiculite-gibbsite	2.78	4.48	5.15	2.76	2.77

The negative logarithm of the molar activity is denoted by p. The Al^{3+} is corrected for hydrolysis. The ionic strength, essentially determined by KCl released from the reference electrode during pH measurements, was 0.047 for sample 4 and 0.036 for the rest.

amorphous silica), but alkaline pH prevents the measurement of Al^{3+} and Fe^{3+} and usually Fe^{2+} (depending upon the Eh).

The strategy adopted for equilibrating vermiculite under alkaline pH and high silica conditions, where it is most likely to be stable, was first to add hematite to the sample and assume control of $\text{pH}-1/3\text{pFe}^{3+}$ at the hematite level. Fe^{2+} can be calculated from Fe^{3+} and an Eh measurement, when the sample reaches equilibrium. Next, amorphous SiO_2 was added to control H_4SiO_4 . The H_4SiO_4 was initially raised to the level of slight supersaturation with respect to amorphous silica by the addition of Na_2SiO_3 . No assumptions were necessary with respect to control of H_4SiO_4 by amorphous silica, since the H_4SiO_4 could be measured. The level of $\text{pH}-1/3\text{pAl}^{3+}$ was assumed to be fixed by the addition of Belle Fourche montmorillonite of known stability (Kittrick, 1971a). The initial Mg^{2+} level was set at 0.0100 M by the addition of MgCl_2 . The uncontrolled variable in the system was pH, permitting the course of equilibration to be followed by periodic pH measurements.

Montmorillonite and amorphous silica were added to the vermiculite samples so that at equilibrium the solution composition should be somewhere along the montmorillonite–amorphous silica join in Fig. 2. Specifically, if vermiculite is a stable mineral, then at equilibrium the solution composition should be at the montmorillonite–vermiculite–amorphous silica triple point, at some value of $\text{pH}-1/2\text{pMg}^{2+}$ below that supported by magnesite. The stability plane of vermiculite resulting from this hypothetical value of $\text{pH}-1/2\text{pMg}^{2+}$ would then be bounded by the dashed lines in Fig. 2. If vermiculite were unstable under the conditions of these experiments, the $\text{pH}-1/2\text{pMg}^{2+}$ of

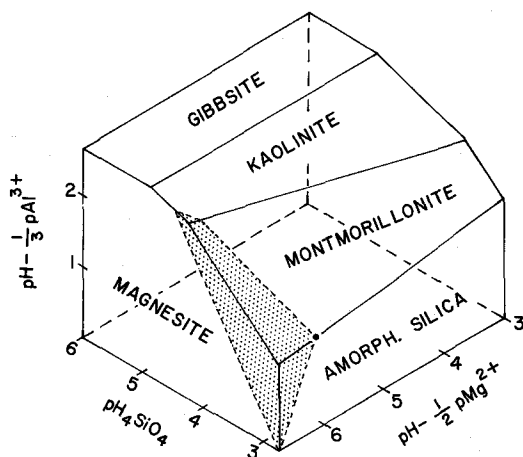


Fig. 2. Diagram indicating a possible vermiculite stability plane (shaded). The hypothetical montmorillonite–vermiculite–amorphous silica triple point is indicated by the dot.

the solution would increase until the montmorillonite–amorphous silica–magnesite triple point was reached. Further dissolution of vermiculite at this point should result in the precipitation of one or more of these triple-point minerals.

The $\text{pH}-1/2\text{pMg}^{2+}$ of magnesite. Since solutions of $\text{pH}-1/2\text{pMg}^{2+}$ greater than that supported by magnesite are supersaturated with respect to magnesite, the area encompassed by the vermiculite stability plane will then depend upon how much lower, if any, are the $\text{pH}-1/2\text{pMg}^{2+}$ values of the solutions of Table 2 as compared to the $\text{pH}-1/2\text{pMg}^{2+}$ supported by magnesite under similar conditions.

