

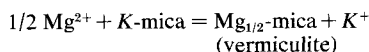
LABORATORY ALTERATION OF TRIOCTAHEDRAL MICAS

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Abstract—Artificial alteration of thirty-five trioctahedral and one dioctahedral micas by solutions varying in strength from 0.001 to 1.00 molal magnesium sulfate was found to approximate a normal exchange reaction after surface effects are eliminated. The equilibrium constants for the reaction:



range from 0.0001 to 0.0028 and average 0.0010 in value. X-ray diffraction study reveals that iron-rich micas tend to develop a 1:1 mixed-layer biotite-vermiculite structure in weak magnesium sulfate solutions whereas magnesium-rich biotite and phlogopite alter to vermiculite. Mica composition also influences the degree of alteration of mica to vermiculite. High fluorine and octahedral multivalent cation contents tend to retard the reaction whereas high magnesium content and perhaps high calcium contents tend to favor the alteration. The equilibrium constant data indicate that vermiculite and hydrobiotite are more stable than trioctahedral micas in most weathering environments.

INTRODUCTION

THE FORMATION of vermiculite has been attributed to the chemical alteration of mica by many investigators. Studies of vermiculite from Libby, Montana (Bassett, 1959), Scottish soils (Walker, 1950), Day Book mine, North Carolina (Kulp and Brobst, 1954) and various other localities indicate that vermiculite forms by the actions of dilute aqueous solutions on biotite or phlogopite. The alteration is effected primarily by the loss of potassium and the uptake of hydrated magnesium ions by the mica phyllosilicate structure. Artificial alteration of micas to simulate the natural processes has been carried out by several investigators in the past (Barshad, 1954; Bassett, 1959; Boettcher, 1966). However, the experiments were conducted on a limited scale and consequently little is known about the physico-chemical environment under which this transformation takes place. The present investigation is mainly an attempt to correlate the extent of alteration of a mica with its chemical composition and the ionic strength of the altering solutions. The experiments were conducted on one dioctahedral mica and thirty-five trioctahedral micas of widely varying composition.

MATERIALS AND EXPERIMENTAL PROCEDURE

Specimens. Micas were collected from a variety of locations in the eastern U.S. and purchased from several mineral dealers. Samples were purified, when necessary, using magnetic, heavy liquid,

and mechanical means of mineral separation. Microscopic examination showed each purified sample to be at least 98 per cent mica. All the specimens were chemically analyzed using a combination of rapid silicate analyses (Shiparo and Brannock, 1962) and X-ray fluorescence techniques. Structural formulas were calculated following Foster's (1960) method. The chemical analyses, structural formulas and source locations of the micas are given in Tables 1, 2, and 3, respectively.

Preparation and experimental procedure. The purified micas were ground in a micro-mill and sieved to obtain the less than 43 μm sizes. A split of each sample was immersed in 200 mm of magnesium sulfate solution. Most experiments were conducted using 0.100 g of sample, but one series was run using 0.500 g to examine the effects of increased surface area of mica. Four different solution strengths, ranging from 1.0 to 0.001 molal, were used for each sample. The grain size, the weight of the sample, and the volume of the altering solutions were kept constant throughout each experimental run. Solutions were stored in polyethylene bottles to avoid possible cation release from glass. Most of the work was conducted at room temperature; however, to speed up the reaction and to study the effect of temperature, one set of samples was altered at 65°C. Except for the 65°C run, the bottles were placed in a large drum and continuously rotated about a horizontal axis at approximately five rpm to insure maximum ex-

Table 1. Chemical composition of the mica samples

Constituent	1	2	3	4	5	6	7	8	9
SiO ₂	35.76	34.90	35.47	37.18	41.60	40.60	36.61	40.03	40.46
TiO ₂	3.23	3.54	2.45	2.74	3.12	2.35	2.62	3.31	1.82
Al ₂ O ₃	17.84	15.26	12.19	12.44	15.52	12.13	19.66	11.71	15.26
Fe ₂ O ₃	5.02	10.03	5.95	3.49	0.31	1.09	4.39	4.04	1.76
FeO	23.93	15.26	23.00	21.24	4.30	16.20	15.51	18.97	13.48
MnO	0.28	0.55	1.71	0.62	0.01	0.73	0.12	0.35	0.30
MgO	1.96	7.35	3.76	6.73	22.83	10.97	7.82	7.95	12.99
CaO	0.27	0.04	0.04	0.05	0.02	0.10	0.02	0.05	1.51
Na ₂ O	0.11	0.12	0.49	0.15	0.79	0.49	0.23	0.13	0.43
K ₂ O	9.16	9.76	9.40	11.09	9.04	9.45	9.72	8.82	8.45
H ₂ O	3.10	2.32	4.80	2.79	1.38	1.94	3.55	3.75	2.55
F	0.38	0.25	0.25	0.42	0.78	3.62	0.38	0.68	0.22
O ≡ F	-0.22	-0.14	-0.14	-0.24	-0.45	-2.07	-0.22	-0.39	-0.13
Total	100.88	99.42	99.40	98.76	99.37	98.12	100.47	99.50	99.14
	10	11	12	13	14	15	16	17	18
SiO ₂	40.89	35.76	37.05	42.74	39.46	42.03	36.90	33.34	40.90
TiO ₂	0.64	1.81	2.20	0.00	1.96	0.48	3.37	0.30	1.24
Al ₂ O ₃	16.20	17.68	17.59	12.43	23.00	12.72	12.10	18.32	17.39
Fe ₂ O ₃	13.11	17.72	1.58	0.19	0.61	1.56	14.40	4.11	0.68
FeO	0.15	2.20	15.65	0.00	14.06	2.58	14.49	26.76	11.32
MnO	0.24	0.23	0.42	0.00	0.18	0.51	0.73	1.19	0.24
MgO	15.02	8.73	9.06	28.93	7.88	25.27	4.66	1.26	13.42
CaO	0.07	0.04	1.67	0.02	1.07	1.17	0.14	0.06	0.20
Na ₂ O	0.13	0.10	0.39	0.04	0.21	0.42	0.46	0.41	0.16
K ₂ O	10.45	10.22	9.96	11.15	8.71	9.44	9.75	9.29	10.55
H ₂ O	2.17	4.50	1.72	0.35	2.97	0.98	3.14	2.65	2.28
F	1.87	0.07	3.07	9.55	1.20	3.62	0.22	3.45	1.86
O ≡ F	-1.08	-0.04	-1.78	-5.53	-0.70	-2.10	-0.13	-2.00	-1.08
Total	100.35	99.03	99.07	101.38	100.81	99.26	100.27	101.01	99.46
	19	20	21	22	23	24	25	26	27
SiO ₂	43.59	35.90	36.19	34.90	38.89	35.90	40.89	42.74	40.60
TiO ₂	0.19	3.76	1.82	2.38	1.90	1.69	2.42	0.99	1.28
Al ₂ O ₃	12.61	15.57	16.84	20.10	18.31	18.16	16.28	14.68	14.69
Fe ₂ O ₃	0.00	0.87	15.29	0.00	2.08	1.87	1.00	1.47	2.34
FeO	3.43	25.86	4.69	18.43	14.11	20.29	13.48	3.27	0.12
MnO	0.07	0.22	0.19	0.00	0.25	0.49	0.17	0.07	0.04
MgO	26.34	3.83	8.46	9.17	10.00	6.77	13.47	23.14	25.85
CaO	0.34	0.07	0.06	0.05	0.09	0.12	0.51	0.10	0.57
Na ₂ O	0.26	0.11	0.16	0.21	0.34	0.10	0.29	0.63	0.27
K ₂ O	10.39	9.25	9.60	10.54	10.59	10.64	8.33	9.38	10.72
H ₂ O	0.58	3.66	5.94	3.50	2.53	3.37	2.34	1.04	0.92
F	5.24	0.11	0.13	0.16	0.29	0.26	0.50	2.80	3.19
O ≡ F	-3.03	-0.06	-0.08	-0.09	-0.17	-0.15	-0.29	-1.62	-1.85
Total	100.83	99.16	99.30	99.37	99.26	99.55	99.47	99.40	99.25
	28	29	30	31	32	33	34	35	36
SiO ₂	38.81	41.03	35.33	39.32	38.75	41.89	40.89	40.89	39.46
TiO ₂	1.29	1.22	1.94	1.19	2.33	2.08	0.85	0.95	2.15
Al ₂ O ₃	17.30	14.55	21.54	19.85	11.24	16.53	14.91	18.88	18.22
Fe ₂ O ₃	0.00	0.67	2.76	0.77	2.22	3.23	0.28	0.54	1.58
FeO	5.08	1.38	16.40	13.61	14.43	9.79	0.24	1.14	17.19
MnO	0.02	0.02	0.31	0.07	0.32	0.08	0.01	0.01	0.13
MgO	24.20	27.50	7.54	12.89	12.08	14.20	27.91	24.92	8.40
CaO	0.77	0.08	0.00	0.26	0.25	3.49	2.76	0.17	2.30

Table 1 (contd.)

