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ARTIFICIAL ALTERATION OF BIOTITE INTO A 14 Å LAYER SILICATE WITH HYDROXY–ALUMINIUM INTERLAYERS

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Abstract—Biotite was altered by boiling in 0·2 M $AlCl_3$ solution, and the products were examined by X-ray powder and single-crystal diffraction, chemical analysis and thermogravimetry. The altered material is a 14 Å clay mineral with hydroxy–Al interlayers. It has a stacking sequence characteristic of vermiculite and its silicate layers are similar in chemical composition to trioctahedral vermiculite. The results of extracting the interlayer material with sodium citrate solution, X-ray examinations after heating and thermogravimetry show that the interlayer material is composed of Al associated with OH and H_2O. The chemistry and kinetics of the alteration reaction and the orientational between the altered and original biotites are also discussed.

INTRODUCTION

The alteration of biotite has been the subject of many studies on chemical weathering, because it is a common rock-forming mineral and acts as an important source of soluble K in soils (Arnold, 1960). It is now established that biotite usually weathers into vermiculite either directly (Walker, 1949, 1950; Wilson, 1966) or possibly through an intermediate stage of hydrobiotite (Coleman, le Roux and Cady, 1963; Kato, 1965 a; Wilson, 1970).

The weathering of biotite into vermiculite can be reproduced in the laboratory by extracting the interlayer K with salt solution (Barshad, 1948; Mortland, 1958; Scott and Smith, 1966; Hoda and Hood, 1972), and this reaction can be accelerated by using sodium tetraphenylboron solution, in which the released K is precipitated as potassium tetraphenylboron (DeMumbrum, 1959, 1963; Scott, Hunziker and Hanway, 1960; Scott and Reed, 1962). The kinetics of the alteration reaction were studied by Mortland (1958), Reed and Scott (1962), Rausell-Colom *et al.* (1965) and Wells and Norrish (1968), and the chemistry of the alteration was studied by Newman and Brown (1966) and Newman (1967). These investigations on the artificial alteration of biotite constitute an important contribution to the understanding of weathering processes.

Rich (1968) has reviewed the occurrence of 14 Å clay minerals with hydroxy–Al interlayers in soils and their artificial preparation from montmorillonite or vermiculite. Kato (1965b) and Wilson (1966) reported the occurrence of a similar mineral formed as a weathering product of biotite, but only Robert (1971) has reported laboratory experiments in which minerals with hydroxy–Al interlayers may have been formed from micas.

Biotite was altered by boiling in aluminum soln and a 14 Å mineral with hydroxy–Al interlayers was produced. This paper gives the result of the experiments with reference to the kinetics and chemistry of the alteration reaction, and to the orientational relationship of the product to the original biotite.

EXPERIMENTAL

Material. Magnesium biotite from Madagascar was used throughout this study. It is of 1 M polymorph with $a = 5{\cdot}29$ Å, $b = 9{\cdot}22$ Å, $c = 10{\cdot}16$ Å, $\beta = 99{\cdot}5°$ and has the chemical composition shown in Table 3. Two kinds of sample were prepared from a single large flake of this biotite. A powder sample of 100–300 mesh fraction was prepared by grinding the flake with a Culatti grinder and sieving. Also, small square pieces with average linear dimensions 0·8 × 0·8 mm × 25–50 μm in thickness were prepared by cutting the flake with an S.S. White Industrial Airbrasive Unit using Al oxide as abrasive.

Solutions. Aluminum solutions were prepared from A.R. grade Al wire and dilute HCl (three parts of A.R. HCl were diluted with seven parts of distilled water) by heating under reflux (Treadwell and Lien, 1931); after filtering, the solutions were diluted to a

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total Al concentration of 0·2 M. Two such solutions were prepared, with pH 3·6 and 3·8; the pH depended on the amount of Al dissolved during the preparation. We calculated from the data of Aveston (1965) that at 25°C the ratio of OH/Al was 1 and the concentration of Al^{3+} was 0·1 M in the solution of pH 3·6, whereas at pH 3·8, OH/Al was 2, the concentration of Al^{3+} was 0·03 M and 75 per cent of the aluminium was present as polynuclear hydroxycomplex; the proportions at 100°C may differ from these owing to displacement of the equilibria.

Alteration experiments. The biotite samples were altered by boiling in the aluminium solution pH 3·6 and 3·8.

(1) In the first series, powder samples were boiled in the solutions of pH 3·6 and 3·8 for a total of 847 and 844 hr respectively, the solutions being changed nine times during this period. The final products collected by centrifuging were washed once with dilute HCl of the same pH as the extracting solution, once with water, then with 90 per cent ethanol until chloride-free, and air-dried. The amounts of sample taken (1 g for 1500 ml of solution of pH 3·6 and 0·67 g for 1000 ml of solution of pH 3·8) allowed detailed mineralogical examinations of the products.

(2) In the second series of experiments we examined the effect of different extraction periods. Fifty-mg samples of the powder were boiled in 1500 ml of the solution of pH 3·6 for 1, 5 or 20 days without changing the solution.

In these two series of experiments, gibbsite and a small amount of boehmite formed a coating on the wall of the flask, and a part of the coating material mixed with the sample powder. In addition, gibbsite was precipitated in the experiments with solutions initially at pH 3·8. These impurities were largely eliminated by sieving and hand-picking after washing, and after drying, the altered biotite was concentrated by passing the samples through a Cook magnetic mineral separator.

(3) In the third series of experiments single crystals were altered for kinetic and single-crystal X-ray studies. A single-crystal piece of biotite was boiled in the aluminum solution of pH 3·6 or 3·8. After periods ranging from 6 to 715 hr, the crystal was taken out and examined under the microscope or by X-ray diffraction, and then boiled again as before. This was repeated several times.

Removal of hydroxy–Al interlayers. The hydroxy–Al interlayers of the alteration products in the first series of experiments were extracted with 1 N sodium citrate soln (pH 7·3) for 6 hr near its boiling point (Tamura, 1958). The solution was renewed every 2 hr. The products, after washing with water and 90 per cent ethanol, were used for CEC determination and X-ray examination.

Chemical analysis. The biotite and its alteration products in the first series of experiments were analysed by the semi-micro analysis procedure given by Pruden and King (1969). H_2O^+ was obtained from the loss on ignition after correcting for the increase in weight caused by the oxidation of Fe^{2+}. H_2O^- and loss on ignition were determined by thermogravimetry, in which samples were kept at 110 and 1000°C until the weights became constant.

