NEGATIVE CHARGE OF DIOCTAHEDRAL MICAS AS RELATED TO WEATHERING

by

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ABSTRACT

Negative charge and related characteristics of dioctahedral micas have been investigated by conducting artificial weathering studies on a muscovite from Ontario, Canada, and saprolitic micas from Virginia. Emphasis is given to the relationship between loss of potassium, increase in net negative charge, or cation exchange capacity, and expansion characteristics.

Boiling solutions of acetic acid, sodium chloride and magnesium chloride removed potassium and sodium from a saprolitic mica but produced a negligible increase in cation exchange capacity. Expansion of the mica structure occurred following treatment with salt solutions but not with acid solutions. Boiling solutions of sodium citrate removed potassium effectively, produced marked expansion, and caused a large increase in cation exchange capacity. The small increase in cation exchange capacity resulting from acid and salt treatments is attributed to the hydrolysis of exchangeable aluminum to form hydroxy-aluminum polymeric groups, which can occupy exchange sites but remain non-exchangeable. The results of the sodium citrate tratement are attributed to the complexing of aluminum by citrate, thus releasing the hydroxy-aluminum polymeric groups from exchange positions and permitting an increase in cation exchange capacity.

Molten lithium nitrate treatment of specimen muscovite produced a greater increase in cation exchange capacity than in the case of muscovite separated from soil-forming mica phyllite. The observed difference in charge characteristics, concomitant with the greater expansion of the muscovite, suggest that soil micas and specimen-type micas differ in their alteration tendencies.

When interlayer hydroxy groups are eliminated and account is taken of residual sodium, potassium, and water, dioctahedral micas apparently lose no negative charge on expansion to vermiculite-like minerals.

INTRODUCTION

Dioctahedral micas are important primary minerals found in rocks that upon weathering, give rise to soil parent material. Micas undergo considerable change from the time they are exposed to weathering as part of the parent rock until they are transformed into soil materials. One of the interesting changes occurring in dioctahedral micas that is perplexing to soil chemists and mineralogists is the apparent decrease in negative charge of the mica upon weathering. This apparent decrease in charge arises when the loss of potassium

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or other interlayer cations in the mica is not balanced equally by an increase in cation exchange capacity.

The present study is concerned with the negative charge characteristics of saprolitic micas from Virginia as they undergo treatment in the laboratory. An artificial weathering approach is used in order to have controlled conditions in contrast to the complex soil and rock environments in nature. Emphasis is given to the following parameters: loss of potassium (also sodium in certain cases), increase in cation exchange capacity, and expansion.

MATERIALS

An attempt was made to obtain fresh dioctahedral mica specimens that had not undergone weathering to any appreciable extent so that the weathering products formed could be attributed to the mica component only. Samples completely free of weathered materials could not be obtained, but reasonably fresh mica samples were taken from several exposures in the Virginia Piedmont. The work reported herein was conducted on a specimen of phyllite containing approximately equal amounts of paragonite and muscovite, and a soil mica containing muscovite only. Both samples were taken in Orange County, Virginia. The phyllite has been designated as the Loudoun formation by Stose (1928), and this name will be used in this paper. The soil mica will be referred to as Mica OR for distinction purposes.

The sample on Ontario, Canada, muscovite was obtained from Ward's Natural Science Establishment, Rochester, New York.

EXPERIMENTAL

Pretreatment of Samples

The massive samples were first lightly ground in an agate mortar, then were further broken down with alternate manual grinding and mixing in a Waring blender. Grinding was kept to a minimum to avoid breakdown or alteration of the original mica structure. Dispersion was accomplished using NH_4OH or Na_2CO_3 to adjust the dispersant to pH 10. Ammonium hydroxide was used in those cases where sodium analyses were critical and it was desired to keep the samples free of extraneous sodium. Particle size fractionation of the samples was conducted according to the procedures of Jackson (1956). Both specimens contained materials extraneous to the mica that required removal prior to laboratory weathering. The NaOH dissolution technique of Hashimoto and Jackson (1960) was employed to remove kaolinite, interlayered material, and amorphous silica. Free iron oxides were subsequently removed according to the method of Mehra and Jackson (1960).

Following free iron removal, each sample was calcium saturated by washing it five times with N $CaCl_2$ solution. Excess salts were removed with one wash of water followed by 100 per cent methanol washes until the supernatant liquid was chloride free as indicated by no precipitation when a few drops of 0.5 N $AgNO_3$ were added.

Analytical Methods

The cation exchange capacity was determined by the method of Rich (1961), in which 20 mg of calcium saturated sample was transferred to a 15 ml centrifuge tube, 5 ml N $Mg(OAc)_2$ added, and the tube stoppered and shaken for 18 hr. The suspension was centrifuged and the supernatant extract analyzed for calcium on a Beckman DU flame photometer.

The Mg-saturated sample remaining in the tube was glycerol solvated and transferred to a glass slide for X-ray diffraction analysis. X-ray diffraction patterns were obtained with a General Electric XRD-3 instrument using nickel-filtered copper radiation. Intensities were recorded logarithmically. The (060) reflections were measured using an orientation technique devised by Rich (1957). The sample was preheated at 550°C to destroy kaolinite, which has a reflection at 1.49 Å, and may interfere with the (060) for muscovite at 1.50 Å.

Total potassium and sodium were determined by the semimicrochemical method of Corey and Jackson (1953). Percentages of potassium and sodium, and cation exchange capacity values are reported on the basis of a sample dried at 300°C for at least 4 hr.