Constituent	28	29	30	31	32	33	34	35	36
Na ₂ O	0.34	0.21	0.19	0.70	0.43	0.73	0.92	0.38	0.70
K ₂ O	9.78	10.24	10.80	8.33	9.59	6.00	8.47	10.38	8.05
H ₂ O	0.90	0.48	3.21	2.94	2.00	2.84	1.41	1.27	2.36
F	2.06	3.65	0.06	0.28	2.50	0.21	2.19	0.50	0.32
O ≡ F	-1.19	-2.11	-0.04	-0.16	-1.45	-0.12	-1.27	-0.29	-0.23
Total	99.68	99.49	100.06	100.09	95.09	100.98	99.92	99.82	100.77
	37	38	39						
SiO ₂	39.04	48.01	43.02						
TiO ₂	2.12	0.00	0.99						
Al ₂ O ₃	17.35	28.01	14.42						
Fe ₂ O ₃	1.21	6.31	1.08						
FeO	12.02	1.46	0.20						
MnO	0.21	0.00	0.00						
MgO	16.44	2.73	27.50						
CaO	0.50	0.00	0.13						
Na ₂ O	0.31	0.30	1.00						
K ₂ O	9.06	10.36	9.49						
H ₂ O	1.82	2.74	0.70						
F	0.22	0.21	2.69						
O ≡ F	-0.13	-0.12	-1.58						
Total	100.21	100.04	100.09						

posure of the samples to the altering solutions. The set of samples run at 65°C were intermittently removed from the oven and shaken by hand.

In a typical experimental run, a sample was placed in the magnesium sulfate solution and continuously agitated by rotating it in the drum. Once a week a small portion was removed and the solid material X-rayed to ascertain whether vermiculite was present (a necessary condition for equilibrium) and to determine the relative amounts of biotite and vermiculite. When these became constant, equilibrium was assumed to have been reached. This usually happened in about four weeks, although the samples were allowed to remain in the solutions for three months in order to increase the likelihood that they had attained equilibrium. One set of samples, after having been analyzed at the end of six months, was allowed to remain in the solutions five more months and reanalyzed. The results, within analytical precision, were identical.

At the end of the three month period, each solution was filtered and the filtrates analyzed for potassium and magnesium. The solid residue of mica and vermiculite, except for that from the 1.0 molal solutions, was added to a fresh batch of solutions and the experiment repeated. The repetition of the experiments was necessary because appreciable amounts of potassium can be released from surfaces and edges of the mica flakes (Phillips and Hood, 1965) and interfere with the interlayer exchange of potassium for magnesium.

One set of samples, weighing 0.5 g, was altered at 65°C by changing solutions every week. This

was done in part to obtain a series of vermiculite samples to use to reverse the exchange reaction. Samples of these vermiculites, each weighing 0.100 g as before, were placed in 0.10 molal magnesium sulfate solution to which potassium chloride had been added. The amount of potassium chloride in each solution was greater than the last amount released by the mica during the last cycle of treatment but less than the amount of potassium necessary to completely convert the vermiculite back to mica. These were allowed to come to equilibrium and analyzed as above.

Potassium ion analysis. All solutions except the thousandth molal were analyzed for potassium ion concentration using a Coleman flame emission photometer. The average of two or more determinations on each solution was used to determine the potassium concentration in each solution. The reproducibility of the analyses was $\pm 2\%$ of the amount present. With the anticipation that the potassium released by the thousandth molal solutions would be very low, a Perkin-Elmer atomic absorption spectrophotometer was used to obtain greater accuracy and precision in these samples.

Magnesium ion determination. The magnesium ion concentration in 0.01 molal and stronger solutions was calculated by subtracting one-half the number of moles of potassium released into the solution from the initial concentration of magnesium (two moles of potassium are displaced by one mole of magnesium in the exchange). Considering the large proportion of magnesium relative to potassium in the solutions, this value should not

Table 2. Structural formulas of mica samples

Constituent	1	2	3	4	5	6	7	8	9	10
Tetrahedral										
Si	2.75	2.67	2.88	2.92	2.86	3.09	2.72	3.06	2.95	2.89
Al	1.25	1.33	1.12	1.08	1.14	0.91	1.28	0.94	1.05	1.11
Octahedral										
Al	0.37	0.04	0.04	0.07	0.12	0.18	0.44	0.11	0.26	0.24
Ti	0.19	0.20	0.15	0.16	0.16	0.13	0.15	0.19	0.10	0.03
Fe ⁺³	0.29	0.58	0.36	0.21	0.02	0.06	0.25	0.23	0.10	0.70
Fe ⁺²	1.54	0.97	1.56	1.40	0.25	1.03	0.96	1.21	0.82	0.01
Mg	0.22	0.84	0.45	0.79	2.34	1.24	0.87	0.90	1.41	1.58
Mn	0.02	0.04	0.12	0.04	0.00	0.05	0.01	0.02	0.02	0.01
Interlayer										
K	0.90	0.95	0.97	1.11	0.79	0.92	0.92	0.86	0.79	0.94
Na	0.02	0.02	0.08	0.02	0.11	0.07	0.03	0.02	0.06	0.02
Ca	0.02	0.00	0.00	0.00	0.00	0.01	0.10	0.00	0.12	0.01
	11	12	13	14	15	16	17	18	19	20
Tetrahedral										
Si	2.67	2.80	2.98	2.82	2.95	2.84	2.70	2.96	3.01	2.83
Al	1.33	1.20	1.02	1.18	1.05	1.16*	1.30	1.04	0.99	1.17
Octahedral										
Al	0.23	0.36	0.00	0.76	0.00	0.00	0.45	0.45	0.04	0.28
Ti	0.10	0.12	0.00	0.11	0.03	0.19	0.02	0.07	0.01	0.22
Fe ⁺³	1.00	0.09	0.01	0.03	0.08	0.77	0.25	0.04	0.00	0.05
Fe ⁺²	0.14	0.99	0.00	0.84	0.15	0.93	1.81	0.69	0.20	1.70
Mg	0.97	1.02	3.00	0.84	2.64	0.53	0.15	1.45	2.71	0.45
Mn	0.01	0.03	0.00	0.01	0.03	0.05	0.08	0.01	0.00	0.01
Interlayer										
K	0.97	0.96	0.99	0.79	0.84	0.96	0.96	0.97	0.92	0.93
Na	0.01	0.06	0.01	0.03	0.06	0.07	0.06	0.02	0.03	0.02
Ca	0.00	0.13	0.00	0.08	0.09	0.01	0.01	0.02	0.03	0.01
	21	22	23	24	25	26	27	28	29	30
Tetrahedral										
Si	2.74	2.65	2.86	2.76	2.94	2.96	2.83	2.71	2.83	2.64
Al	1.26	1.35	1.14	1.24	1.06	1.04	1.17	1.29	1.17	1.36
Octahedral										
Al	0.25	0.45	0.45	0.41	0.32	0.16	0.03	0.13	0.02	0.54
Ti	0.10	0.14	0.11	0.10	0.13	0.05	0.07	0.07	0.06	0.11
Fe ⁺³	0.87	0.00	0.12	0.11	0.05	0.08	0.12	0.00	0.03	0.16
Fe ⁺²	0.30	1.17	0.87	1.30	0.81	0.19	0.01	0.30	0.08	1.03
Mg	0.95	1.04	1.10	0.78	1.44	2.41	2.68	2.51	2.83	0.84
Mn	0.01	0.00	0.02	0.03	0.01	0.00	0.00	0.00	0.00	0.02
Interlayer										
K	0.93	1.02	0.99	1.04	0.76	0.83	0.95	0.87	0.90	1.03
Na	0.02	0.03	0.05	0.01	0.04	0.08	0.04	0.05	0.03	0.03
Ca	0.00	0.00	0.01	0.01	0.04	0.01	0.04	0.06	0.01	0.00
	31	32	33	34	35	36	37	38	39	
Tetrahedral										
Si	2.82	3.03	2.93	2.80	2.77	2.87	2.78	3.20	2.91	
Al	1.18	0.97	1.07	1.20	1.23	1.13	1.22	0.80	1.09	
Octahedral										
Al	0.50	0.07	0.29	0.00	0.28	0.43	0.23	1.41	0.06	
Ti	0.06	0.14	0.11	0.04	0.05	0.12	0.11	0.00	0.05	
Fe ⁺³	0.04	0.13	0.17	0.01	0.03	0.09	0.06	0.32	0.05	
Fe ⁺²	0.82	0.94	0.57	0.01	0.06	1.04	0.71	0.08	0.01	

Table 2 (contd.)