Cation exchange capacities of the alteration products before and after the removal of the hydroxy–Al interlayers were determined on Mg-saturated samples. The Mg was removed by washing four times with 0·1 N $CaCl_2$ solution, and the CEC was calculated from the total amount of Mg in the leachate.

The K, Mg and Fe contents of the $AlCl_3$ extracts in the first series of alteration experiments, the Al contents of the sodium citrate extracts and total Mg in the 0·1 N $CaCl_2$ extracts were determined by atomic absorption.

X-ray diffraction examination. Powder samples of the biotite and its alteration products were examined by X-ray diffraction before and after removing the hydroxy–Al interlayers. X-ray diffraction diagrams of oriented aggregates on glass slides were recorded with an X-ray diffractometer, using Ni filtered Cu radiation and a proportional counter. Powder photographs of unoriented powder samples were taken with a powder camera of 114·83 mm diameter, using Ni filtered Cu radiation. Heated oriented aggregates of the alteration products were also examined. The glass slides on which oriented aggregates of samples were prepared were placed on a Variac-controlled heating stage mounted on the diffractometer (Brown *et al.*, 1972), and X-ray diffraction diagrams of these samples were recorded during heating at temperatures up to 250°C. The temperature of the slide surface was calibrated against the setting of the Variac by using the melting points of stearic acid, cholesterol, $AgNO_3$ and phenolphthalein. After setting the Variac at the required voltage the specimens were left on the stage for 45 min to reach equilibrium before recording the diffraction pattern. For temperatures above 250°C samples previously heated to selected temperatures up to 550°C for 1 hr were cooled in a desiccator and the X-ray patterns were recorded with the samples on the heating stage at 250°C. For temperatures above 550°C, oriented aggregates for X-ray diffraction were prepared on silica glass slides, and heated at the selected temperatures for 1 hr.

Normal-beam and equi-inclination Weissenberg photographs were taken for single-crystal pieces of

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biotite and their alteration products, using Ni filtered Cu radiation.

Thermogravimetry. Thermogravimetry of the alteration products of the first series of experiments was made using a silica spiral thermobalance (Greene-Kelly and Weir, 1956). The samples were kept at 110°C until the weights became constant and then heated at the rate of 2·2°C min^{-1}. Corrections based on the results of blank experiments were made for buoyancy and convection.

RESULTS AND DISCUSSION

Mineralogy of the alteration products

The results of X-ray diffraction examination of the products of the first series of alteration experiments, before and after the extraction with sodium citrate solution, are shown in Figs. 1 and 2, and Tables 1 and 2. The alteration product prepared in the pH 3·6 solution gives 14·1 Å and rational higher order basal reflections that change little after Mg-saturation, followed by ethylene glycol treatment. This basal spacing gradually collapses on heating and reaches 10·1 Å at 750°C, but the materials heated below 550°C are readily rehydrated and re-expanded to about 13·8 Å on leaving in air. After extracting the interlayer material with sodium citrate, the basal reflection appears at 14·2 Å on Mg-saturation; however, the removal of the interlayer material was not complete, as indicated by the incomplete collapse of basal reflection after K-saturation (Table 1 and Fig. 1). Further interlayer material was removed by a more prolonged extraction; i.e. boiling for 10 hr in a large excess of sodium citrate solution which was renewed every 2 hr. The product of this extraction gives a basal reflection at 14·4 Å on Mg-saturation a distinctly larger spacing than that obtained before the citrate extraction. The 14·4 Å spacing, which changes to 10·2 Å after K-saturation, does not change after ethylene glycol treatment.

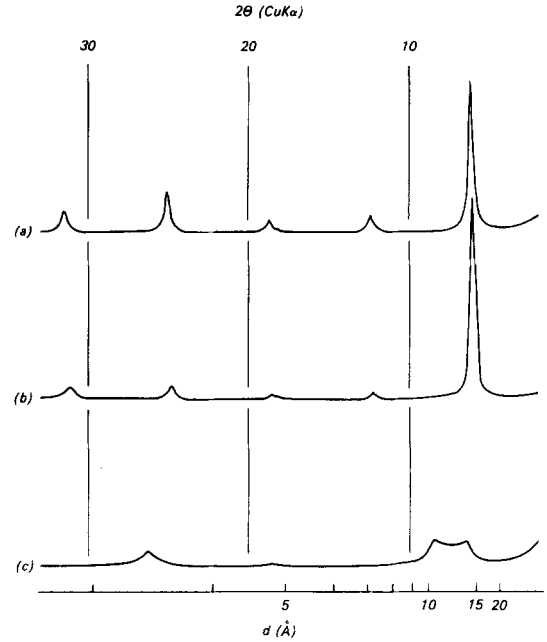


Fig. 1. X-ray powder diagrams for (a) altered biotite prepared in the pH 3·6 solution, (b) citrate-treated Mg-saturated altered biotite and (c) citrate-treated K-saturated altered biotite.

The properties indicate that the alteration product is a 14 Å clay mineral with hydroxy–Al interlayers resembling that referred to as the intergradient chlorite-expansible 2:1 layer silicate of Dixon and Jackson (1962).

The X-ray patterns of the alteration product prepared in the pH 3·8 solution were similar; they differ in that the pH 3·8 material has a slightly smaller basal

Table 1. Basal spacings of the altered biotites

	Altered biotite (pH 3·6) (Å)	Altered biotite (pH 3·8) (Å)
Untreated, room temp.	14·1	14·0
Untreated, 250°C	13·4	13·2
Untreated, 550°C	11·3	10·8
K-saturation	14·0	14·0
Mg-saturation, then E.G.	14·0	13·9
Sodium citrate, then Mg-saturation	14·2	14·1
Sodium citrate, Mg-saturation, then E.G.	14·1	13·9
Sodium citrate, then K-saturation	10·3, 13·3	14·0

E.G.—ethylene glycol.