To determine the $\text{pH}-1/2\text{pMg}^{2+}$ supported by magnesite in equilibrium with atmospheric CO_2 , consider the following (where standard free energy of formation values, herein indicated for simplicity as ΔG , are taken from Robie and Waldbaum (1968) and ΔG_r is the standard free energy of the reaction):

$$\begin{aligned} \text{MgCO}_3 &= \text{Mg}^{2+} + \text{CO}_3^{2-} \\ \Delta G_r &= \Delta G_{\text{Mg}^{2+}} + \Delta G_{\text{CO}_3^{2-}} - \Delta G_{\text{MgCO}_3} \\ &= 108.9 \pm 0.2 - 126.2 \pm 0.15 \\ &\quad + 246.1 \pm 0.3 \\ &= 11.0 \pm 0.65 \text{ kcal.} \end{aligned}$$

Where K is the equilibrium constant, (K values taken from Garrels and Christ, 1965), and considering the activity of the solid phase to be unity,

$$\begin{aligned} \text{p}K &= \Delta G_r/1.364 = 8.06 \pm 0.48 \text{ and} \\ \text{pMg}^{2+} + \text{pCO}_3^{2-} &= 8.06 \pm 0.48. \quad (2) \end{aligned}$$

When the CO_2 in the air at an average pressure of $10^{-3.5}$ atm dissolves in water,

$$\begin{aligned} \text{CO}_2 + \text{H}_2\text{O} &= \text{H}_2\text{CO}_3 \\ \text{p}K &= 1.47 = \text{pH}_2\text{CO}_3 - \text{pCO}_2 \text{ and} \\ \text{pH}_2\text{CO}_3 &= 1.47 + 3.50 = 4.97. \end{aligned}$$

Further,

$$\begin{aligned} \text{H}_2\text{CO}_3 &= \text{H}^+ + \text{HCO}_3^- \\ \text{p}K &= 6.4 = \text{pH}^+ + \text{pH}_2\text{CO}_3 - \text{pHCO}_3^- \text{ and} \\ \text{pH}^+ + \text{pHCO}_3^- &= 6.4 + 4.97 = 11.37. \end{aligned}$$

Then,

$$\begin{aligned} \text{HCO}_3^- &= \text{H}^+ + \text{CO}_3^{2-} \\ \text{p}K &= 10.3 = \text{pH}^+ + \text{pCO}_3^{2-} - \text{pHCO}_3^- \\ \text{pHCO}_3^- &= -10.3 + \text{pH}^+ + \text{pCO}_3^{2-} \\ \text{pHCO}_3^- + \text{pH}^+ &= -10.3 + 2\text{pH}^+ + \text{pCO}_3^{2-} = 11.37 \\ \text{pCO}_3^{2-} &= 21.67 - 2 \text{pH}. \end{aligned}$$

Substituting in (2),

$$\begin{aligned} \text{pMg}^{2+} + 21.7 - 2 \text{pH}^+ &= 8.06 \pm 0.48 \\ \text{and } \text{pH}-1/2\text{pMg}^{2+} &= 6.8 \pm 0.24 \approx 6.6 \text{ to } 7.0 \quad (3) \end{aligned}$$

where uncertainties in the ΔG values, but not in the K values are considered.

Table 2. Composition of the solution in contact with Palabora and Libby vermiculites at alkaline pH. The samples also contained montmorillonite, amorphous silica and hematite

Equilibration time (days)	pH ₄ SiO ₄	pMg ²⁺	pH	pH-1/2pMg ²⁺
Initial solution				
0	2.52	2.24	7.90	6.78
Palabora vermiculite				
8	2.72		7.55	
19	2.70	2.56	7.84	6.56
42	2.69	2.60	7.89	6.59
73	2.75	2.64	7.90	6.58
Libby vermiculite				
8	2.74		7.43	
19	2.73	2.63	7.87	6.55
42	2.73	2.73	7.89	6.53
73	2.75	2.73	7.97	6.60

The negative logarithm of the molar activity is denoted by p. The ionic strength was initially determined by the equilibrating solution (mainly 0.0100 M MgCl₂) at 0.030 for both samples. In spite of compositional changes during equilibration, the final ionic strength was still 0.030.