Constituent	31	32	33	34	35	36	37	38	39
Mg	1.38	1.41	1.48	2.84	2.51	0.91	1.74	0.27	2.77
Mn	0.00	0.02	0.00	0.00	0.00	0.01	0.01	0.00	0.00
Interlayer									
K	0.76	0.96	0.53	0.74	0.90	0.75	0.82	0.88	0.82
Na	0.10	0.07	0.10	0.12	0.05	0.10	0.04	0.04	0.13
Ca	0.02	0.02	0.26	0.20	0.01	0.18	0.04	0.00	0.01

*Includes 0.06 Fe⁺³.

be significantly different from the true values. It is probably much more precise than any analysis would have been. However, in the 0.001 molal solutions, a greater accuracy was desirable in view of the small quantities involved, so the magnesium concentration was determined volumetrically with

an EDTA titration using the method described by Shapiro and Brannock (1962).

RESULTS

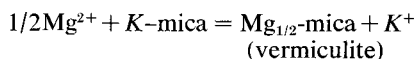
"Equilibrium Constant" Determination

Making the assumption that mica and vermi-

Table 3. Descriptions and locations of mica samples

Sample number	Description	Location
1.	Lepidomelane, brownish black	Adirondack Mountains, N.Y.
2.	Biotite, dark greenish brown	Near Algonquin Park, Ont.
3.	Lepidomelane, greenish black	Arendal, Norway
4.	Biotite, dark brown	Auburn, Maine
5.	Phlogopite, reddish brown	Bamle, Norway
6.	Biotite, yellow brown	Bancroft, Ontario
7.	Biotite, black	Big Ridge Mine, Haywood Co., N.C.
8.	Biotite, brownish black	Chalk Mt., near Spruce Pine, N.C.
9.	Biotite, black	Dysartsville, N.C.
10.	Biotite, bronze	Emerald Mine, near Spruce Pine, N.C.
11.	Biotite, tan (weathered)	Emery County, Utah
12.	Biotite, bronze	Faraday Twp., Ontario
13.	Fluorophlogopite, colorless	Synthetic
14.	Biotite, reddish brown	Foote Mineral Company Mine, Kings Mountain, N.C.
15.	Phlogopite, dark brown	Franklin, N.J.
16.	Lepidomelane, black	Gjerstadt, Norway
17.	Biotite, black	Gunnison County, Colo.
18.	Biotite, gray	Hoot Owl Mine, Mitchell Co., N.C.
19.	Phlogopite, yellow brown	Huddersfield Twp., Quebec
20.	Lepidomelane, yellow black	Johnstown, Calif.
21.	Biotite, tan (weathered)	Pacolma Canyon, Los Angeles County, Calif.
22.	Biotite, brown	Number Two Prospect, Mitchell County, N.C.
23.	Biotite, black	Number Eight Mine, Mitchell County, North Carolina
24.	Biotite, black	McKinney Mine, near Spruce Pine, N.C.
25.	Biotite, black	N. L. Teer Quarry, Raleigh, N.C.
26.	Phlogopite, brown	Natural Bridge, Jefferson Co., N.Y.
27.	Phlogopite, silvery white	North Burgess, Ontario
28.	Biotite, reddish brown	Ogdensburg, N.J.
29.	Phlogopite, reddish brown	Pitkin, Colo.
30.	Biotite, reddish brown	Spruce Pine, N.C.
31.	Biotite, gray	Six miles southwest of Spruce Pine, N.C.
32.	Biotite, brownish black	Silver Crater Mine, Faraday Twp., Ontario
33.	Biotite, light brown	Superior Stone Company Quarry, Kings Mountain, N.C.
34.	Phlogopite, silvery white	Sydenham, Ontario
35.	Phlogopite, light brown	Texas, Md.
36.	Biotite, dark reddish brown	Weaverville, N.C.
37.	Biotite, black	Vulcan Materials Company Quarry, Winston-Salem, N.C.
38.	Muscovite, light green	Wind River Mountains, Wyo.
39.	Phlogopite, silvery white	York, Ontario

culite, both being solids, each have an activity of one, the "equilibrium constant" for the reaction:



would be:

$$K = \frac{\gamma K^+(K^+)}{\sqrt{\gamma \text{Mg}^{2+}(\text{Mg}^{2+})}}$$

where γK^+ and γMg^{2+} are the activity coefficients and (K^+) and (Mg^{2+}) are the molal concentrations of potassium and magnesium, respectively. Values for concentration of potassium and magnesium were obtained as described under experimental procedures; Latimer's (1952) data for mean ionic activity coefficients were used in making the calculations. It must be pointed out that the "equilibrium constant" as used here is not a true equilibrium constant in the strict sense of the term. Ion exchange equilibrium depends on the specific set of experimental conditions, i.e. concentration, relative amounts of exchange cations, etc. (Helfferick, 1962). In order to calculate a true equilibrium constant, the activities of each of the exchange ions in the silicate framework would have to be known. The supposition that the solids each have an activity of one in reality assumes the exchange ions each have the same activity in the solids. This is obviously an oversimplification, but it does allow the data to be handled in such a way that permits comparisons of behavior of different micas to be made.

The equilibrium constant data are summarized in Table 4, where nine independent determinations for each mica are tabulated. Values obtained range from 0.0001 to 0.0028, with the mean value being 0.0010. It would appear at a first glance that the values for the equilibrium constant for any given sample do not have acceptable precision. However, a closer examination of the data reveals that the equilibrium constants for the reverse reactions are not much different from those calculated from the second cycle of treatment, which is in accordance with expectations. Release of adsorbed potassium from surfaces and edges of a mica flake occurs in addition to the release of potassium from the interlayer position in the first cycle of exchange. The measured values of potassium from the first treatment therefore tend to be higher than the values for interlayer exchange alone. Consequently, the deviation of the equilibrium constants from the true values depends on the amount of adsorbed potassium ions that are released; this may or may not be significant. The same samples treated for a second time with fresh solutions should give a much more dependable set of values for interlayer exchange,

as should the artificial vermiculite samples for the reverse reaction, because easily exchanged surface cations have been removed.

The effect of adsorbed potassium ions should be less in stronger solutions because the proportion of potassium released from the interlayer position in these cases will be larger. It is evident from the experimental data that the equilibrium constants for the 1.0 m (and in some cases the 0.1 m) solutions are much closer to those from the second treatment than are the values of the equilibrium constant for weaker solutions. For this same reason there is a general increase in value of equilibrium constants from 1.0 to 0.000 m solutions in the first cycle of treatment. Similarly, samples with 0.5 g mica have higher equilibrium constants than those with 0.1 g. In very weak solutions, the first cycle of treatment may not have dislodged all the adsorbed potassium, so calculated equilibrium constants for dilute second cycle solutions may not be as reliable as those for more concentration solutions.