Laboratory Weathering Methods

Boiling treatments.—Approximately 1 g of pretreated material was placed in a 6-liter flask containing 5 liters of the appropriate solution and heated to boiling on an electric hotplate. A reflux condenser was inserted through the rubber stopper closing the flask in order to prevent evaporation during boiling. Aliquots of the boiling suspension were taken at various intervals and 5 liters of fresh replacing solution was added.

Molten $LiNO_3$ treatment.—A method similar to that used by White (1956) was employed. A 0.5 g sample was dry-mixed with 50 g solid $LiNO_3$ in platinum crucibles. The crucibles and their contents were heated at 300°C for varying periods of time. After cooling, the solidified melt was dissolved in water and two additional water washes were given the sample to remove excess salt. Total lithium was determined flame photometrically following hydrofluoric acid digestion.

RESULTS AND DISCUSSION

The nature of the Loudoun phyllite ($< 2\mu$) before and after pretreatment is shown in Fig. 1. Noteworthy is the presence of the sodium mica, paragonite (9.80 Å), which has a slightly smaller c-spacing than muscovite (10.0 Å), and thus produces a series of ordered peaks forming doublets with those of muscovite. The sample also contained kaolinite (7.15 Å) and regularly interstratified vermiculite–montmorillonite, as indicated by the integral reflections at 32.7, 16.3, and 8.18 Å. There was a small amount of quartz present. The pretreatment appeared to have an insignificant destructive effect on the mica. The removal of vermiculite by the pretreatment is attributed to its small particle

size and, consequently, large surface area. The dioctahedral nature of the mica is evidenced by the (060) spacing of 1.500 Å. Trioctahedral micas give an (060) spacing near 1.53 Å.
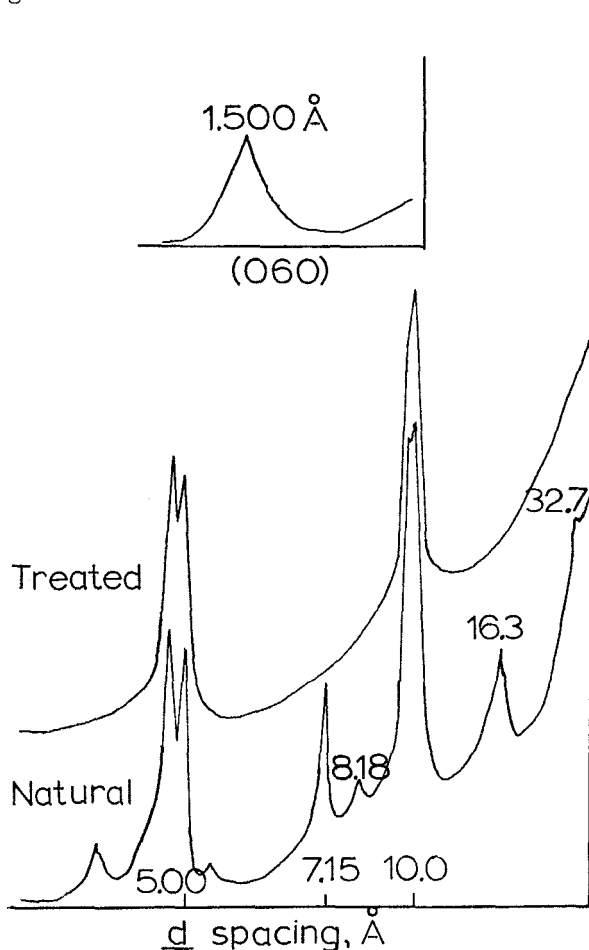

FIGURE 1.—Smoothed X-ray diffractometer traces of Loudoun phyllite ($<2\mu$) showing effect of NaOH treatment and free Fe-oxide removal. Inset shows (060) spacing.

Boiling Treatments

Loudoun Phyllite. A boiling 0.2 N HOAc solution (pH 3.0) was allowed to react with the $< 2\mu$ fraction of phyllite for 30 days. Aliquots were taken every five days for chemical and X-ray diffraction analyses, and the boiling flask was refilled with fresh solution. The results of the treatment on potassium and

sodium removal and the cation exchange capacity are given in Table 1. Approximately 100 meq/100 g of potassium and sodium were removed; however, the cation exchange capacity was increased by only 7 meq/100 g. The non-stoichiometry of the reactions is reflected in the $\frac{CEC\ gain}{K + Na\ loss}$ ratio. The ratio would be 1 in a stoichiometric relationship. A likely explanation for the negligible increase in cation exchange capacity is that the HOAc solution, at pH 3.0, brought into solution large amounts of Al^{+++}, which subsequently reacted to form hydroxy-aluminum polymeric groups. These groups can occupy exchange sites but are non-exchangeable. Although the cation exchange

TABLE 1.—EFFECT OF BOILING 0.2 N HOAc ON K CONTENT, Na CONTENT, AND CEC OF LOUDOUN PHYLLITE ($<2\mu$)

Boiling Period, Days	K	Na	K + Na	CEC	$\dfrac{CEC\ gain}{K + Na\ loss}$
		meq/100 g			
0	86.2	93.8	180	5.8	—
5	86.0	84.4	170	5.8	0
10	65.6	79.2	145	5.9	0
15	43.0	73.1	116	6.0	0
20	31.5	65.2	97	7.0	0.01
30	30.7	49.4	80	12.8	0.07

capacity increased only slightly, considerable expansion occurred, as indicated in Fig. 2. Furthermore, the interlayer material formed was resistant to collapse, particularly after 30 days. The difficult contraction indicates a stable aluminum interlayer configuration as a result of HOAc treatment.