Vermiculite-montmorillonite-amorphous silica-hematite equilibria. A series of preliminary experiments (not shown) compared samples with two particle sizes of each of two montmorillonites, plus hematite and each of the two vermiculites. The samples did not contain amorphous silica, but initial solutions contained Si at the amorphous silica equilibrium level; that is, a pH₄SiO₄ of 2.72 (Kittrick, 1969b). The initial pH-1/2pMg²⁺ of the solutions was 5.87 and after 4½ hr of equilibration this value rose to 6.49. The difference between pH-1/2pMg²⁺ of 6.49 and that of magnesite at 6.6-7.0 leaves only a very small possible stability area for the two vermiculites.

The results of the preliminary experiments were independent of the two particle-size fractions of each of the two montmorillonites so the final experiments reported in Table 2 used only a single type and particle size of montmorillonite. After 144 days the pH₄SiO₄ of the preliminary samples had increased to between 3.02 and 3.59, so amorphous silica was included in the final samples in an effort to maintain the samples on the amorphous silica plane and thereby permit clearcut interpretation of results.

Natural and experimental solutions often show some degree of silica supersaturation, but the solutions in Table 2 (which were supersaturated initially) apparently were controlled at the theoretical value by the amorphous silica added to the samples. The montmorillonite and hematite equilibria could not be measured, but both have been shown to come to equilibrium with similar solutions under similar conditions in about 2 weeks (Kittrick, 1971b). Provided that the pH-1/3pAl³⁺ of the solutions was controlled by the montmorillonite added for that purpose, the solution

compositions lie along the montmorillonite-amorphous silica join as originally anticipated.

When the initial solution of Table 2 was added to the acidified mineral mixture, the pH dropped. After 8 days the pH of the Palabora sample had risen to 7.55. Due to an oversight, no Mg²⁺ analyses were made at that time, but the pMg²⁺ must have been between the 2.24 of the initial solution and the 2.56 found at 19 days. The pH-1/2pMg²⁺ at 8 days therefore must have been between 6.27 and 6.43. Values of pH-1/2pMg²⁺ were probably lower than this prior to 8 days. Similar arguments apply to the Libby sample. It is evident that the samples of Table 2 were definitely undersaturated with respect to magnesite initially, and with time approached the lower range of values for magnesite saturation in equilibrium with atmospheric CO₂; that is, a pH-1/2pMg²⁺ of 6.6.

Two factors would tend to make experimental values controlled by magnesite appear near the lower limit of the magnesite stability range. First and most important is the fact that the ΔG of a mineral corresponding to the solution conditions under which it precipitates may range from a few tenths to more than a kcal more negative than the ΔG determined for a particular mineral specimen (see Kittrick, 1970). For every kcal difference, the pH-1/2pMg²⁺ calculated in (3) would be lowered 0.37 unit. Secondly, one must also consider that the air in a laboratory will ordinarily be higher in CO₂ than the average air content of 0.035 per cent used in arriving at the value of the pH-1/2pMg²⁺ for magnesite in (3). A CO₂ content of 0.045 per cent would decrease this value by about 0.10 unit.

After 8 days, the pH of the samples increased with time as the pMg increased. This had the effect of main-

taining the $\text{pH}-1/2\text{pMg}^{2+}$ essentially constant and suggests control by some solid phase, presumably magnesite.* However, it was not possible to detect the formation of any magnesite in the samples by X-ray diffraction. It may be that the magnesite, if precipitated, was not crystalline. However, even crystalline magnesite in small amounts would have been difficult to detect, because the strongest X-ray diffraction peaks of magnesite are coincident with or close to the much stronger peaks of the vermiculite, montmorillonite and hematite which comprise the sample. It is evident from Table 2 that *some* Mg-containing phase is precipitating, because the Mg content of the solutions is decreasing with time.