Hower (1967) points out that illites should contain zero percent expandable layers when the mineral contains about 0.8 mole of potassium per $\text{O}_{10}(\text{OH})_2$ rather than the 1.0 moles necessary to fill all the voids in the tetrahedral sheet. It is possible that a similar situation might exist in the case of vermiculite returning to mica during the reverse reaction; that is, it may take less than one mole of potassium per $\text{O}_{10}(\text{OH})_2$ to collapse the structure back to 10 Å. If this occurs, the result would be a higher value of the equilibrium constant for the reverse reaction as compared to the forward reaction. To test this possibility, the results of runs f, g, and h were averaged; the mean value was 0.00096. The mean value of run i, the back conversion, was also 0.00096. Because there is an appreciable amount of scatter in the data, the possibility of reconstituted mica being potassium deficient cannot be completely ruled out, but the similarity of the average values of the equilibrium constant for forward and reverse runs indicates any effect due to less than one mole of potassium collapsing the structure is not large.

The situation discussed above is one possible case of non-ideal behavior of the solid phases involved in the reaction. Other possibilities, such as magnesium entering the solution from the octahedral layer of the structure or the value of the equilibrium constant changing with different mica to solution ratios, might exist and, if so, would have the effect of giving the exchange ions in the solid phases activity values other than unity as was assumed. However, when the obvious problem of surface potassium in the first cycle data is eliminated, the values for the various forward and reverse reactions seem to be close enough to allow

Table 4. Equilibrium constant data

Experimental Procedure	EQUILIBRIUM CONSTANTS FOR SAMPLE NUMBER							
	1.	2.	3.	4.	5.	6.	9.	
First treatment								
a. 1.0 m	0.0015	0.0013	0.0004	0.0010	0.0017	0.0003	0.0018	
b. 0.1 m	0.0014	0.0012	0.0004	0.0009	0.0023	0.0003	0.0034	
c. 0.1 m (0.5 g)	0.0027	0.0017	0.0026	0.0009	0.0031	0.0007	0.0073	
d. 0.01 m	0.0022	0.0010	0.0014	0.0011	0.0048	0.0007	0.0082	
e. 0.001 m	0.0031	0.0019	0.0036	0.0021	0.0045	0.0017	0.0110	
Second treatment								
f. 0.1 m (0.5 g)	0.0016	0.0012	0.0007	0.0010	0.0023	0.0005	0.0048	
g. 0.01 m	0.0004	0.0002	0.0002	0.0001	0.0023	0.0001	0.0022	
h. 0.001 m	0.0004	0.0002	0.0003	0.0001	0.0025	0.0002	0.0027	
Back conversion								
i. 0.1 m, 100 ppm K ⁺	0.0010	0.0015	0.0005	0.0010	0.0020	0.0005	0.0020	
Average of a, b, f, g, h, i	0.0011	0.0009	0.0004	0.0007	0.0022	0.0003	0.0028	
	10.	11.	12.	13.	14.	15.	16.	
First treatment								
a. 1.0 m	0.0008	0.0001	0.0003	0.0001	0.0001	0.0003	0.0018	
b. 0.1 m	0.0007	0.0003	0.0002	0.0001	0.0002	0.0005	0.0026	
c. 0.1 m (0.5 g)	0.0024	0.0003	0.0007	0.0005	0.0009	0.0029	0.0028	
d. 0.01 m	0.0021	0.0003	0.0004	0.0003	0.0007	0.0032	0.0032	
e. 0.001 m	0.0038	0.0008	0.0015	0.0013	0.0019	0.0050	0.0032	
Second treatment								
f. 0.1 m (0.5 g)	0.0006	0.0002	0.0005	0.0001	0.0002	0.0005	0.0012	
g. 0.01 m	0.0005	0.0001	0.0001	0.0002	0.0001	0.0004	0.0012	
h. 0.001 m	0.0011	0.0002	0.0003	0.0001	0.0003	0.0007	0.0008	
Back conversion								
i. 0.1 m, 100 ppm K ⁺	0.0006	0.0003	0.0004	0.0001	0.0001	0.0004	0.0020	
Average of a, b, f, g, h, i	0.0007	0.0002	0.0003	0.0001	0.0002	0.0005	0.0016	
	18.	19.	20.	21.	22.	23.	24.	
First treatment								
a. 1.0 m	0.0004	0.0001	0.0014	0.0001	0.0014	0.0014	0.0013	
b. 0.1 m	0.0004	0.0001	0.0027	0.0002	0.0015	0.0017	0.0016	
c. 0.1 m (0.5 g)	0.0008	0.0005	0.0054	0.0004	0.0037	0.0035	0.0029	
d. 0.01 m	0.0010	0.0005	0.0057	0.0005	0.0023	0.0034	0.0026	
e. 0.001 m	0.0022	0.0010	0.0077	0.0007	0.0027	0.0037	0.0043	
Second treatment								
f. 0.1 m (0.5 g)	0.0006	0.0002	0.0027	0.0004	0.0025	0.0027	0.0012	
g. 0.01 m	0.0003	0.0002	0.0007	0.0001	0.0007	0.0017	0.0005	
h. 0.001 m	0.0001	0.0010	0.0008	0.0001	0.0008	0.0009	0.0008	
Back conversion								
i. 0.1 m, 100 ppm K ⁺	0.0005	0.0002	0.0016	0.0002	0.0017	0.0016	0.0010	
Average of a, b, f, g, h, i	0.0004	0.0003	0.0017	0.0002	0.0014	0.0017	0.0011	
	25.	26.	27.	28.	29.	30.	31.	
First treatment								
a. 1.0 m	0.0010	0.0007	0.0005	0.0004	0.0002	0.0016	0.0016	
b. 0.1 m	0.0015	0.0005	0.0004	0.0002	0.0002	0.0018	0.0024	
c. 0.1 m (0.5 g)	0.0025	0.0012	0.0007	0.0008	0.0006	0.0030	0.0070	
d. 0.01 m	0.0028	0.0026	0.0009	0.0005	0.0005	0.0032	0.0074	
e. 0.0001 m	0.0044	0.0025	0.0015	0.0010	0.0014	0.0028	0.0092	

Table 4 (contd.)

Experimental Procedure	EQUILIBRIUM CONSTANTS FOR SAMPLE NUMBER							
	25.	26.	27.	28.	29.	30.	31.	
Second treatment								
f. 0.1 m (0.5 g)	0.0026	0.0012	0.0006	0.0009	0.0004	0.0019	0.0044	
g. 0.01 m	0.0006	0.0006	0.0001	0.0001	0.0001	0.0028	0.0018	
h. 0.001 m	0.0013	0.0006	0.0001	0.0001	0.0001	0.0019	0.0046	
Back conversion								
i. 0.1 m, 100 ppm K ⁺	0.0010	0.0010	0.0007	0.0005	0.0004	0.0015	0.0015	
Average of a, b, f, g, h, i	0.0013	0.0008	0.0004	0.0004	0.0004	0.0019	0.0027	
	32.	33.	34.	35.	36.	37.	38.	39.
First treatment								
a. 1.0 m	0.0003	0.0014	0.0008	0.0019	0.0014	0.0008	0.0001	0.0009
b. 0.1 m	0.0002	0.0025	0.0007	0.0022	0.0027	0.0016	0.0001	0.0004
c. 0.1 m (0.5 g)	0.0008	0.0102	0.0016	0.0029	0.0066	0.0057	0.0008	0.0011
d. 0.01 m	0.0007	0.0089	0.0016	0.0055	0.0063	0.0056	0.0003	0.0009
e. 0.001 m	0.0015	0.0142	0.0025	0.0034	0.0063	0.0081	0.0008	0.0012
Second treatment								
f. 0.1 m (0.5 g)	0.0005	0.0029	0.0012	0.0024	0.0037	0.0022	0.0001	0.0013
g. 0.01 m	0.0005	0.0007	0.0001	0.0015	0.0020	0.0002	0.0003	0.0004
h. 0.001 m	0.0002	0.0008	0.0003	0.0008	0.0008	0.0004	0.0008	0.0001
Back conversion								
i. 0.1 m, 100 ppm K ⁺	0.0005	0.0020	0.0008	0.0022	0.0015	0.0010	0.0001	0.0015
Average of a, b, f, g, h, i	0.0004	0.0017	0.0007	0.0018	0.0020	0.0010	0.0002	0.0008

the assumption of ideal solid behavior to stand, at least as a first approximation. Any effects that might be due to non-ideal behavior are not large enough to influence the conclusions reached in the discussion to follow.