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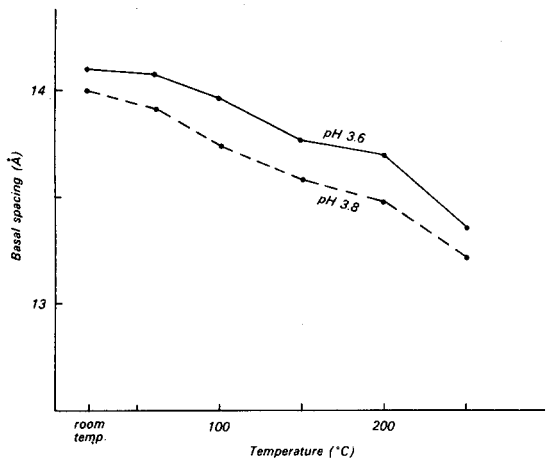


Fig. 2. Collapse of basal spacing of altered biotites on heating.

spacing of 14·0 Å (Table 1 and Fig. 2) and does not collapse after citrate treatment followed by K-saturation. A minor phase also occurs in the pH 3·8 material. This impurity shows a weak diffuse reflection at about 10 Å (Table 2) that is unaltered by K-saturation but disappears when saturated with Mg and treated with ethylene glycol. The spacing of the reflection decreases on heating, reaching 8·5 Å at 200°C, and then disappears.

The alteration products prepared in solutions of pH 3·6 and 3·8 gave powder diffraction patterns characteristic of the Ia chlorite of Brown and Bailey (1962) (Table 2). The 060 reflection appears at 1·537 Å (pH 3·6) and 1·538 Å (pH 3·8), values that are nearly the same as those for the original biotite with d (060) = 1·536 Å. These 060 spacings show that the altered biotites are trioctahedral, a conclusion that is supported by the chemical composition. Powder photographs of the pH 3·6 alteration product were taken after the more prolonged sodium citrate extraction mentioned above and saturation with Mg or K. Citrate treatment increased the 060 spacing of material in the Mg-saturated form from 1·537 to 1·541 Å. The citrate-treated Mg-saturated sample also has a powder pattern characteristic of a 14 Å structure composed of Ia-type layers (Brown and Bailey, 1962); Shirozu and Bailey (1966) showed that natural vermiculites were of this type. Material treated with K after citrate treatment gave a powder pattern resembling that of 1 M or 3T micas.

The structural type of the alteration products prepared in both solutions was determined from Weissen-

Table 2. X-ray powder diffraction data of the altered biotites

Altered biotite (pH 3·6)		Altered biotite (pH 3·8)		
d (Å)	I	d (Å)	I	hkl
14·1	10	14·0	10	002
		9·84	*2B*	
7·10	2	7·08	2	004
		4·83	2	*G*
4·76	1/2			006
4·59	3	4·61	3	02*l*; 11*l*
		4·37	1	*G*
		4·17	1/2	
3·53	4	3·53	3	008
2·831	2	2·831	2	0, 0, 10
2·644	4	2·643	4	200; 13$\bar{2}$
2·583	3	2·586	3	132; 20$\bar{4}$
2·539	3	2·541	3	13$\bar{4}$; 202
		2·456	1/2	*G*
2·380	5	2·381	5	0, 0, 12; 13$\bar{6}$; 204; *G*
2·254	1/2	2·252	1/2	136; 20$\bar{8}$
2·194	1/2	2·187	1/2	13$\bar{8}$; 206
2·066	1	2·058	1	138; 2, 0, $\bar{10}$
2·002	1	2·000	2	1, 3, $\bar{10}$; 208
		1·836	1/2	2, 0, 10
1·740	1/2	1·744	1	15*l*; 24*l*; 31*l*
1·661	1	1·662	1	1, 3, $\bar{14}$; 2, 0, 12
1·537	4	1·538	4	060; 330; 33$\bar{2}$; 33$\bar{4}$
1·505	1/2	1·505	1/2	064; 332

I—visually estimated intensity; *B*—broad line; *G*—gibbsite line.

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berg photographs of the altered single-crystal pieces, although the diffuse reflections did not permit the determination of atomic coordinates. Zero to third layer Weissenberg photographs taken of a crystal rotated about the *b*-axis of the original biotite showed that, although the basal spacing of single crystals altered in the pH 3·6 solution was 14·1 Å, a two-layer cell with $a = 5{\cdot}33$ Å, $b = 9{\cdot}22$ Å, $c = 28{\cdot}5$ Å, $\beta = 97°$ was required to allow the reflections on the first and second layer lines to be indexed. Reflections with $h + k = 2n + 1$ were absent, as were those with $k = 0, 3n$ and $l = 2n + 1$, and reflections with $k \neq 0, 3n$ were more diffuse than those with $k = 0, 3n$. The absences are consistent with space groups *Cc* and *C2/c* with additional non-space group absences, as noted by Shirozu and Bailey (1966) for vermiculite, that are due to disorder. The intensities of the *h0l* reflections confirm the conclusion from the powder patterns that the altered biotite consists of Ia-type chlorite layers. The alteration product therefore consists of Ia-type layers forming a two-layer monoclinic structure with $\beta = 97°$; this is the same as is found for natural vermiculites (Mathieson and Walker, 1954; Smith Aitken, 1965; Shirozu and Bailey, 1966). Mathieson and Walker showed that there are four possible ways of stacking Ia-type layers by means of a *c* glide into a two-layer structure, which they designated *p*, *q*, *r* and *s*. The intensities of the 02*l* reflections of the alteration products agree with those calculated for the ideal *s*-type structure, and with the observed intensities of the Llano-vermiculite determined by Shirozu and Bailey (1966) to be of *s*-type (Shirozu, private communication). The alteration products therefore have the stacking sequence of the *s*-type two-layer vermiculite, or,

Table 3. Chemical compositions of the biotite and its alteration products

	Wt (%)				Atomic ratios		
	Original biotite	Altered biotite (pH 3·6)	Altered biotite (pH 3·8)		Original biotite	Altered biotite (pH 3·6)	Altered biotite (pH 3·8)
SiO_2	37·35	31·50	20·64	Si	5·35	(5·35)	(5·35)
Al_2O_3	18·87	25·35	38·60	Al	2·65	2·65	2·65
TiO_2	1·29	1·27	0·78				
Fe_2O_3	3·26	7·64	5·08		8·00	8·00	8·00
FeO	6·81	0·69	0·37				
CaO	0·45	0·07	0·02	Al	0·53	(0·53)	(0·53)
MgO	18·22	14·44	9·93	Ti	0·14	0·16	0·15
MnO	0·52	0·29	0·18	Fe^{3+}	0·35	0·98	0·99
Na_2O	0·19	0·01	0·01	Fe^{2+}	0·82	0·10	0·08
K_2O	9·54	0·15	0·12	Mn	0·06	0·04	0·04
H_2O-	0·69	4·56	5·65	Mg	3·89	3·65	3·83
H_2O+	1·58	14·50	19·02				
					5·79	5·46	5·62
F	1·85	—	—				
				Ca	0·07	0·01	0·01
Total	100·62	100·47	100·40	Na	0·05	0·00	0·01
				K	1·74	0·03	0·04
Less O = F	0·78						
					1·86	0·04	0·06
	99·84						
				F	0·84	—	—
				Total Al	3·18	4·92	6·40
				Interlayer Al	—	1·74	3·22
				Charges, assuming an anion charge of 44			
				Tetrahedral	−2·65	−2·65	−2·65
				Octahedral	+0·72	+0·75	+1·06
				Interlayer	+1·93	+0·05	+0·07
				Net charge	0·00	−1·85	−1·52
				(Net charge)/ (Increase Al)	—	1·063	0·472