It has been illustrated (Barshad, 1949) that $MgCl_2$ is effective in altering hydrobiotite to vermiculite. Thus, a solution of approximately 5 N $MgCl_2$, pH 4.8, was boiled with a sample of Loudoun phyllite ($< 2\mu$) for 17 days. The results are shown in Table 2. Considerably more potassium than sodium was lost through $MgCl_2$ boiling, indicating that the potassium layers are more easily penetrated than the sodium layers. Approximately equal total amounts of potassium and sodium were removed as with HOAc, but a significantly greater increase in exchange capacity was observed.

TABLE 2.—EFFECT OF BOILING 5N $MgCl_2$ ON K CONTENT, NA CONTENT, AND CEC OF LOUDOUN PHYLLITE ($< 2\mu$)

Boiling Period, Days	K	Na	K + Na	CEC	$\dfrac{CEC\ gain}{K + Na\ loss}$
		meq/100 g			
0	86.2	93.8	180	5.8	—
10	30.7	71.3	102	26.5	0.27
17	27.6	64.2	92	32.6	0.31

The low $\frac{\text{CEC gain}}{\text{K + Na loss}}$ ratio is attributed also to aluminum hydrolysis. In fact, Rich (1960) demonstrated that sodium salts actually promote the hydrolysis reaction. Magnesium salts cause similar hydrolysis enhancement; however, it is likely that not as much aluminum was brought into solution as in the case of HOAc, because the salt solution had a higher pH. As a consequence, there was a greater increase in cation exchange capacity.
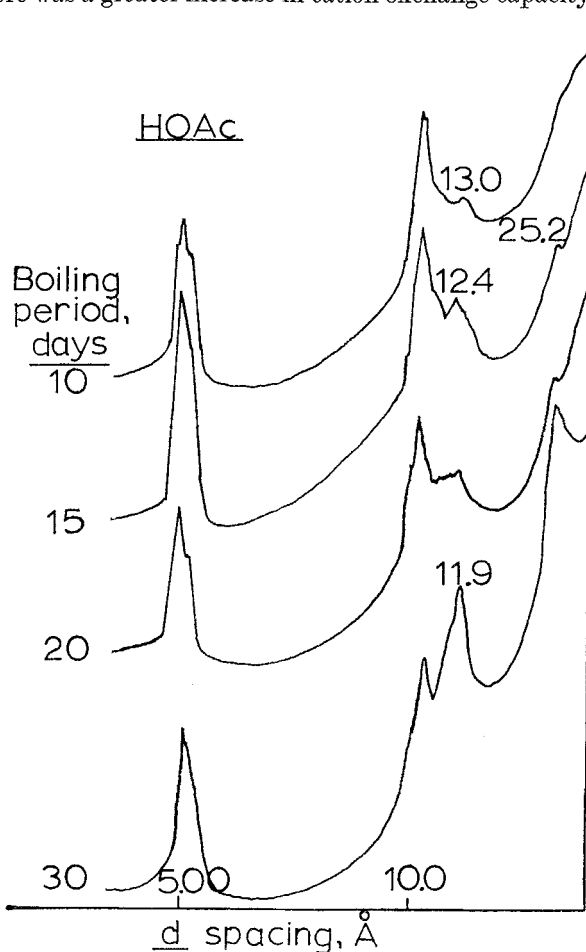

FIGURE 2.—Expansion of Loudoun phyllite ($<2\mu$) following boiling 0.2 N HOAc treatment, as indicated by smoothed X-ray diffractometer traces of Mg-saturated and glycerol-solvated samples.

The mica was almost completely altered after 10 days treatment, as indicated in Fig. 3. The interstratified mica–vermiculite resisted collapse, presumably due to the hydroxy-aluminum material in the interlayer positions.

The phyllite was treated also with boiling 5 N NaCl. The mica–vermiculite mixture formed from $MgCl_2$ treatment produced more prominent peaks and was slightly more resistant to collapse with heat treatment. However, there were insignificant differences in potassium and sodium losses and cation exchange capacity gain, suggesting that the weathering action of the two salts is essentially the same.
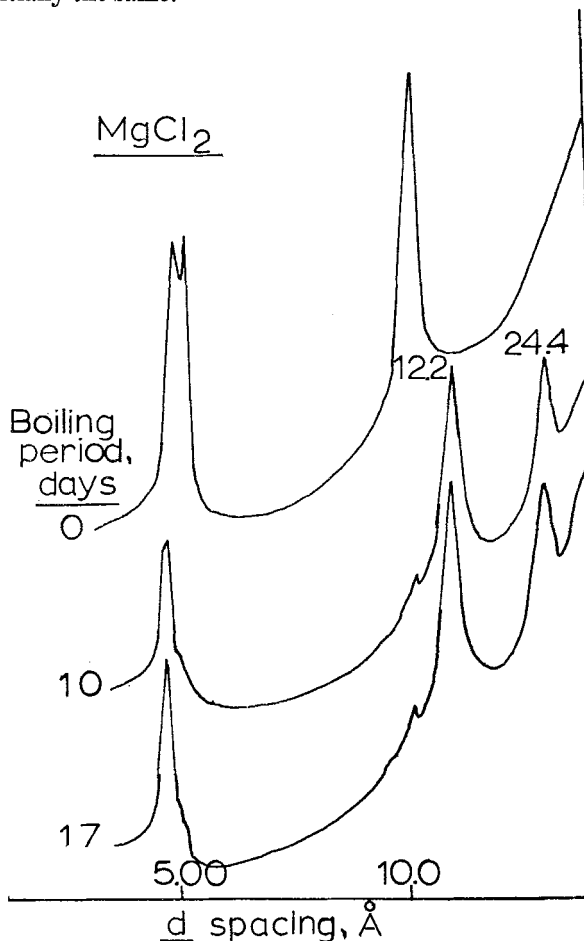

FIGURE 3.—Expansion of Loudoun phyllite ($<2\mu$) following boiling 5 N $MgCl_2$ treatment, as indicated by smoothed X-ray diffractometer traces of Mg-saturated and glycerol-solvated samples.