In summary, the equilibrium constants from the back conversion of vermiculite to mica and the second exchange treatment of the mica samples, if not entirely precise, at least are generally consistent and probably show the range within which the true values lie. The values are also consistent enough to indicate the assumption that the micas and vermiculite behave as solids with activities of one is reasonable once the adsorbed surface cations have been eliminated.

DISCUSSION

X-ray Diffraction Studies

An examination of the X-ray diffractometer tracings reveals some very interesting differences in the behavior of the different types of micas. Minerals of the lepidomelane group initially develop a 14 Å vermiculite peak in 0.1 molal magnesium sulfate solutions (Fig. 1, a). However, in the course of the time the 14 Å peak decreases in intensity and a 12 Å peak due to 1:1 mixed layer mica-vermiculite develops in its place (Fig. 1, b). In a more dilute solution, 0.01 molal, the 12 Å peak appears in the very beginning of alteration and the 14 Å peak either does not appear or remains sub-

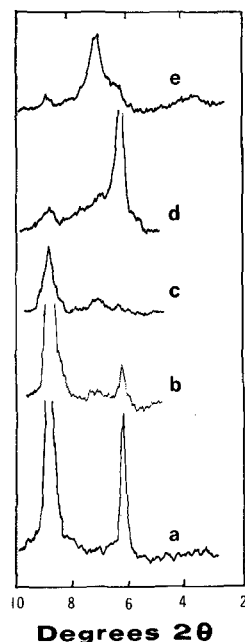


Fig. 1. X-ray diffraction patterns of a lepidomelane (sample no. 1) showing behavior in different altering solutions. a. 0.1 m MgSO₄ for four weeks. b. 0.1 m MgSO₄ for seven weeks. c. 0.01 m MgSO₄ for three weeks. d. 0.1 m MgSO₄ at 65°C, changed weekly for five weeks. e. Sample d in 0.1 m MgSO₄ and 100 ppm potassium for one week.

ordinate (Fig. 1.c). Upon changing solutions several times, these micas show a strong 14 Å vermiculite peak which has a trailing toward lower *d*-spacing (Fig. 1.d). On treatment with weak potassium solutions, the vermiculite produced from lepidomelane tends to develop a 12 Å mixed-layer mica-vermiculite structure rather than reverting completely to mica (Fig. 1.e).

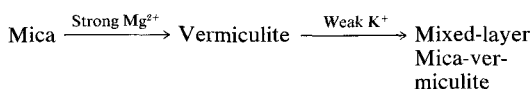
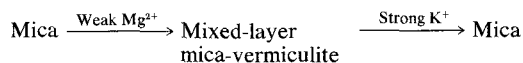
High-iron biotites seem to follow the lepidomelane group except in certain respects. The initial 14 Å peak again diminishes in intensity with time, but in this case does not become subordinate to the 12 Å mixed-layer peak (Fig. 2.a,b). In the weaker 0.01 molal solutions, both the 14 Å and the 12 Å peaks appear with about the same low intensity (Fig. 2,c). Weak potassium treatment again causes formation of a 12 Å mixed layer structure from the 14 Å vermiculite.

Phlogopites develop, in 0.1 molal solutions, a 14 Å peak which increases in intensity with time (Fig. 3,a,b). In the weaker 0.01 molal solutions they do not, in contrast to iron-rich samples, show

the development of a mixed-layer structure (Fig. 3,c). During complete conversion to vermiculite they show a sharp symmetrical peak (Fig. 3,d) in contrast to the broad peak with tailings toward lower spacings shown by vermiculite formed from iron-rich samples. During the reverse reaction with weak potassium treatment, they develop a 10 Å peak, showing a return to the mica structure (Fig. 3,e). Magnesium-rich biotites follow the phlogopites except that they do not develop a sharp symmetrical 14 Å peak but have a relatively broad peak which tails toward lower spacings.

The lone sample of muscovite behaved like phlogopite but showed a much smaller degree of alteration than low-fluorine phlogopites.

It appears, therefore, that in iron-rich trioctahedral micas the reaction is:



whereas in magnesium-rich micas it is:

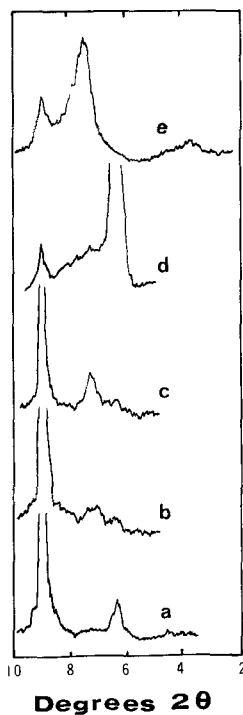
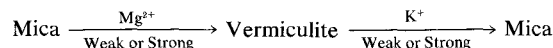


Fig. 2. X-ray diffraction patterns of an iron-rich biotite (sample no. 24) showing behavior in different altering solutions. a. 0.1 m MgSO_4 for four weeks. b. 0.1 m MgSO_4 for seven weeks. c. 0.01 m MgSO_4 for three weeks. d. 0.1 m MgSO_4 at 65°C, changed weekly for five weeks. e. Sample d in 0.1 m MgSO_4 and 100 ppm potassium for one week.

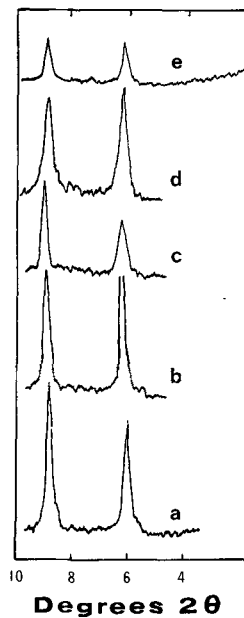


Fig. 3. X-ray diffraction patterns of a phlogopite (sample no. 15) showing behavior in different altering solutions. a. 0.1 m MgSO_4 for four weeks. b. 0.1 m MgSO_4 for seven weeks. c. 0.01 m MgSO_4 for three weeks. d. 0.1 m MgSO_4 at 65°C, changed weekly for five weeks. e. Sample d in 0.1 m MgSO_4 and 100 ppm potassium for one week.

Regarding the formation of mixed layer sheets, Rausell-Colom *et al.* (1965, p. 68–69) state:

“In strong salt solution the replacement of potassium is orderly and appears to take place between every silicate sheet at the same rate, so that a well-defined boundary is observed. In natural weathering the salt solutions will usually be dilute and the replacement very slow against the back reaction of potassium in solution. In these circumstances, the replacement is not so orderly and once a particular sheet has been opened, continued replacement in that region will be favored over the opening up of other interlayer regions. Therefore, interstratification would be expected during natural weathering, and is commonly found.”

The results of the present investigation are in agreement with the above statement as far as it goes. However, it does not explain why ordered mixed-layering should occur. Regularly interstratified biotite-vermiculite was formed in some of the experiments by Rausell-Colom *et al.* (1965) as well as by Bassett (1958) and Sawhney (1967). Bassett (1959) and Sawhney (1967) both suggest that when potassium enters an interlayer position and causes collapse, a decrease in bonding energy occurs in the adjacent interlayer position. The next layer to collapse would not be the adjacent layer with decreased bonding energy, but rather the next one beyond. The bonds would thus be alternately strong and weak and yield alternately mica and vermiculite.

At least three factors influence the formation of ordered mixed-layer mica-vermiculite. First is the composition of the mica. With magnesium as the exchange cation, ordered interstratification took place when the original mica contained less than approximately ten percent magnesium oxide. It did not occur in phlogopites. The second factor is the concentration of the altering cation. Mixed-layering is more likely to occur in dilute solutions than in concentrated solutions. The third factor is nature of the altering cation. A few samples were leached by sodium and calcium as well as magnesium solutions. Vermiculites formed from those leached by sodium and ordered mixed-layer biotite-vermiculite formed when the leaching cation was calcium. In contrast to the previously discussed situation with magnesium as the altering cation, even phlogopites formed ordered mixed-layer biotite-vermiculite when leached with calcium solutions. Similarly, Bassett (1959) obtained only vermiculite from Libby, Montana, biotite using magnesium as the altering cation while Sawhney obtained ordered mixed-layer structures from the same mica using calcium solutions.