Analyst: G. Pruden. Atomic ratios for the alteration products corrected for free $Al(OH)_3$ (see text).

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Table 4. Result of sodium citrate extractions from the altered biotites

	Altered biotite (pH3·6)	Altered biotite (pH 3·8)
Total amount of Al extracted	4·61%	9·33%
CEC before sodium citrate extraction	1 m-equiv 100 g^{-1}	2 m-equiv 100 g^{-1}
CEC after sodium citrate extraction	131 m-equiv 100 g^{-1}	17 m-equiv 100 g^{-1}

All of these values are referred to the weights of air-dried altered biotites.

in the notation of Brown and Bailey (1962), the altered material consists of alternate Ia-4 and Ia-6 layers. There is a shift of $-a/3$ parallel to the symmetry plane within each of the talc-like layers, and shifts alternately $+b/3$ and $-b/3$ occur between the talc-like layers.

Chemical composition

Chemical compositions of the original and altered biotites are shown in Table 3. The atomic ratios for the original biotite were calculated on the basis of the anionic composition O_{20} (OH, F)$_4$, while those of the altered biotites, after correction for free $Al(OH)_3$, were calculated by assuming that the proportion of Si was unchanged by the alteration (Newman and Brown, 1966). The amount of free $Al(OH)_3$ in the product formed in the pH 3·6 solution was estimated to be 1·16 per cent $Al(OH)_3$ from thermogravimetry. For the product formed in the pH 3·8 solution, citrate extraction caused very little increase in exchange capacity (Table 4), indicating that the treatment selectively removed free $Al(OH)_3$, and the composition of this product was corrected by subtracting the citrate-soluble Al. Interlayer K was almost entirely removed by alteration with both aluminum soln whereas the amount of total Al increased (Table 3); the total Fe content changed very little, but Fe^{2+} was oxidized to Fe^{3+}, and there was a small decrease in the Mg content of the product formed in the pH 3·6 solution. Assuming that the additional Al is external to the aluminosilicate layers, these compositions lie within the range found in natural trioctahedral vermiculites (Foster, 1963; Norrish, 1972) and are close to that of the vermiculite-like product formed from a biotite of similar composition by removing K with sodium tetraphenylboron (cf. mica M3 and product AM3; Newman and Brown, 1966). The chemical analyses thus confirm the X-ray evidence that the products are vermiculite containing interlayer aluminum.

The apparent layer charge of the alteration product in the pH 3·6 solution is 1·90 if the anion framework of the 2:1 layers is equivalent to 44 negative charges, but as shown by Newman and Brown (1966), calculating the atomic ratios of altered micas by reference to the Si ratio for 44 negative charges in the unaltered mica often leads to formulae in which the net anion charge is less than 44. For a mica of composition similar to that used in the present work (M3 and its alteration product AM3) Newman and Brown (1966) found that the effective anion charge of the product was 43·67, a decrease of 0·33; a similar decrease for the mica used here would give a net layer charge of 1·90 − 0·33 = 1·57 in the alteration product. A net layer charge of 1·90 is equivalent to an exchange capacity of about 180 m-equiv 100 g^{-1}, and of 1·57 to 150 m-equiv. 100 g^{-1}. Both values are larger than the exchange capacity of the citrate-extracted alteration product formed in the pH 3·6 solution, which was 131 m-equiv 100 g^{-1} (Table 4), suggesting that some interlayer Al remained after the citrate extraction. This conclusion is supported by the X-ray diffraction evidence (Fig. 1) that the citrate-extracted altered biotite still contained 14 Å layers after K-saturation.

A considerable proportion of the original biotite was dissolved in the aluminum solutions used to extract K. Determination of Mg and Fe in the pH 3·8 extracts showed that 31 per cent of the Mg and 34 per cent of the total Fe in the original biotite was dissolved. As the atomic ratios show, the composition of the aluminosilicate layers remained largely unchanged during the alteration except for the oxidation of Fe. The amounts of Mg and Fe are therefore believed to represent bulk dissolution of the biotite in the acid soln used for alteration.

The nature of hydroxy–Al interlayers

As mentioned above, the basal spacing of the altered biotites collapses gradually on heating, reaching about 10 Å at 750°C. This suggests that interlayer water, H_2O bound to the interlayer Al, OH anion coordinated to the Al, etc. may exist together between the layers. In the second series of alteration experiments, three extractions were made for the periods of 1 day, 5 days and 20 days. The collapse of the basal spacing of the altered biotites on heating is shown in Fig. 3;

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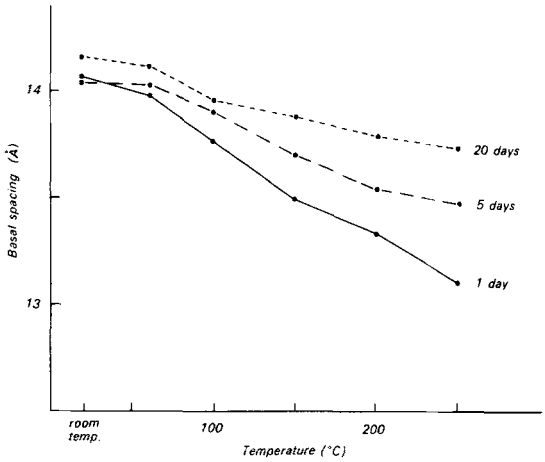


Fig. 3. Effect of length of treatment on the collapse of basal spacing of biotites altered in the pH 3·6 solution.

these indicate that the altered biotite prepared by the shorter extraction collapses more easily on heating. This suggests that the structural integrity of the interlayer material increases with prolonged boiling in the extracting solution, probably because the size of the hydroxy polymer increases with time.