It appears then that when the slightly acid mineral mixture was mixed with the initial solution, the samples approached the montmorillonite-amorphous silica join at a point well below the calculated position of the magnesite plane. Vermiculite dissolution moved the solution composition along the montmorillonite-amorphous silica join toward a vermiculite plane. Before the vermiculite plane could be reached, the solution composition intercepted the magnesite plane, remaining at the montmorillonite-magnesite-amorphous silica triple point. Thus, the two mica-derived vermiculites studied appear to have no stability area at room T and P .

When the stability of a mineral is determined by solubility methods, it is usually possible to show that the equilibrium was indeed controlled by the mineral in question. For example, this may be done by noting the behavior of solution compositions in relation to a theoretical stability line or plane whose slope is dependent upon the particular composition of the mineral. The negative assertion, that a mineral is not stable at all, cannot be proved with equal assurance because it is not possible to prove that non-equilibrium behavior is controlled by a particular mineral phase. It is possible that the dissolution of some unstable, undetected phase in each of the vermiculite samples controlled sample behavior. It seems much more likely that sample behavior was controlled by the large amounts of vermiculite present, and that the two vermiculites were unstable.

THE FORMATION OF MICA-DERIVED VERMICULITES: A HYPOTHESIS

A mineral is stable in a system if it can persist there at equilibrium, but in some cases a near-infinite

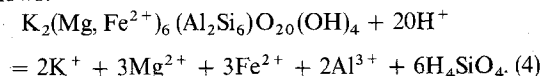
* The only other Mg-containing phase in the samples initially was Belle Fourche montmorillonite. Solubility determinations on this mineral in the absence of vermiculite did not encounter an equilibrium value of $\text{pH}-1/2\text{pMg}^{2+}$ greater than 1.55 (Kittrick, 1971a).

amount of time may be required to reach equilibrium. Thus, persistence of a mineral on a geologic time scale does not necessarily mean thermodynamic stability. Muscovite mica can be stable relative to other minerals that form in soils and sediments if solution conditions are suitable (Routson, 1970). However, these conditions rarely obtain in river and upper ground waters, or even in ocean waters. The stabilities of biotite and ordinary phlogopite have not been determined, but weathering relationships indicate these minerals are even less stable than muscovite. With biotite and phlogopite rarely, if ever, stable in the soil solution, it is not surprising to find experimentally that the vermiculites derived from them are unstable in solution also. These considerations lead to the following hypothesis: *all mica-derived vermiculites are unstable as a result of the unique way in which micas degrade during weathering.*

It is the nature of hypotheses that they be continually tested by comparison with newly-observed facts. Thus, when more observations are available, it may be necessary to alter or even discard this hypothesis, especially since the hypothesis contains two absolutes; that is, *all* mica-derived vermiculites and the weathering environment (*all* naturally occurring solutions at essentially room T and P). Obviously, direct stability determinations such as those reported herein are needed on a wider variety of mica-derived vermiculites, particularly those that are dioctahedral and small in size. At the moment, it is instructive to examine the compatibility of this hypothesis with what is known of mica degradation.

Mica degradation reactions

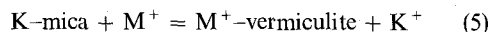
Complete dissolution. One might expect biotite, for example, merely to dissolve in the soil solution as follows:



This reaction (see Huang, Crosson and Rennie, 1968) apparently does occur as written to some extent (for example, Newman, 1969). However, dissolution of biotite more often takes place in a series of steps. Some of the Fe^{2+} is oxidized while still in the mica structure (Boettcher, 1966; Farmer and Wilson, 1970), some octahedral cations may go into solution before the tetrahedral cations (Sawhney and Voigt, 1969) and some of the OH^- groups may be neutralized by the addition of H^+ (Newman and Brown, 1966).

K replacement. If the level of K^+ (or ions of lower hydration energy) in solution is low, the most striking mica degradation reaction of all is the rapid exchange of structural K^+ by ions of higher hydration energy.