The observation that iron-rich micas tend to develop mixed-layer mica-vermiculite may be the

explanation of why Foster (1963) indicated natural vermiculites are invariably magnesium-rich. Foster disregarded any vermiculite that contained over one percent potassium oxide. Vermiculites derived from iron-rich micas are likely to form mixed layer mica-vermiculite and retain appreciable amounts of potassium. Therefore, they would have been excluded from Foster's compilation.

The mixed layer mica-vermiculite formed in this study seems to have a regular 1:1 interstratification of biotite and vermiculite layers, for it shows development of both the 12 Å (*d*002) and 24 Å (*d*001) peaks. The term “hydrobiotite” (Gruner, 1934) is commonly used for such material. Thus, the results of this investigation provide the evidence Boettcher (1966) lacked when he remarked that no experimental evidence could be cited to show that hydrobiotite could be produced in the laboratory at low temperatures. His contention that hydrobiotites are not a product of weathering would therefore appear to be untenable in view of the present investigation.

Influence of mica composition and other factors on alteration

A comparison was made between the equilibrium constants and percent of fluorine, octahedral multivalent cation content, octahedral ferrous iron content, octahedral magnesium content, and the percent of CaO. Coefficients of correlation were computed for each of these pairs of variables to determine which composition variable exerted the greatest degree of influence on the equilibrium constant. All five of the above compositional variables influence the experimentally determined equilibrium constants to some extent, making this a rather complex system. The fact that the dependent variable, the equilibrium constant, is influenced by several independent variables results in a considerable amount of scatter of the data when any two variables are compared. This scatter makes it difficult to determine if any variables other than those five influence the equilibrium constant. The experimental data gathered in this investigation do not seem to indicate that any other compositional variable is very important.

Fluorine. When the equilibrium constants for all mica samples used in this investigation are compared with the five compositional variables listed above, the largest correlation coefficient, -0.51 , is between the equilibrium constant and the percent of fluorine in the mica. As this value is nearly twice that of any other pair of variables, fluorine content appears to be the most important composition factor in the alteration of trioctahedral mica to vermiculite. The equilibrium constant shows an inverse correlation with the fluorine content (Fig.

4). The relationship appears to be a hyperbolic relationship; therefore, high fluorine micas should be extremely resistant to chemical alteration to vermiculite. If the fluorine content of a mica exceeds one percent, the equilibrium constant usually does not exceed 0.0005 and never exceeds 0.0008, regardless of the effects of other variables. On the other hand, low fluorine micas show a wide range of equilibrium constants and thus vary greatly in their susceptibility to alteration. Bassett (1960) observed the resistance of artificial fluor-phlogopite to alteration and explained it by pointing out that fluorine occurs as a substitute for hydroxyl ions that are located adjacent to the inter-layer potassium ions. In trioctahedral micas the orientation of the hydroxyl is such that the proton remains close to the potassium ion, thereby weakening the bonding strength of the potassium to the mica structure by placing two positive charges close to one another. In dioctahedral micas the hydroxyl ions are inclined to the basal plane of the mica structure so that the proton is located farther away from the potassium. The potassium is therefore placed in a more electrically negative environment in the dioctahedral micas, which results in a stronger attraction between the silicate structure and the potassium ion. This makes the dioctahedral micas generally more resistant to alteration than trioctahedral micas. When fluorine substitutes for hydroxyl there is no proton present to weaken the bonding force between potassium and the silicate structure. Therefore, high fluorine micas are very resistant to alteration.

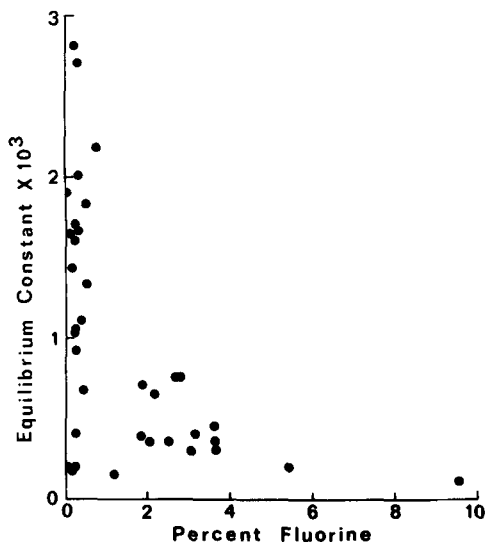


Fig. 4. Equilibrium constants plotted as a function of the percentage of fluorine in the original mica.

Multivalent octahedral cations. Because fluorine is the dominant factor in the alteration of trioctahedral micas but obviously does not explain all the variation observed in the data, the data for samples containing fluorine in quantities of more than one percent were omitted and the correlation coefficients recalculated.

In this case, the highest correlation coefficient (-0.59) is between the equilibrium constant and the multivalent octahedral cations (aluminum, titanium, and ferric iron). The correlation is a negative one; with increasing amounts of multivalent ions in the octahedral position, the equilibrium constant becomes smaller (Fig. 5) and the mica becomes increasingly difficult to alter. As larger amounts of multivalent ions are incorporated into the structure, the trioctahedral micas become closer in character to the dioctahedral micas. This should influence the orientation of the proton of the hydroxyl, as was discussed in the section on fluorine content, and should make the micas progressively harder to alter.

Structural magnesium and divalent iron. Three of the samples with high multivalent cation content appear to be atypical; one is the muscovite and two are biotites that visually appear to be weathered. The data for these samples were omitted as before and the correlation coefficients were recomputed. The highest values for the recomputed coefficients, -0.49 and 0.44 , were between the equilibrium constant and the octahedral ferrous iron content and the equilibrium constant and octahedral magnesium content of the octahedral layer, respective-

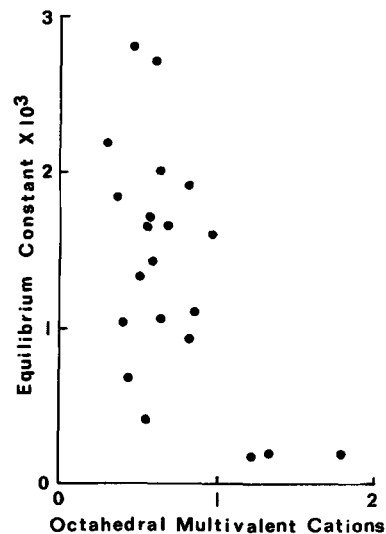


Fig. 5. Equilibrium constants of low-fluorine micas plotted as a function of the octahedral multivalent cation content of the original mica.

ly. The magnesium content and the ferrous iron content of the octahedral layer are very closely related; as the magnesium content goes up, the ferrous iron content goes down and vice versa. These two variables show opposite relationships to the equilibrium constant. As the iron content increases the equilibrium constant goes down (Fig. 6) and as the magnesium content goes up, the equilibrium constant increases. Thus, samples high in ferrous iron and low in magnesium are more difficult to alter than samples rich in magnesium. A similar observation was made by Bergseth (1964).

In order to explain the formation of vermiculite, Roy and Romo (1957) proposed the migration of magnesium from the octahedral to the interlayer position with concomitant oxidation of ferrous iron to the ferric state to balance the charge deficiency created by the migration of magnesium. This simplifies the problem of accounting for the source of interlayer magnesium in vermiculite but also necessitates the presence of at least an equivalent amount of ferrous iron in the octahedral layer. The present study indicates the alteration of samples with little ferrous iron takes place with greater ease than samples with larger amounts of ferrous iron; therefore, the oxidation of ferrous iron is considered to be a separate process in the formation of vermiculite and not a requirement of alteration.

Calcium content. A crude relationship (correlation coefficient 0.30) exists between the equilibrium constant and the calcium oxide content of the micas after the fluorine and multivalent cation corrections

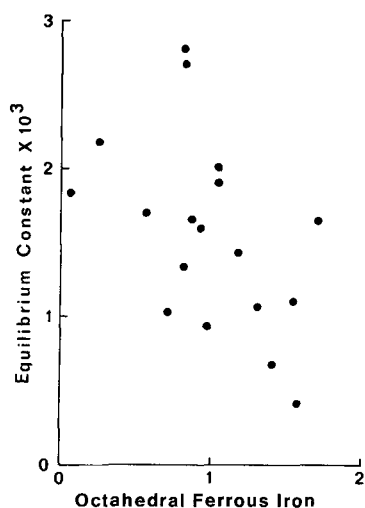


Fig. 6. Equilibrium constants of low-fluorine micas plotted as a function of octahedral ferrous iron content of the original mica.

are made. The effect was shown best by samples 9, 33, and 36, which released potassium very rapidly at first during the conversion to vermiculite. All three of these samples have low fluorine contents (less than one percent) and greater than one percent calcium oxide. Two of the four high fluorine samples that contain greater than one percent calcium oxide also released considerably larger than average amounts of potassium into solution in the early stages of alteration. We have no good explanation as to why calcium-rich micas should be abnormally susceptible to potassium loss during early stages of alteration.