Mica OR. Since it would be necessary to define the role of sodium in weathering of the phyllite, it was decided to avoid this difficulty by using a mica containing only potassium in other boiling experiments. Mica OR was

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treated for removal of kaolinite and extraneous materials in like manner as the first sample. Particle size was increased from $< 2\mu$ to $5-2\mu$ since the most likely source of clay is the fine silt fraction. Boiling treatments were carried out in a similar manner to those conducted on Loudoun phyllite. An important exception was that the solution was changed daily to keep the potassium content of the solution low. Rich and Cook (1962) observed that 10 ppm potassium in solution is sufficient to block exchange.

It is recalled that a 0.2N HOAc solution removed potassium and sodium effectively but produced a negligible effect on the cation exchange capacity. To note the effect of a more concentrated HOAc solution, N HOAc, pH 2.4, was boiled with the sample for eight days. The amount of potassium extracted in comparison with the increase in cation exchange capacity is given in Table 3. The rather small amount of potassium removed is attributed to the

TABLE 3.—Effect of Boiling N HOAc on K and Na Content and CEC of Mica or $(5-2\mu)$

Boiling Period, Days	K	Na	CEC	CEC gain
		meq/100 g		K + Na loss
0	134	9.6	9.2	—
2	118	7.3	23.3	0.77
4	112	7.5	24.5	0.64
6	102	7.0	33.0	0.69
8	100	6.4	36.0	0.72

coarser particle size. The significantly greater increase in cation exchange capacity with N HOAc than with 0.2 N HOAc is attributed to the lower pH of the system. In an HOAc solution of pH 2.4, the formation of hydroxy-aluminum is small, the aluminum remaining largely in trivalent form, which is capable of being exchanged. There may have been some hydroxy-aluminum fixation and also some additional hydrolysis on calcium saturation. These reactions may have caused the discrepancy between loss of potassium and increase in cation exchange capacity.

Expansion of the mica following HOAc treatment produced weak and variable spacings (Fig. 4). After eight days, a pronounced 12.2 Å spacing appeared, suggesting a mica–vermiculite type of interstratification. Potassium saturation and heating to 300°C contracted the material, tending to confirm the conclusion that blockage of exchange sites by interlayer hydroxy-aluminum groups was small.

A boiling treatment using N sodium citrate, pH 7.6, was then employed to compare the products formed previously upon acid treatment with those formed upon slightly alkaline treatment. Sodium citrate was chosen also because it is a complexer of aluminum, and thus should give insight into the proposition that hydroxy-aluminum groups were formed during the previous

boiling treatments. The effectiveness of sodium citrate in complexing aluminum has been utilized in the removal of aluminum interlayers from soil clays (Tamura, 1958).

The effect of the sodium citrate treatment on loss of potassium and increase in cation exchange capacity is shown in Table 4. Whereas previous treatments removed increments of potassium in excess of exchange capacity gain, sodium citrate produced a somewhat greater exchange capacity increase than could be accounted for by potassium removal. The explanation offered for this unexpected occurrence is that amorphous material, possessing weight but no charge, was present initially causing the initial potassium content to be lower than it would have been had the sample been pure mica. As the amorphous material was removed during boiling, the percentage of potassium measured in the aliquot was high relative to the initial value. That amorphous materials were removed through boiling is indicated by an increase in size and intensity of the X-ray diffraction peaks after treatment compared with those before treatment.

TABLE 4.—EFFECT OF BOILING N Na-CITRATE ON K AND Na
CONTENT AND CEC OF MICA OR $(5-2\mu)$

Boiling Period, Days	K	Na	CEC	CEC gain / K + Na loss
		meq/100 g		
0	134	9.6	9.2	—
2	112	10.4	32.5	1.06
4	102	8.8	47.3	1.19
8	93	9.2	56.5	1.16
12	89	9.6	63.5	1.18
16	88	10.1	69.0	1.36

Although the increase in cation exchange capacity of Mica OR with sodium citrate was greater than with the other treatments, it is possible to obtain values on the order of 140 meq/100 g with sodium citrate (Rich and Cook, 1962). Among the factors affecting the magnitude of cation exchange capacity, the solution : sample ratio is one of the most critical. The high values were obtained using 100 mg samples in 100 ml of solution, with daily change of the solution.

Expansion occurred readily as a result of the sodium citrate treatment, as shown in Fig. 5. A vermiculitic component and a mica–vermiculite interstratification are indicated by the 14.4 Å and 12.2 Å spacings, respectively. The amount of interstratified material increased with time of treatment. Furthermore, it collapsed readily, apparently indicating that aluminum was complexed and hence no restricting interlayer material was formed. Potassium saturation of the samples and heating to 100°C induced collapse of the 16-day treated material as well as that following two days of treatment.