The thermogravimetric curves of the altered biotites (Fig. 4) also show a gradual loss of water from the interlayer region. The rate of dehydration is largest between 400 and 450°C. The altered biotite prepared in the pH 3·8 solution shows a larger weight loss than that prepared in the pH 3·6 solution especially in the temperature range between 300 and 600°C. This may be due to the presence of a larger amount of hydroxyl in the interlayer region of altered biotite prepared in the pH 3·8 solution. The gibbsite impurity is also indicated on these curves by sharp inflections in the region 280–300°C.

The interlayer material of the altered biotites was only partly extracted with sodium citrate solution. The amounts of Al extracted and the cation exchange capacity values of the altered biotites before and after the extraction are shown in Table 4. Much Al was extracted from the altered biotite prepared in the pH 3·8 solution, although the gain of CEC is very small. This result may be explained by the presence of gibbsite impurity to which the large Al content of the sodium citrate extract is attributed. The above mentioned resistance against the collapse of basal spacing caused by K-saturation suggests that much material is left in the interlayer space. In contrast the large increase in CEC and the collapse after K-saturation of the altered biotite prepared in the pH 3·6 solution shows that the major part of the interlayer material was extracted by citrate treatment. The amount of Al present as gibbsite impurity was estimated as 0·40 per cent, by thermogravimetry. By subtracting this from the Al content of citrate extract, the amount of Al extracted from the interlayer region is estimated as 4·21 per cent or 158 mg atom 100 g^{-1}. This value is a little smaller than the value of interlayer Al calculated from chemical composition of the altered biotite, 4·60 per cent. This discrepancy may be explained by the incomplete extraction of interlayer material, indicated by the incomplete collapse on K-saturation (Fig. 1).

The large amount of interlayer Al, 1·7 atoms for the pH 3·6 material and 3·2 atoms for the pH 3·8 material (Table 3) should be compared with the corresponding

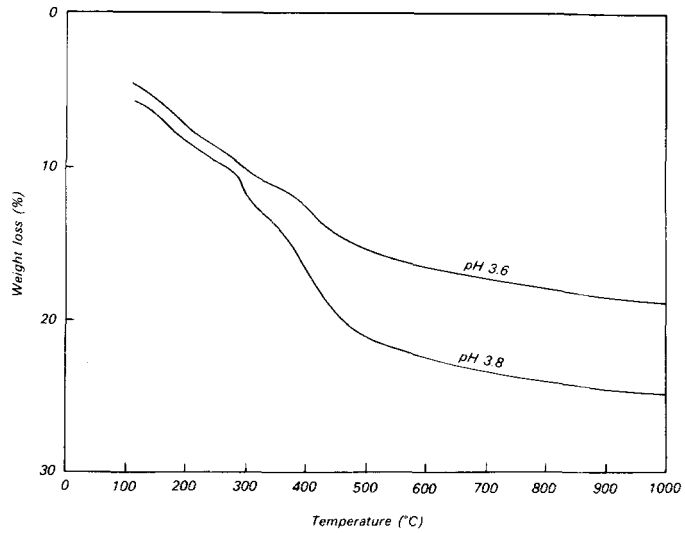


Fig. 4. Thermogravimetric curves of altered biotites.

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values for interlayer cations in vermiculites, 0·6–0·9 divalent cations, and for chlorites with dioctahedral hydroxide interlayers, where the ideal number of interlayer cations is 4. Information on the nature of the interlayer Al species in the alteration products can be obtained from the structural formulae in Table 3 in which the allocation of cations to structural sites is based on the assumption that the Al in the aluminosilicate layers is the same as in the original biotite. The number of interlayer Al atoms in Table 3 is the difference between total Al atoms found from the atomic ratios calculated from chemical analyses, and those in the aluminosilicate layers given in Table 3. Assuming that the anionic charge totals 44, the net charge balanced by interlayer Al atom can be found, and hence the charge per Al atom. For the material altered in the pH 3·6 solution the charge is 1·06 per Al atom, giving an average formula $(Al(OH)_{1.94})^{+1.06}$ for the interlayer species; for the material altered in the pH 3·8 solution the charge per Al atom is 0·47, leading to a formula $(Al(OH)_{2.53})^{+0.47}$. If the total anionic charge is assumed to be 43·67, these formulae become $(Al(OH)_{2.13})^{+0.87}$ and $(Al(OH)_{2.63})^{+0.37}$ respectively.

Independent evidence from the increase in the cation exchange capacity of the pH 3·6 material after extraction of interlayer Al, broadly supports these deductions. The extraction of 158 mg atom Al 100 g^{-1} increased the cation exchange capacity by 130 m-equiv 100 g^{-1} (Table 4), so that the charge per Al atom is 130/158 = 0·822 and the composition of the material that was removed may be written as $[Al(OH)_{2.178}]^{+0.822}$ or approx. $[Al_6(OH)_{13}]^{5+}$.

Alteration kinetics

In the third series of alteration experiments a single-crystal flake was examined under the microscope as the alteration proceeded in the pH 3·6 solution. The width of the alteration rim observed with the polarizing microscope increased with repeated extraction. This is similar to the observations of Rausell-Colom *et al.* (1965) and Scott and Smith (1967), and indicates that the reaction proceeds along the basal plane. Single-crystal X-ray examination confirmed that the rim was composed of the altered material, although the core part of the flake also produces weak reflections of the altered material, which shows that the reaction also proceeds perpendicular to the basal plane to a limited extent.

When the square of the width of the reaction rim was plotted against time, the graph showed a convexity towards the time axis for measurements up to 600 hr, similar to that found by Wells and Norrish (1968) and Newman (1970b), but thereafter the boundary movement slowed. This suggests that the initial rate of alteration was controlled by the same factors that govern the rate of reaction in exchange experiments with other cations, but that after 600 hr, exchange was hindered, perhaps by obstruction from hydrolyzed interlayer Al.