Multiple linear regression. A multiple linear regression was performed on the data in an attempt to develop an equation that can be used to predict equilibrium constants when the mica composition is known. The equilibrium constant was taken as a dependent variable and all others were considered to be independent variables. The calculated equation is:

$$1000K = -3.59 - 0.25F + 0.13Ca + 1.74Mg + 1.94Fe + 1.79M$$

where K is the equilibrium constant, F is the weight per cent fluorine, Ca is the weight per cent calcium oxide, Mg is the octahedral magnesium content, Fe is the octahedral ferrous iron content, and M is the octahedral multivalent ion content. The last three values are from Table 2. At first glance, this equation appears to be in conflict with preceding discussions in several ways. The discrepancies are not real, however, as the following discussion will show.

In the discussion on fluorine, it was pointed out that fluorine is the most important composition variable controlling the alteration of mica to vermiculite. The low coefficient for fluorine in the regression equation would seem to indicate just the opposite. This discrepancy can be explained when it is remembered that in trioctahedral micas, the sum of octahedral magnesium, ferrous iron, and multivalent cations should ideally have an almost constant value of three. Because the coefficients of these three variables are nearly the same, their contribution should in each case be nearly 5.4. This allows the equation to be simplified to the approximation: $1000K = 1.8 - 0.25F + 0.13Ca$. Since the value for F varies from zero to +9, its importance is at once evident.

In the regression equation, octahedral multivalent cations appear to show a positive correlation with the equilibrium constant, which is contrary to the relationship established earlier. This is because an increase in octahedral multivalent

cations is usually coupled with a decrease in the total octahedral occupancy, so that an increase in M is more than compensated by decreases in Mg and Fe and results in a decrease in the value of the equilibrium constant. To illustrate this effect, consider an ideal dioctahedral mica with an octahedral occupancy of two, having no fluorine, calcium, magnesium, or divalent iron. The equilibrium constant would have a predicted value of -0.00001 , or essentially zero. In such a mica, it would be nearly impossible to exchange magnesium for potassium. Natural muscovites, although not ideal, do appear to be very difficult to alter. The single muscovite sample used in this study has a low equilibrium constant, 0.0002 , which is in agreement with the above argument.

It was indicated earlier that the octahedral divalent iron content of a trioctahedral mica shows a negative correlation with the equilibrium constant. The regression equation seems to indicate just the opposite. The explanation for this apparent discrepancy is also to be found in the interrelated nature of some of the composition variables. Because the ratio of divalent to trivalent iron is reasonably constant in unaltered micas, as divalent iron increases, the trivalent iron content does also (Foster, 1960). An increase in trivalent cation content is coupled with an increase in the number of vacancies in the octahedral layer, thus increasing the dioctahedral nature of the mica. Therefore, an increase in ferrous iron is coupled with a decrease in octahedral occupancy and hence a decrease in the equilibrium constant.

The above equation is not the final answer to the problem of the influence of mica composition on magnesium-potassium exchange in micas. The predicted values of the equilibrium constant at very high and very low values of the fluorine content are not very satisfactory, because the multiple linear regression treats the fluorine data as a straight line when it is more nearly hyperbolic. As more data are accumulated, it is hoped this equation can be refined to more perfectly explain the variations in equilibrium constant as a function of mica composition.

Phase stability diagram

A phase stability diagram can be constructed using the equilibrium constant data collected in this investigation (Fig. 7). This diagram shows the fields of stability of mica and vermiculite as a function of the magnesium and potassium concentrations of solutions in contact with the minerals. With a range in equilibrium constants there obviously will be a family of curves separating the stability fields of the two minerals. Only three of the possible lines are shown; these are the

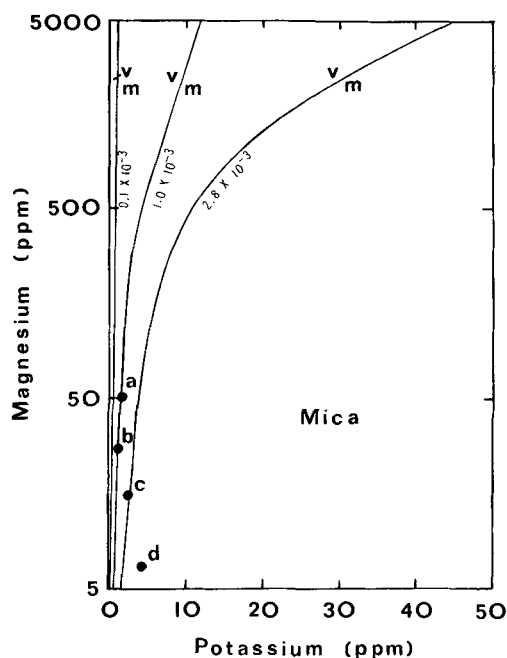


Fig. 7. Phase stability diagram showing mica and vermiculite stability fields corresponding to the highest, average, and lowest values of the equilibrium constants determined in this investigation. Also shown are average ground water compositions for dolomites (a), mafic and ultramafic rocks (b), gneisses and schists (c), and granitic rocks (d).

lowest value, average value, and highest value of the equilibrium constant. These three curves are close to one another at low magnesium concentrations and diverge with increasing concentrations of magnesium in solution. The lowest values of the equilibrium constant were obtained for samples high in fluorine and multivalent octahedral cations; these micas have the largest stability field. The highest values of the equilibrium constant were obtained from micas with little fluorine, large amounts of magnesium and divalent iron, and low octahedral multivalent cations. Such micas have a much smaller field of stability relative to vermiculite.

At this stage of the discussion, it is worthwhile to examine the agent of alteration, i.e., natural waters. The average salt content of streams is about 100 ppm and seldom exceeds 10,000 ppm (Krauskopf, 1967). The composition of the dissolved material varies with climate, vegetation, and rock type. Analyses of river waters show that magnesium ranges from 0.5 to 30 ppm, while potassium ranges from 0.0 to 11.8 ppm; the world average is estimated at 4.1 ppm magnesium and 2.3 ppm potassium (Livingstone, 1963).

Ground water shows a greater range in concentration of elements than rivers and in general tends to be more concentrated. Typical analyses of ground waters from different rock types have been assembled by White, Hem, and Waring (1963); some of their data are summarized in Table 5. Ground waters from granitic rocks have magnesium and potassium contents that are both low and nearly equal. Mafic and ultramafic rocks, as well as dolomites, yield waters that contain relatively large quantities of magnesium but little potassium. Waters from gneisses and schists are in between these extremes with modest amounts of magnesium and intermediate amounts of potassium.

When the average values of potassium and magnesium concentrations for these waters are plotted on the stability diagram (Fig. 7), it can be seen that the values for these elements in waters from dolomitic rocks, gabbros and ultramafic rocks, gneisses and schists, and river water plot very close to the average biotite-vermiculite stability boundary and within the vermiculite field for easily altered micas. Ground water from granitic rocks, on the other hand, plots in the mica field. This indicates that surface and ground waters in rocks in which trioctahedral micas are likely to occur are generally sufficiently rich in magnesium and low in potassium to convert at least some micas to vermiculite. This, of course, ignores the effects of other cations. Since both sodium and calcium can replace magnesium in vermiculite (Foster, 1963), it is reasonable to assume the presence of these elements in ground water would have the effect of shifting the water composition points toward higher magnesium concentrations, i.e. toward the vermiculite stability field. Therefore, a mica with a composition such that it would have an average equilibrium constant would be quite likely to alter to vermiculite in many weathering environments. Only in water from rocks such as granite, where the potassium content is high relative to magnesium, would the alteration be retarded. Alteration of trioctahedral mica to vermiculite would not be as common in granitic rocks as it would in gneisses and schists. It would be quite common in mafic, ultramafic, and dolo-

mitic rocks. This is in good agreement with reported natural vermiculite occurrences (Bassett, 1963).