Due to the fact that the source material was not the same for all the boiling treatments, a comparison of the different solutions is somewhat restricted. However, several general statements can be made relative to the greater effectiveness of certain treatments over others. In general, the boiling treatments produced greater alteration the higher the solution to sample ratio.
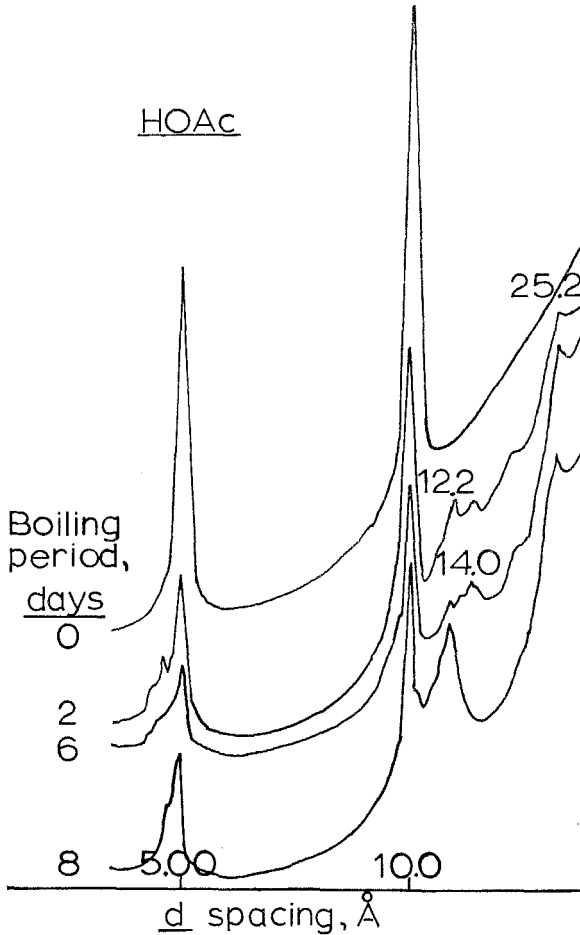

FIGURE 4.—Effect of N HOAc boiling treatment on Mica OR (5–2μ), as indicated by smoothed X-ray diffractometer traces of Mg-saturated and glycerol-solvated samples.

The boiling $MgCl_2$ and NaCl salt solutions more effectively replaced potassium than did sodium citrate. This is believed to be due to the greater concentration of the first two salts and, hence, greater ionic strengths of Mg^{++} and Na^+. Sodium-citrate is advantageous over NaCl, though, in that citrate

complexes aluminum and iron. This characteristic of sodium citrate makes it a better reactant from the standpoint of cation exchange capacity studies, as revealed in a comparison of Tables 1 through 4.
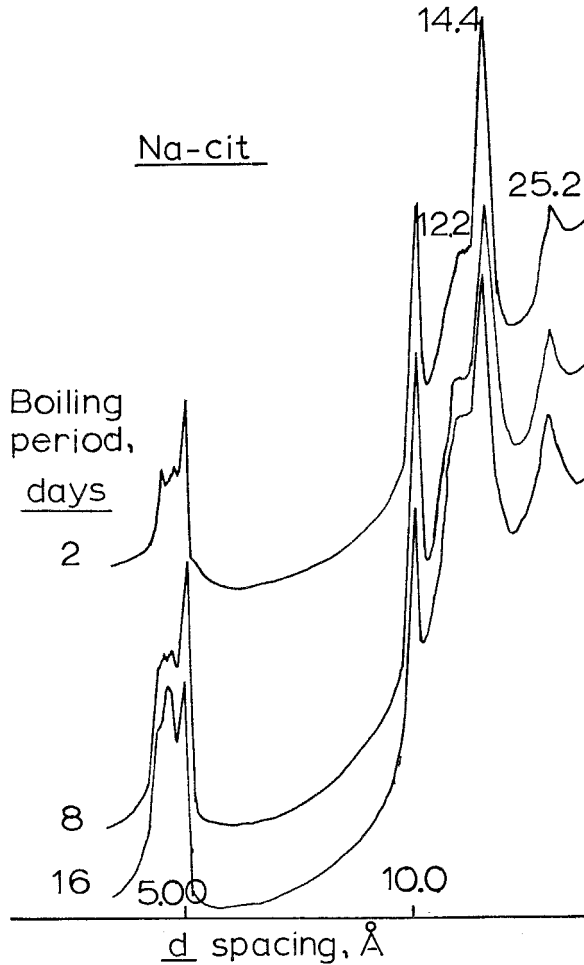

FIGURE 5.—Influence of boiling N Na-citrate on Mica OR ($5-2\mu$), as shown by smoothed X-ray diffractometer traces of Mg-saturated and glycerol-solvated samples.

From the standpoint of ionization, one might conclude that HCl should be more effective in weathering than HOAc. This was tested by treating Mica OR with boiling 10 per cent HCl. Little substitution of interlayer ions occurred; rather, the entire structure of the mineral was attacked.