For edge alteration of micas, Wells and Norrish (1968) found that the rate of boundary movement could be expressed by the empirical equation

$$\delta = kt^y \qquad (1)$$

where δ is the observed boundary width, t the time, y a fractional index and k a constant. In the reaction studied here, the parameters $y = 0{\cdot}637$ and $k = 1{\cdot}20 \times 10^{-3}$ in equation (1) expressed the reaction rate up to 600 hr quite accurately (Fig. 5). For comparison, the rate of boundary movement at 100°C in a mica of similar composition (B3a; Newman, 1970b), altered in 0·25 M NaCl of pH 3·4, gave the parameters $y = 0{\cdot}699$ and $k = 18{\cdot}15$; in this latter experiment, a boundary 0·08 mm wide had developed after only 8 hr, whereas 800 hr alteration by aluminum soln was required for the same boundary width, so that aluminum, presumably as Al^{3+}, reacted very much more slowly than Na.

In the second series of alteration experiments, the products of extraction for 1 and 5 days consist of both altered and unaltered biotites. A weak 11·8 Å reflection is observed in the X-ray powder diagrams of these products. This reflection is not accompanied by rational

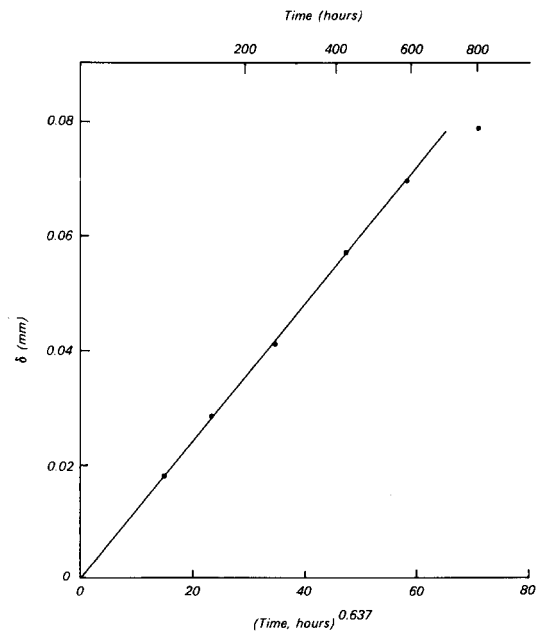


Fig. 5. Plot of boundary width δ against t^y for $y = 0{\cdot}637$ in the single-crystal alteration experiments in the pH 3·6 solution.

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higher order reflections, but a reflection appears at 3·45 Å, i.e. between fourth order of 14 Å and third order of 10 Å reflections. The 11·8 Å reflection, therefore, may be due to a random interstratification of altered and unaltered biotites. The occurrence of this 11·8 Å phase is of minor importance to the kinetics of the alteration reaction, because it may simply imply that the front of the 14 Å phase is diffuse and may be independent of the rate of movement of the front.

The kinetics of the alteration reaction were also studied for the rate of K release from powder samples. In the first series of alteration experiments, the interlayer K has been removed almost completely by 10 extractions with total duration of 847 hr (pH 3·6) and 844 hr (pH 3·8).

The relation between boundary movement δ_k and the fraction of total K remaining in the mica, $\bar{X}_K$, assuming the mica particles are discs of radius R (Newman, 1970 a) is

$$\delta_K = R(1 - \sqrt{\bar{X}_K}). \quad (2)$$

As noted above, substantial amounts of Mg and Fe were dissolved during the alteration experiments, indicating that bulk dissolution of biotite was occurring, so that the observed boundary width, δ, was smaller than δ_K by δ_d, the width of the rim of dissolved material. According to Ross (1967), the kinetics of the acid dissolution of chlorites can be described quite accurately by a diffusion-controlled reaction, so that

$$\delta_d = k_d\, t^{1/2} \quad (3)$$

where

$$\delta_d = \delta_K - \delta. \quad (4)$$

Eliminating δ_K, δ and δ_d from equations (1–4), we get

$$R(1 - \sqrt{\bar{X}_K}) = k\, t^y + k_d\, t^{1/2}$$

which can be rearranged to the form

$$(1 - \sqrt{\bar{X}_K})/t^y = (k + k_d\, t^{(1/2 - y)})/R. \quad (5)$$

If bulk dissolution is slow relative to the K-replacement reaction, $(1 - \sqrt{\bar{X}_K}/t^y$ should be independent of time and a plot of $(1 - \sqrt{\bar{X}_K})$ against t^y will give a straight line. Figure 6 shows that this is so for reaction times up to 300 hr. The gradient of the approximately linear part of the curve, 0·018, divided by the value of k found from measurements on a single flake, gave a value of about 130 μm for the diameter of the mica particles, which agrees reasonably closely with the median value of the diameters of mica particles in the size range 50–53 μm (100–300 mesh). It seems therefore that for relatively short reaction times there is a reasonable agreement between the two types of kinetic measurements.

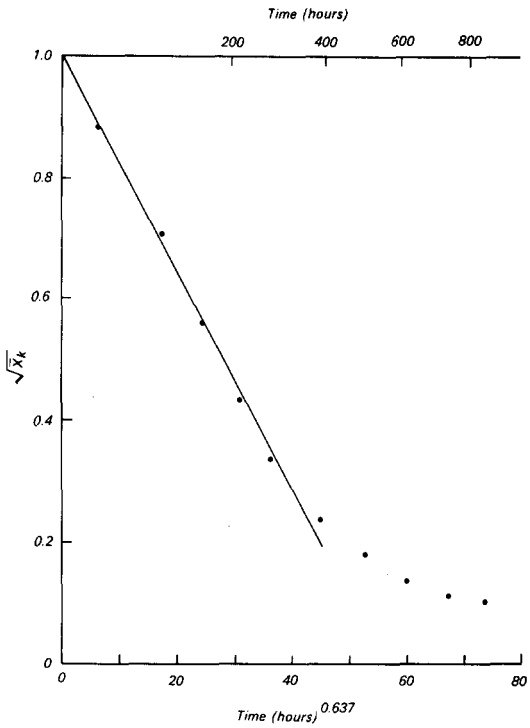


Fig. 6. Graph of (the fraction of total K remaining in mica)$^{1/2}$ against $t^{0.637}$ in the alteration experiments in the pH 3·6 solution.