K⁺-replacement depends in part upon concurrent progress of reactions mentioned previously. For example, the replacement of K⁺ is hastened by the incorporation of protons into the mica structure (Raman and Jackson, 1966; Newman, 1970b) and slowed by the oxidation of Fe²⁺ (Gilkes *et al.*, 1973). Nevertheless, K⁺-replacement can be illustrated as



where M⁺ is not restricted to monovalent cations. Reaction (5) is not strictly reversible since the original mica prior to K⁺-removal is not exactly reconstituted following K⁺ sorption (Newman, 1970a; Brown and Newman, 1970). Additional internal alterations in the vermiculite structure further diminish the likelihood of reversibility. The same is true for hydroxy interlayers, which persist on a geologic time scale even though they may be unstable. Although reactions (4) and (5) involve the same mica, to a large extent they appear to take place independently of each other. That is, (5) can be at equilibrium when (4) is proceeding to the right. However, if (4) is proceeding to the left or is at equilibrium, it seems reasonable to assume that (5) will be at equilibrium also.

The sensitivity of (5) to the concentration of K⁺ and other weakly hydrated ions in solution appears to originate at the interface of unexpanded and expanded portions of the mica (Jackson, 1963; Wells and Norrish, 1968). The micas have a great selectivity for weakly hydrated ions, apparently because such ions may pass between partially expanded mica layers more readily by shedding much or all of their hydration shell. Thus, the concentration of Cs⁺ may be greater than that of the more highly hydrated Na⁺ at the site of K⁺ exchange in micas even when the concentration of Na⁺ is 10,000 times greater than Cs⁺ in the external solution (see data of Wells and Norrish, 1968).

The rate limiting step in (5) is not the actual exchange of K⁺ by M⁺, but appears to involve the diffusion of M⁺ into the mica structure and especially the outward diffusion of K⁺. Experimental data have been fitted to several diffusion models (Mortland and Ellis, 1959; Reed and Scott, 1962; Quirk and Chute, 1968). There are numerous experiments demonstrating the more rapid replacement of K⁺ in trioctahedral micas compared to dioctahedral micas. For example, Quirk and Chute (1968) find the diffusion coefficient for K⁺ release in several illites to be nine to ten orders of magnitude smaller (10⁻¹⁹ vs 10⁻¹⁰ cm²/sec) than those reported for biotite and phlogopite by Rausell-Colom *et al.* (1965). Thus, the K⁺-replacement reaction has a strong structural bias.

Critical K⁺ levels and the K⁺ content of natural waters

The critical K⁺ level is the level of K⁺ in solution

required to stop the replacement of K⁺ in the mica structure by M⁺ in solution. It is the equilibrium K⁺ level of (5). The critical K⁺ level of a particular mica-vermiculite reaction combines the contributions of many factors of mineral composition and structure (including particle size and strain), as well as solution composition. Some of these factors have been studied sufficiently to permit considerable understanding of the mechanism involved. Examples of such effects are tetrahedra rotation and OH⁻ tilt in dioctahedral micas and the F⁻ content of trioctahedral micas.

The critical K⁺ level decreases with decreasing temperature, decreasing M⁺ concentration, and varies with the nature of M⁺. Critical K⁺ levels have not been established for room temperature and the M⁺ concentration in natural waters, but approximate levels can be estimated for these conditions. The level of about 0.02 ppm K⁺ maintained by sodium tetraphenylboron permits the extraction of K⁺ from illites and muscovites, whereas Mackintosh *et al.* (1971) found the critical K⁺ level for a muscovite to be <3 ppm (lower still for a lepidolite). With the critical K⁺ level for the muscovite thus apparently somewhere between 0.02 and 3 ppm, it is satisfying to note that Rausell-Colom *et al.* (1965) found a critical K level of almost 1 ppm K⁺ for muscovite under high salt, high temperature conditions. Since Rausell-Colom *et al.* found the critical K⁺ level to decrease with decrease in temperature and concentration of extracting salt, the critical K⁺ level of muscovite is probably closer to 0.02 ppm than to 1 ppm K⁺.