It is not implied that the treatments described are characteristic of the

reactions occurring during natural weathering. However, an interesting feature of the products formed by the boiling treatments, particularly sodium citrate, is their similarity to the naturally weathered products formed in soils (Fig. 6). The 2–0.2μ fraction of the surface soil overlying Mica OR closely resembles the 5–2μ fraction of Mica OR treated 16 days with sodium citrate.
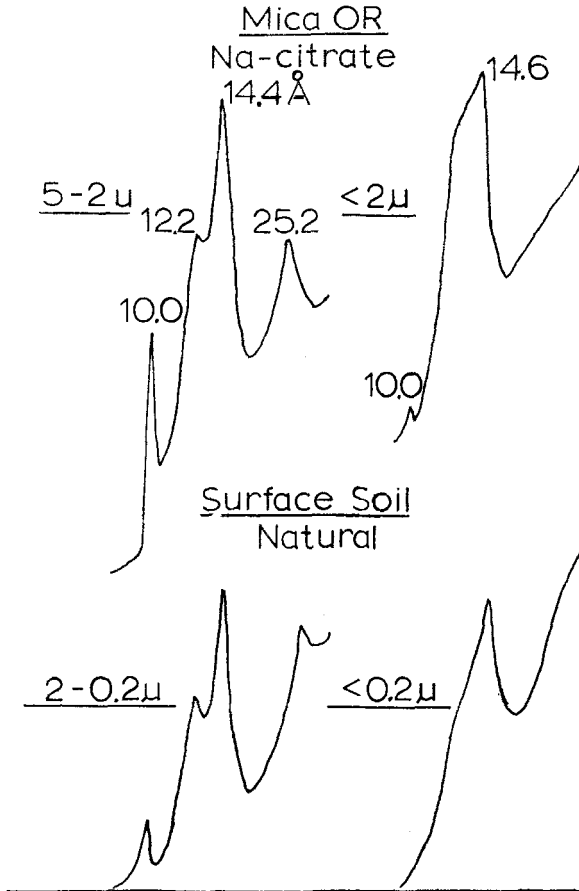

FIGURE 6.—Comparison of natural weathering products with those pro-
duced with boiling Na-citrate in the laboratory. Samples are Mg-saturated
and glycerol-solvated.

Likewise, the soil $< 0.2\mu$ fraction is analogous to the $< 2\mu$ fraction of Mica OR treated eight days with sodium citrate. Other examples are given elsewhere (Rich and Cook, 1962). The residual Ontario muscovite was altered little by boiling treatments. This contrasting behavior to the soil micas indicates marked differences in the stability of dioctahedral mica specimens.

Molten Lithium Nitrate Treatment

Loudoun Phyllite. The effect of molten $LiNO_3$ on the chemical composition of the phyllite is indicated in Table 5. The treatment removed potassium more effectively than sodium, indicating that the potassium layers are more accessible to lithium than the sodium layers. The difference in interlayer accessibility apparently is due to differences in the ionic sizes of potassium and sodium. The potassium ion has an ionic diameter of 2.66 Å, which is slightly larger than the 1.94 Å diameter of sodium. Thus, the tetrahedral layers of muscovite are held apart further than is the case for paragonite. As a result, greater energy would be required to initiate expansion along sodium-containing layers than potassium-containing layers.

TABLE 5.—CHEMICAL COMPOSITION OF LOUDOUN PHYLLITE ($<2\mu$) AS AFFECTED BY MOLTEN LiNO₃ (1:100 RATIO) AT 300°C

Time, hours	K	Na	Li	CEC	Layer Charge (Σ K, Na, CEC)	Total Charge (Σ K, Na, Li, CEC)
				meq/100 g		
0	86.2	93.8	4.1	5.8	186	190
½	67.0	80.0	24.4	21.4	168	193
1	57.5	77.9	30.4	26.7	162	193
6	39.0	72.4	41.3	39.4	151	192
24	28.8	66.9	45.6	53.7	149	194
48	23.4	64.6	47.0	60.8	149	196
96	19.5	57.7	60.6	71.0	148	209
144	15.9	56.0	95.5	79.6	152	247

The rapid changes in potassium content and cation exchange capacity occurring initially probably indicate reaction with finer particles. White(1958) observed a stoichiometric relationship between the amount of lithium migrating into the muscovite lattice and the decrease in the sum of fixed and exchangeable potassium. He also found that the layer charge decreased to a minimum of about 155 meq/100 g. A similar minimum was reached in the present experiment but other reactions continued. After 6 hr, when the layer charge had reached a minimum, the cation exchange capacity and lithium, continued to increase, whereas potassium and sodium decreased. After the layer charge reached a minimum, the main effect apparently was an exchange of lithium for potassium and sodium in the interlayer position. If potassium and/or sodium are replaced by cation exchange or the negative charge on the layer decreased internally by penetration of lithium into the structure, the summation of milliequivalents of sodium, potassium, lithium and cation exchange capacity should be constant. A relatively constant sum was maintained through two days treatment, but a sharp rise to 247 meq was noted after the 6-day period. This latter figure of 247 meq approached the

total charge of muscovite, approximately 250 meq/100 g as calculated from its theoretical formula.