Orientational relationship of the alteration product to the original biotite

Weissenberg photographs were taken for single-crystal pieces in which altered and unaltered biotites coexist. These photographs show that the $+a$- and $+b$-axes of the altered biotite are parallel to the corresponding axes of the original biotite. The $+c$-axis of the altered material lies in the obtuse angle side of the β-angle of the biotite and makes an angle of 2·5° with the $+c$-axis of the biotite. As described above, the original biotite is of 1 M polymorph and the altered material is of *s*-type two-layer monoclinic vermiculite structure. The alteration of the former into the latter with the orientational relationship just described is the most probable way of transformation, as was discussed by Shirozu and Bailey (1966), and this orientational relationship was also found in natural weathering product from phlogopite by Smith Aitken (1965).

Gibbsite was precipitated in the solution in the alteration experiments in the pH 3·8 solution. In the single-crystal alteration experiments, a part of this gibbsite precipitate coated the surface of the biotite flake. Oscillation and Weissenberg photographs of this flake showed that the basal plane of the gibbsite tends to be

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parallel to the basal plane of the original biotite. Similar, but more pronounced preferred orientation was found in natural weathered biotite–gibbsite intergrowths by Wilson (1966) and Tsuzuki, Nagasawa and Isobe (1968).

CONCLUSIONS

The products of the present alteration experiments gave the basal reflection at 14·0–14·1 Å, which was changed neither by K-saturation nor by ethylene glycol treatment, but which gradually collapsed on heating. After extracting the interlayer material with sodium citrate, K-saturation caused it to collapse to 10·2 Å. These results show that this mineral is similar to the natural 14 Å clay mineral with hydroxy–Al interlayers, reported by Kato (1965 b) and Wilson (1966) to occur in soils as a weathering product from biotite. The marked dissolution of the biotite during alteration will also occur in natural acid environments. The present experiments, therefore, may be considered as a simulation of natural weathering of biotite.

Examination of the alteration products revealed the following properties. The structure type is two-layer monoclinic with β angle of 97°, the stacking sequence being an alternation of Ia-4 and Ia-6 chlorites. The silicate layers are trioctahedral, Mg and Fe^{3+} being dominant octahedral cations. These properties are in accord with those of natural macroscopic vermiculite. The interlayer material is composed of Al associated with OH and H_2O, and it is therefore intermediate between the exchangeable cation plus water of vermiculite and the gibbsite- or brucite-like layers of chlorite. The interlayer material of the product prepared in the pH 3·6 solution has an approximate composition of $[Al_6(OH)_{13}.nH_2O]^{5+}$, and that prepared in the solution of higher pH contains more OH.

The alteration reaction consists essentially of the replacement of the interlayer K by Al, OH and H_2O, and the oxidation of the octahedral Fe; the reaction front proceeds inward along the basal plane obeying the empirical equation by Wells and Norrish (1968), at least in the early stage. The alteration is topotactic, the *a*- and *b*-axes of the products being parallel to the corresponding axes of the original biotite. Atomic displacements involved are small; layers remain intact, their separation to accommodate the hydroxy–aluminium being accompanied by small linear displacements.

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REFERENCES

Arnold, P. W. (1960) Nature and mode of weathering of soil-potassium reserves: *J. Sci. Food Agric.* **11,** 285–292.

Aveston, J. (1965) Hydrolysis of the aluminium ion: ultracentrifugation and acidity measurement: *J. Chem. Soc.* 4438–4443.

Barshad, I. (1948) Vermiculite and its relation to biotite as revealed by base exchange reactions, X-ray analyses, differential thermal curves, and water content: *Am. Mineralogist* **33,** 655–678.

Brown, B. E. and Bailey, S. W. (1962) Chlorite polytypism—I. Regular and semi-random one-layer structures: *Am. Mineralogist* **47,** 819–850.

Brown, G., Edwards, B., Ormerod, E. C. and Weir, A. H. (1972) A simple diffractometer heating stage: *Clay Minerals* **9,** 407–414.

Coleman, N. T., leRoux, F. H. and Cady, J. G. (1963) Biotite–hydrobiotite–vermiculite in soils: *Nature* **198,** 409–410.

DeMumbrum, L. E. (1959) Exchangeable potassium levels in vermiculite and K-depleted micas, and implications relative to potassium levels in soils: *Soil Sci. Soc. Am. Proc.* **23,** 192–194.

DeMumbrum, L. E. (1963) Conversion of mica to vermiculite by potassium removal: *Soil Sci.* **96,** 275–276.

Dixon, J. B. and Jackson, M. L. (1962) Properties of intergradient chlorite-expansible layer silicates of soils: *Soil Sci. Soc. Am. Proc.* **26,** 358–362.

Foster, M. D. (1963) Interpretation of the composition of vermiculites and hydrobiotites: *Clays and Clay Minerals* **10,** 70–89.

Greene-Kelly, R., and Weir, A. H. (1956) A silica spiral thermo-balance for studies on the dehydration of clay minerals: *Clay Minerals Bull.* **3,** 68–78.

Hoda, S. N. and Hood, W. C. (1972) Laboratory alteration of trioctahedral micas: *Clays and Clay Minerals* **20,** 343–358.

Kato, Y. (1965a) Mineralogical study of weathering products of granodiorite at Shinshiro City (III): Weathering of primary minerals (2) Mineralogical characteristics of weathered mineral grains: *Soil Sci. Plant Nutr. (Tokyo)* **11,** 30–40.

Kato, Y. (1965 b) *Ibid.* (V): Trioctahedral aluminum–vermiculite as a weathering product of biotite: *Soil Sci. Plant Nutr. (Tokyo)* **11,** 114–122.

Mathieson, A. McL. and Walker, G. F. (1954) Crystal structure of magnesium–vermiculite: *Am. Mineralogist* **39,** 231–255.

Mortland, M. M. (1958) Kinetics of potassium release from biotite: *Soil Sci. Soc. Am. Proc.* **22,** 503–508.

Newman, A. C. D. (1967) Changes in phlogopites during their artificial alteration: *Clay Minerals* **7,** 215–227.

Newman, A. C. D. (1970 a) Cation exchange properties of micas–II. Hysteresis and irreversibility during potassium exchange: *Clay Minerals* **8,** 267–272.

Newman, A. C. D. (1970 b) The synergetic effect of hydrogen ions on the cation exchange of potassium in micas: *Clay Minerals* **8,** 361–373.

Newman, A. C. D. and Brown, G. (1966) Chemical changes during the alteration of micas: *Clay Minerals* **6,** 297–310.