The average K⁺ content of river water is 2.3 ppm (Livingston, 1963), with many ground waters a little higher (see White *et al.*, 1963). These average K⁺ levels are probably higher than the critical K⁺ levels of most dioctahedral micas, hence the conclusion by Rausell-Colom *et al.* (1965) that muscovites will not exchange their K⁺ in most natural waters. However, the K⁺ content of rain-water may often be low enough to exchange K⁺ from dioctahedral micas at the soil surface.

Mackintosh *et al.* (1971) found the critical K⁺ level for a biotite to be 290 ppm and Rausell-Colom *et al.* (1965) found that the critical K⁺ level for a series of biotites and phlogopites ranged from almost that level down to about 2.4 ppm (depending upon temperature, salt concentration and F⁻ content). The critical K⁺ levels of trioctahedral micas in natural waters are no doubt nearer the lower end of this range, as indicated by Hoda and Hood (1973). Since these critical K⁺ levels still exceed the K⁺ content of most natural waters, it seems evident that many trioctahedral micas should exchange their K⁺ in natural fresh water, which they do.

Weathering and the formation of mica-derived vermiculites

If all mica-derived vermiculites are unstable intermediates, resulting from the unique way in which micas degrade, then in essence mica-derived vermiculites owe their existence to the rapidity of reactions corresponding to (5) as compared to reactions corresponding to (4). It seems likely that eventually the mica-derived vermiculites either dissolve to furnish essentially the same ions in solution that the parent mica does in equation (D) (except for ions already lost, such as K^+), or they may alter internally toward some mineral that is stable under the prevailing solution conditions, such as montmorillonite (for example see Sridhar *et al.*, 1972). However, if dissolution of dioctahedral micas and dioctahedral vermiculites is slow, dioctahedral vermiculites could predominate after trioctahedral micas and vermiculites dissolve away. It is unfortunate that our present understanding of dioctahedral vermiculites is so rudimentary.

If future investigations confirm that mica-derived vermiculites are unstable, fast-forming intermediates in the degradation of mica, as suggested here, it does not necessarily follow that all 'vermiculites' are unstable. Non-mica-derived materials, that by present diagnostic criteria are called vermiculite, may also exist in soils and sediments. Unlike the mica-derived vermiculites, these vermiculites may precipitate from solution and have a stability field in the weathering environment. It has not yet been possible to obtain a sample of such material that is suitable for stability determinations.

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Résumé—Des déterminations de stabilité ont été effectuées par des méthodes de solubilité sur deux vermiculites dérivées de micas trioctaédriques. La vermiculite dérivée de la phlogopite est instable dans des conditions de solution acide pour lesquelles les stabilités de la montmorillonite, de la kaolinite et de la gibbsite ont été déjà déterminées. On a essayé ensuite de localiser l'éventuel point triple montmorillonite-vermiculite-silice amorphe. Ce point triple implique des conditions de pH alcalin, $\text{pH}_4 \text{SiO}_4$ élevé et Mg^{2+} élevé. Ce sont des conditions dans lesquelles les vermiculites dérivées de phlogopite et biotite doivent très probablement contrôler l'équilibre si ce sont des minéraux stables. Les échantillons montmorillonite-vermiculite-silice amorphe ont évolué vers le point triple montmorillonite-magnésite-silice amorphe, ce qui ne laisse subsister aucune aire de stabilité pour les vermiculites. Les vermiculites à cristaux de grande taille, dérivées de micas trioctaédriques, apparaissent instables dans toutes les conditions de T et P ambiantes.

On présente des arguments qui indiquent que les micas sont instables dans la plupart des environnements d'altération. On fait l'hypothèse que les vermiculites dérivées de micas découlent de l'unique voie selon laquelle les micas instables se dégradent dans ces conditions. On considère que la vermiculite provient d'une série de réactions dont les vitesses relatives entraînent souvent l'abondance de vermiculite. Ces vitesses relatives de réaction sont lentes pour la dissolution du mica, rapides pour l'extraction de K et pour les autres réactions concourant à la formation de la vermiculite, et lentes pour la dissolution de la vermiculite. En termes de chimie, les vermiculites dérivées de mica peuvent être considérées comme des intermédiaires instables à formation rapide.