Expansion of the lithium-treated samples after various reaction times is shown in Fig. 7. Expansion occurred rapidly, which was to be expected
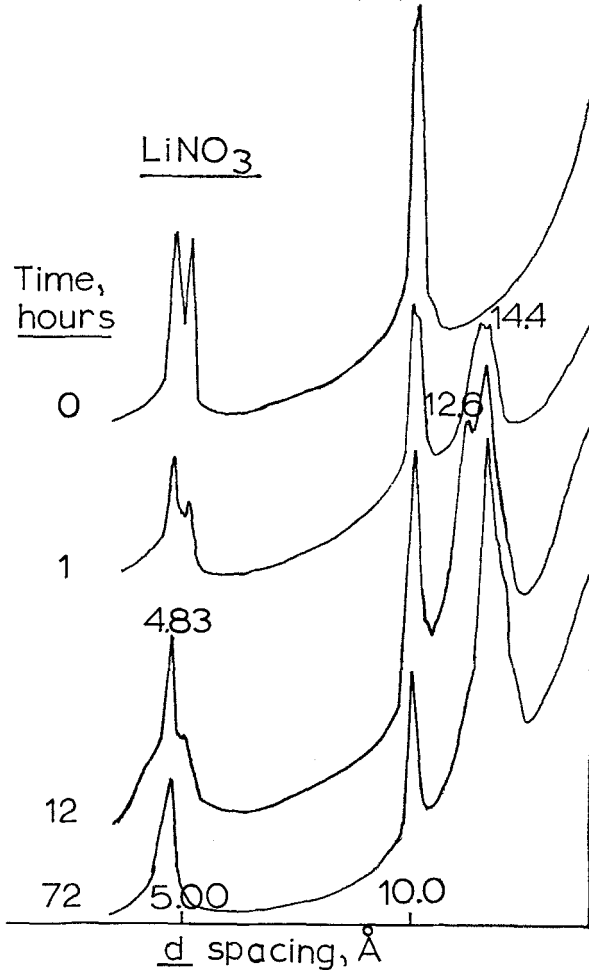

FIGURE 7.—Influence of molten $LiNO_3$ (100 : 1 ratio) on expansion of Loudoun phyllite ($<2\mu$), as shown by smoothed X-ray diffractometer traces of Mg-saturated and glycerol-solvated samples.

according to the rapid initial losses of potassium and sodium and decrease in layer charge (Table 5). The layer charge was computed by summation of potassium, sodium, and cation exchange capacity. This summation was based on the assumption that all of the non-exchangeable lithium migrated to

octahedral positions. A relatively constant layer charge was reached after about 6 hr. This agrees with the findings of White (1958), who attributed the leveling-off in layer charge to attainment of a critical potassium content in the melt. The magnitude of layer charge is an important factor in the inter-lamellar expansion of micaceous minerals. Earlier studies, e.g. Barshad (1954), seemed to indicate that a crystal lattice with a layer charge greater than 150 meq/100 g will remain contracted at 10 Å. However, significant expansion was observed in Loudoun phyllite when the layer charge was 172 meq/100 g. More recent work by Barshad (1960) showed that a vermiculite with a charge of approximately 200 meq/100 g expanded quite readily, suggesting that magnitude of charge may not be the only controlling factor. Perhaps the sites of charge and their distribution are important factors in this respect.

Ontario Muscovite. A specimen type muscovite from Ontario, Canada, was also treated with $LiNO_3$ for periods up to 48 hr. The results are given in Table 6. The high initial cation exchange capacity is believed to be caused by partial opening of the layers and exchange of potassium during fractionation of the sample. Mackenzie and Milne (1953) increased the cation exchange capacity of a muscovite to almost 30 meq/100 g by grinding for only one hour.

TABLE 6.—CHEMICAL COMPOSITION OF AN ONTARIO MUSCOVITE (2–0.2μ) AS AFFECTED BY MOLTEN $LiNO_3$ (1:100 RATIO) AT 300°C

Time, hours	K	Li	CEC	Layer Charge (Σ K, CEC)	Total Charge (Σ K, Li, CEC)
			meq/100 g		
0	150	7.8	37	187	195
1	37	35	145	182	217
5	32	58	150	182	240
24	17	91	165	182	272
48	16	110	170	186	296

The low initial charge of 187 meq/100 g for the Ontario muscovite is noticeable, since it represents a marked discrepancy from the theoretical value for well-crystallized muscovite. Low-charged micas have been observed, however, as in the case of high-silica micas (Schaller, 1950). Total charge increased to the unusually high value of 296 meq/100 g, which is unreasonable to expect. It is possible that in the separation of the 2–0.2μ fraction, some of the potassium was replaced by sodium from the sodium carbonate dispersing solution. Also, an increase in the apparent total charge would occur upon the substitution of lithium for potassium due to the difference in atomic weights of lithium (6.94) and potassium (39.1). Even if lithium replaced all the potassium, though, the total charge would be only 273 meq/100 g. Furthermore, if all the vacant octahedral positions in a dioctahedral mica were filled, it would appear that the structure would be neutral. Since it isn't, perhaps the

negative charge on the tetrahedral layer cannot be balanced completely by lithium in the octahedral layer.

Differences in expansion of the Loudoun phyllite and Ontario muscovite were noted, as shown in Figs. 7 and 8. The Loudoun phyllite did not expand
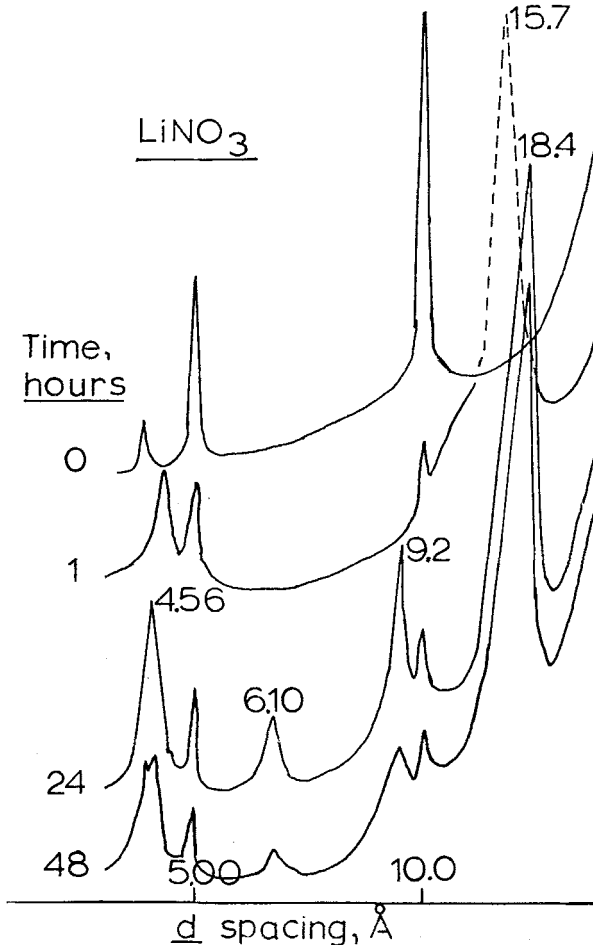