Norrish, K. (1972) Factors in the weathering of mica to vermiculite: *Intern. Clay Conf.*, Madrid, Preprints **2,** 83–101.

https://doi.org/10.1346/CCMN.1974.0220306 Published online by Cambridge University Press

Pruden, G. and King, H. G. C. (1969) A scheme of semi-micro analysis for the major elements in clay minerals based on modifications to conventional methods of silicate analysis: *Clay Minerals* **8,** 1–13.

Rausell-Colom, J., Sweatman, T. R., Wells, C. B. and Norrish, K. (1965) Studies in the artificial weathering of mica: *Experimental Pedology, Proc. 11th School Agric. Sci., Nottingham* (Edited by Hallsworth, H. G. and Crawford, D. V.), pp. 40–72. Butterworth, London.

Reed, M. G. and Scott, A. D. (1962) Kinetics of potassium release from biotite and muscovite in sodium tetraphenylboron solution: *Soil Sci. Soc. Am. Proc.* **26,** 437–440.

Rich, C. I. (1968) Hydroxy interlayers in expansible layer silicates: *Clays and Clay Minerals* **16,** 15–30.

Robert, M. (1971) Étude expérimentale de l'évolution des micas (Biotites)—II. Les autres possibilités d'évolution des micas et leur place par rapport à la vermiculitisation: *Ann. Agron.* **22,** 155–181.

Ross, G. J. (1967) Kinetics of acid dissolution of an orthochlorite mineral: *Canad. J. Chem.* **45,** 3031–3034.

Scott, A. D., Hunziker, R. R. and Hanway, J. J. (1960) Chemical extraction of potassium from soils and micaceous minerals with solutions containing sodium tetraphenylboron—I. Preliminary experiments: *Soil Sci. Soc. Am. Proc.* **24,** 191–194.

Scott, A. D. and Reed, M. G. (1962) *Ibid.*—II. Biotite: *Soil Sci. Soc. Am. Proc.* **26,** 41–45.

Scott, A. D. and Smith, S. J. (1966) Susceptibility of interlayer potassium in micas to exchange with sodium: *Clays and Clay Minerals* **14,** 69–81.

Scott, A. D. and Smith, S. J. (1967) Visible changes in macro mica particles that occur with potassium depletion: *Clays and Clay Minerals* **15,** 357–373.

Shirozu, H. and Bailey, S. W. (1966) Crystal structure of a two-layer Mg-vermiculite: *Am. Mineralogist* **51,** 1124–1143.

Smith Aitken, W. W. (1965) An occurrence of phlogopite and its transformation to vermiculite by weathering: *Mineralog. Mag.* **35,** 151–164.

Tamura, T. (1958) Identification of clay minerals from acid soils: *J. Soil Sci.* **9,** 141–147.

Treadwell, W. D. and Lien, O. T. (1931) Über ein basisches Aluminiumchlorid: *Helv. Chim. Acta* **14,** 473–481.

Tsuzuki, Y., Nagasawa, K. and Isobe, K. (1968) Weathered biotite from Matsusaka, central Japan: *Mineralog. J. (Japan)* **5,** 365–382.

Walker, G. F. (1949) The decomposition of biotite in the soil: *Mineralog. Mag.* **28,** 693–703.

Walker, G. F. (1950) Trioctahedral minerals in the soil-clays of north-east Scotland: *Mineralog. Mag.* **29,** 72–84.

Wells, C. B., and Norrish, K. (1968) Accelerated rates of release of interlayer potassium from micas: *9th Intern. Congr. Soil Sci. Trans.* **2,** 683–694.

Wilson, M. J. (1966) The weathering of biotite in some Aberdeenshire soils: *Mineralog. Mag.* **35,** 1080–1093.

Wilson, M. J. (1970) A study of weathering in a soil derived from a biotite–hornblende rock—I. Weathering of biotite: *Clay Minerals* **8,** 291–303.

Résumé—Une biotite a été altérée à l'ébullition dans une solution $AlCl_3$ 0,2 M et les produits résultants ont été étudiés par diffraction X sur poudre et sur cristal unique, par analyse chimique et thermogravimétrie. Le matériau altéré est un minéral argileux à 14 Å contenant de l'hydroxy-Al interfeuillet. Il a une séquence d'empilement caractéristique de la vermiculite et les feuillets silicatés ont une composition chimique semblable à celle d'une vermiculite trioctaédrique. L'extraction du matériau interfeuillet par une solution de citrate de sodium, les examens aux rayons X après chauffage et la thermogravimétrie, montrent que le matériau interfeuillet est composé d'Al associé à OH et H_2O. On discute également de la chimie et de la cinétique de la réaction d'altération et de la relation existant entre l'orientation des biotites altérées et originelles.

Kurzreferat—Biotit wurde durch Kochen in 0,2 M $AlCl_3$-Lösungen umgewandelt und die Umwandlungsprodukte mit Hilfe der Pulver- und Einkristallröntgenbeugung sowie der chemischen Analyse und der Thermogravimetrie untersucht. Das umgewandelte Material besteht aus einem 14 Å Tonmineral mit Hydroxo-Al-Zwischenschichten. Es besitzt eine für Vermiculit charakteristische Schichtabfolge und seine Silicatschichten ähneln in der chemischen Zusammensetzung denen des trioktaedrischen Vermiculits. Die Ergebnisse einer Extraktion des Zwischenschichtmaterials mit Na-Citratlösung, die röntgenographische Untersuchung nach Erhitzung und die Thermogravimetrie zeigen, daß das Zwischenschichtmaterial aus einer Verbindung von Al mit OH und H_2O besteht. Die Chemie und Kinetik der Umwandlungsreaktion sowie die Beziehungen in der Verteilung der Gitterionen zwischen umgewandelten und ursprünglichen Biotiten werden ebenfalls diskutiert.

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Резюме — Варкой в растворе 0,2M $AlCl_3$ изменили биотит и полученный продукт исследовали методом рентгеновских порошкограмм, дифракцией одного кристалла, химическим анализом и термогравиметрией. Измененный материал является глинистым материалом 14 Å с прослойкой гидрокси-Al. Он имеет характеристику последовательной столбчатой укладки вермикулита и его слой силиката подобен по химическому составу триоктаэдральному вермикулиту. Результаты экстрагирования прослоечного материала раствором лимоннокислого натрия, рентгенографических исследований после нагревания и термогравиметрии показывают, что прослоечный материал состоит из Al ассоциированного с OH и H_2O. Также рассматривали химию и кинетику реакции изменения и ориентационное соотношение между измененным и исходным биотитами.

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