Kurzreferat—An zwei aus trioktaedrischen Glimmern entstandenen Vermiculiten wurden Stabilitätsbestimmungen mit Löslichkeitsmethoden durchgeführt. Der phlogopitbürtige Vermiculit erwies sich als instabil unter sauren Lösungsbedingungen, bei denen früher die Stabilität von Montmorillonit, Kaolinit und Gibbsit bestimmt wurde. Als nächstes wurde versucht, einen gemeinsamen Schnittpunkt für die drei Phasen Montmorillonit-Vermiculit-amorphe Kieselsäure ausfindig zu machen. Dieser Schnittpunkt war durch alkalisches pH, hohes pH_4SiO_4 und hohe Mg^{2+} -Gehalte gekennzeichnet. Dieses sind Bedingungen, unter denen am ehesten mit einer Beeinflussung der Gleichgewichte durch phlogopit- und biotitbürtige Vermiculite zu rechnen ist, soweit diese stabile Minerale darstellen. Die aus Montmorillonit-Vermiculit-amorpher Kieselsäure bestehenden Proben gelangten zum Montmorillonit-Magnesit-amorphe Kieselsäure-Schnittpunkt, ohne irgendein Stabilitätsfeld für die Vermiculite offenzulassen. Diese grobkörnigen, trioktaedrischen, glimmerbürtigen Vermiculite scheinen unter allen Bedingungen von Raumtemperatur und -druck instabil zu sein.

Es werden Argumente dafür beigebracht, daß Glimmer nahezu in jedem Verwitterungsmilieu instabil sind. Eine Hypothese wird vorgestellt, der zufolge glimmerbürtige Vermiculite das Ergebnis einer spezifischen Umwandlung sind, der instabile Glimmer unter solchen Bedingungen beim Abbau unterliegen. Es wird angenommen, daß Vermiculite aus einer Folge von Reaktionen entstehen, deren relative Raten oft zu einem Vermiculitüberschuß führen. Diese relativen Reaktionsraten sind langsam für die Glimmerauflösung, schnell für die K-Freisetzung und andere mit der Vermiculitbildung verbundene Reaktionen, sowie langsam für die Vermiculitauflösung. In der chemischen Terminologie können die glimmerbürtigen Vermiculite als sich schnell bildende, instabile Zwischenstufen betrachtet werden.

Резюме — Методами растворения определялась устойчивость двух переотложенных из слюды вермикулитов. В условиях кислотных растворов ранее применявшихся для определения устойчивости монтмориллонита, каолинита и гидраргиллита, переотложенный из флогопита вермикулит оказался неустойчивым. Затем сделали попытку определить местонахождение тройной точки аморфного кремнезема-монтмориллонита-гермикулита. Эта тройная точка включала условия щелочного pH, высокого pH_4SiO_4 и высокого Mg^{2+} . В этих условиях устойчивые вермикулиты, переотложенные из флогопита и биотита, наверно, более всего регулируют равновесное состояние. Образцы аморфного кремнезема-вермикулита-монтмориллонита перешли на тройную точку аморфного кремнезема-магнезита-монтмориллонита совсем не оставив устойчивой области для вермикулита. Эти крупнозернистые триоктаэдральные верми-

кулиты, отложенные из слюды, очевидно, неустойчивы при всех условиях комнатной температуры и давления.

Приводят доводы указывающие, что слюды являются неустойчивыми почти что во всех условиях выветривания. Выдвигается гипотеза, что отложенные из слюды вермикулиты resultируются вследствие необыкновенного способа распада слюд во всех фациях. Предполагают, что отложение вермикулита происходит вследствие целого ряда интенсивных взаимных реакций, в результате которых часто образуется много вермикулита. Эти относительные степени реакции медленно растворяют слюду, быстро удаляют К и другие реакции следующие за формированием вермикулита, и медленно растворяют вермикулит. В химической терминологии образующиеся из слюды вермикулиты можно считать быстрообразующимися неустойчивыми переходными типами пород.