Rock composition and mica composition, and hence the equilibrium constant, are crudely related (Foster, 1960). Micas from mafic, ultramafic, and dolomitic rocks tend to be high in magnesium. Some, but not all, of these are low in fluorine. In general this would result in relatively high equilibrium constants. On the other hand, trioctahedral micas from granitic rocks are relatively richer in iron and often in multivalent octahedral cations. Thus, they typically have lower equilibrium constants. This means the equilibrium constants and the ground water compositions are complimentary in the alteration of micas; those samples with the lowest equilibrium constants are commonly associated with waters least likely to cause alteration and those micas with high equilibrium constants are associated with waters most likely to cause alteration.

The phase stability diagram may also be used to suggest the possible behavior of biotites and vermiculites in sea water. Sea water contains 1,272 ppm magnesium, 380 ppm potassium, 400 ppm calcium, and 10,556 ppm sodium, (Krauskopf, 1967). If the magnesium and potassium data were considered by themselves, there would be no question but that trioctahedral micas would be far more stable than vermiculite in sea water. However, calcium and sodium influence the system in ways that have not yet been fully evaluated. The data of Raussell-Colom *et al.* (1965) suggest sodium and calcium are only about half as effective as magnesium in displacing potassium from mica. Using this as a guide, the cations that might displace potassium from a mica would have a concentration approximately equivalent to 6,750 ppm magnesium. Ignoring the fact that the activity of these ions will be greatly decreased in a solution as concentrated as sea water, it can be tentatively concluded that the potassium concentration in sea water is too great in relation to the combined amounts of other ions for micas to alter to vermiculite. Hence, mica should be the stable phase in the sea and any vermiculite deposited in marine

Table 5. Magnesium and potassium concentrations in ground water

Rock Type	Magnesium content			Potassium content		
	High (ppm)	Average (ppm)	Low (ppm)	High (ppm)	Average (ppm)	Low (ppm)
Granitic rocks	14	6.3	2.6	14	4.1	0.8
Mafic and Ultramafic rocks	76	27.2	2.6	3.2	1.5	0.0
Gneisses and Schists	57	15.8	0.7	5.8	2.7	0.4
Dolomites	86	51.2	14	3.5	1.8	0.6

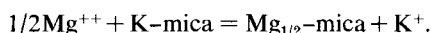
conditions should revert to trioctahedral mica (or perhaps hydrobiotite). The above argument applies only to the trioctahedral mica-vermiculite pair; the possibility of some other mineral (such as chlorite) forming cannot be evaluated with this data.

Some strong words of caution must be added in conclusion. First, the effects of oxidation, which nearly always occurs during the natural weathering process, have not been investigated. The present experiments were conducted over a relatively short period of time and little evidence of oxidation of iron in the micas was observed. If oxidation or any other process should lower the lattice charge, the conclusions drawn herein may not be valid. These conclusions are for materials with high structural charge; extrapolation to materials with lower structural charge must be considered only tentative.

Finally, many trioctahedral micas tend to lose octahedral cations during weathering (Farmer *et al.*, 1971; Newman and Brown, 1966). It is not known whether this happened during these experiments or what effect such a phenomenon would have on the equilibrium constants. Additionally, since most sedimentary phyllosilicates seem to be dioctahedral rather than trioctahedral, loss of octahedral cations might occur in the sea and, if so, might negate the predicted reversion of vermiculite back to trioctahedral mica.

SUMMARY AND CONCLUSIONS

Vermiculite and hydrobiotite can both form as chemical weathering products of micas. In dilute aqueous solutions such as might be expected in the weathering environment, phlogopites and magnesium-rich biotite alter to vermiculite whereas iron-rich micas tend to form hydrobiotite. The alteration can be approximated by the reaction:



Equilibrium constants determined for this reaction vary from 0.0001 to 0.0028. The value of the equilibrium constant depends on mica composition, with micas containing more than one per cent fluorine or high concentrations of multivalent octahedral cations having very low values and magnesium and calcium-rich micas having high values for the equilibrium constant. The equilibrium constant data, when compared with ground water analyses, indicate that vermiculite and hydrobiotite ought to be more stable than trioctahedral mica in most weathering environments. An exception to this is found in rocks where potassium is abundant, such as granite. In such instances, the potassium content in the ground water is likely to be suffi-

ciently high to prevent the alteration. Any vermiculite or hydrobiotite derived from mica on the land surface should revert to mica if transported to a marine environment.

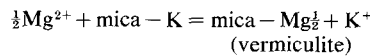
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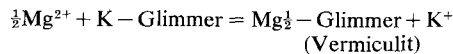
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Résumé—Trente cinq micas trioctaédriques et un mica dioctaédrique ont été altérés artificiellement par des solutions de sulfate de magnésium dont la concentration molale variait de 0,001 à 1,00. On a montré que l'altération pouvait se représenter par une réaction d'échange normale après élimination des effets de surface. Les constantes d'équilibre de la réaction



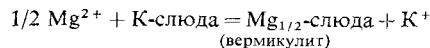
s'étagent de 0,0001 à 0,0028 avec une valeur moyenne de 0,0010. La diffraction des rayons X révèle que les micas riches en fer tendent à développer une structure interstratifiée 1 : 1 biotite-vermiculite dans les solutions de sulfate de magnésium peu concentrées tandis que les biotites riches en magnésium et les phlogopites s'altèrent en vermiculite. La composition du mica a aussi une influence sur le degré d'altération du mica en vermiculite. Les teneurs élevées en fluor et en cations octaédriques plurivalents tendent à retarder la réaction tandis que des teneurs élevées en magnésium et peut être en calcium tendent à la favoriser. Les valeurs des constantes d'équilibre indiquent que la vermiculite et l'hydrobiotite sont plus stables que les micas trioctaédriques dans la plupart des milieux d'altération naturelle.

Kurzreferat—Es wurde festgestellt, dass die künstliche Veränderung von fünfunddreißig trioktaedrischen und einem dioktaedrischen Glimmer durch Lösungen, die in ihrem Gehalt von 0,001 bis 1,00 molar an Magnesiumsulfat variieren, sich einer normalen Austauschreaktion nähert, wenn man von den Oberflächeneffekten absieht. Die Gleichgewichtskonstanten für die Reaktion:



umfassen einen Bereich von 0,0001 bis 0,0028 mit einem Durchschnittswert von 0,0010. Untersuchungen mit Röntgenbeugung zeigen, dass eisenreiche Glimmer die Neigung haben ein 1 : 1 Mischschicht-Biotit-Vermiculit Gefüge in schwachen Magnesiumsulfatlösungen zu entwickeln während magnesiumreicher Biotit und Phlogopit in Vermiculit verändert werden. Die Glimmerzusammensetzung beeinflusst auch den Grad der Veränderung von Glimmer in Vermiculit. Hohe Gehalte an Fluor und oktaedrischen vielwertigen Kationen neigen dazu die Reaktion zu verlangsamen, wohingegen hohe Magnesiumgehalte und vielleicht hohe Calciumgehalte die Veränderung eher begünstigen. Die Gleichgewichtskonstanten deuten darauf hin, dass Vermiculit und Hydrobiotit in den meisten Verwitterungsumgebungen stabiler sind als trioktaedrische Glimmer.

Резюме — Нашли, что искусственное превращение тридцати пяти образцов триоктаэдральных и одного образца диоктаэдральной слюды растворами сернокислого магния различной крепости от 0,001 до 1,00 грамм-молекул приближенно выражает нормальную реакцию обмена после удаления поверхностных эффектов. Константы равновесия реакции следующие:



порядка от 0,0001 до 0,0028 и в среднем 0,0010. Рентгенографическими исследованиями обнаружили, что слюды богатые железом имеют тенденцию развиваться в слабых растворах сернокислого магния смешанные пласты 1 : 1 структуры — биотита-вермикулита, в то время как биотит и флогопит богатые магнием превращаются в вермикулит. Высокое содержание фтора и октаэдрического многовалентного катиона замедляют реакцию, а высокое содержание магния и, может быть, кальция благоприятствуют превращению. Данные, константы равновесия указывают, что вермикулит и гидробиотит оказываются при выветривании более устойчивыми, чем триоктаэдральные слюды.