FIGURE 8.—Influence of molten LiNO₃ (100: 1 ratio) on expansion of Ontario muscovite (2–0.2μ), as shown by smoothed X-ray diffractometer traces of Mg-saturated and glycerol-solvated samples.

beyond 14.7 Å, which is indicative of a vermiculite-like material. Muscovite expanded to 18.4 Å, which is a characteristic spacing of montmorillonite. This difference, as well as the difference in charge characteristics, seems to illustrate that soil micas and specimen-type micas are quite different from an alteration standpoint.

Several possibilities may account for the differences observed. The micas studied originated in meta-sediments, in which more ionic substitution has occurred than in igneous rocks. This greater substitution would lead to warping and misfit and to a less stable mica than one found in crystalline rock. Another factor important in mica alteration is the amount of negative charge originating in the silicate layers because of substitution and vacancies in the tetrahedral and octahedral positions. The weaker stability of the soil micas also could be attributed to ions other than potassium in the interlayer position. Sodium may proxy for potassium to a large extent, and this substitution may affect appreciably the structural relationships of the mica.

CONCLUSIONS

The results of this study indicate that the degree and kind of alteration of dioctahedral micas in the laboratory is dependent upon the weathering agent as well as the mineral itself. Soil micas alter much more readily than specimen-type muscovite suggesting differences in their structure and crystallinity. Both boiling and molten salt treatments produce alteration products resembling those found in nature.

The increase in negative charge of the mica depends upon the reaction of the weathering medium with aluminum. Boiling weak acid and salt solutions promote the hydrolysis of aluminum to form hydroxy-aluminum compounds, which satisfy much of the negative charge. This reaction occurs in acid weathering environments and is at least one of the reasons for the apparent decrease in charge of weathered mica. Sodium citrate is effective in preventing the accumulation of aluminum-containing interlayer materials. When it is used, a reasonably good stoichiometric relationship between interlayer balancers of charge, e.g. potassium and sodium, and increase in cation exchange capacity is obtained.

REFERENCES

Barshad, I. (1959) Vermiculite and its relation to biotite as revealed by base-exchange reactions, X-ray analyses, differential thermal curves, and water content: *Amer. Min.*, v.33, pp.655–678.

Barshad, I. (1954) Cation exchange in micaceous minerals. II. Replaceability of ammonium and potassium from vermiculite, biotite and montmorillonite: *Soil Sci.*, v.78, pp.57–75.

Barshad, I. (1960) X-ray analysis of soil colloids by a modified salted paste method: in *Clays and Clay Minerals*, 7th Conf., Pergamon Press, pp.350–364.

Corey, R. B. and Jackson, M. L. (1953) Silicate analysis by a rapid semimicrochemical system: *Anal. Chem.*, v.25, pp.624–628.

Hashimoto, I. and Jackson, M. L. (1960) Rapid dissolution of allophane and kaolinite-halloysite after dehydration: in *Clays* and *Clay Minerals*, 7th Conf., Pergamon Press, pp.102–113.

Jackson, M. L. (1956) *Soil Chemical Analysis—Advanced Course.* Published by the author. University of Wisconsin, Madison, 991 pp.

Mackenzie, R. C. and Milne, A. A. (1953) The effect of grinding on micas: I. Muscovite: *Min. Mag.*, v.30, pp.178–185.

Mehra, O. P. and Jackson, M. L. (1960) Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium carbonate: in *Clays and Clay Minerals*, 7th Conf., Pergamon Press, pp.317–327.

Rich, C. I. (1957) Determination of (060) reflections of clay minerals by means of counter type X-ray diffraction instruments: *Amer. Min.*, v.42, pp.569–570.

Rich, C. I. (1960) Aluminum in interlayers of vermiculite: *Soil Sci. Soc. Amer. Proc.*, v.24, pp.26–32.

Rich, C. I. (1961) Calcium determination for cation exchange capacity measurements: *Soil Sci.*, v.92, pp.226–231.

Rich, C. I. and Cook, M. G. (1962) Formation of dioctahedral vermiculite in Virginia soils: in *Clays and Clay Minerals*, 10th Conf., Pergamon Press. In press.

Schaller, W. T. (1950) An interpretation of the composition of high silica sericites: *Min. Mag.*, v.29, pp.406–415.

Stose, G. W. (1928) Supervisor of preparation, Geologic Map of Virginia. Virginia Geological Survey.

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

White, J. L. (1956) Reactions of molten salts with layer-lattice silicates: in *Clays and Clay Minerals*, Natl. Acad. Sci.–Natl. Res. Council, pub. 456, pp.133–146.

White, J. L. (1958) Layer charge and interlamellar expansion in a muscovite: in *Clays and Clay Minerals*, Natl. Acad. Sci.–Natl. Res. Council, pub. 566, pp.289–294.