DODECYLAMMONIUM-MICA COMPLEXES—II
CHARACTERIZATION OF THE REACTION PRODUCTS

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Abstract—Interlayer potassium was removed from a wide range of mica minerals by treatment with dilute solutions of n-dodecylammonium chloride. On subsequent reaction with the appropriate metal methoxide, the Na⁺ or Ca²⁺ form of the altered mica was produced. The properties of the original and sodium saturated samples were compared to assess the changes in water content, charge density and chemical composition (particularly ferrous iron) which resulted from the displacement of potassium.

Calculation of structural formulae was not attempted since it was established that for the altered samples accurate distinction could not be made between adsorbed and structural water. Changes in layer charge are thus expressed on the basis of samples ignited to 100°C. Charge losses of up to 76 me/100 g were recorded for biotites, smaller charges were noted for phlogopites and no loss was observed for the two muscovites examined.

Oxidation of ferrous iron occurred for all trioctahedral samples, the greatest oxidation occurring in the samples initially high in iron. There was no consistent relationship between the amount of iron oxidized and the loss of layer charge.

All altered samples contained greater amounts of H₂O⁺ than the original materials suggesting that protonation of structural oxygens occurred during, or following, removal of potassium.

It is concluded that the alteration of micas by reaction with organic cations is a complex process, differing in detail for different micas, and following a similar path to alteration by reaction with inorganic salts.

INTRODUCTION

When potassium is displaced from the interlayer of mica minerals, in addition to the obvious changes which occur in the (001) spacing, other differences have been noted between the original mica and the altered product, e.g. in surface charge density and/or chemical composition of the silicate sheet (Rausell-Colom et al., 1964; Newman and Brown, 1966; Scott and Smith, 1966).

In Part I (Mackintosh et al., 1971) the n-dodecylammonium ion (DA⁺) was shown to be capable of displacing large amounts of potassium from a wide range of micas. To assess the changes which result from the displacement of K⁺ from within the interlayer by DA⁺, the charge density and total chemical composition (and in particular the content of Fe²⁺ ions) have been determined for a range of biotites, phlogopites and muscovites.

MATERIALS AND METHODS

Micas

The eight samples used (3 ferruginous micas, 3 phlogopites and 2 muscovites) were described in Part I (Mackintosh et al., 1971). Chemical analyses of the 53–75μ fraction for each original mica and the corresponding K-depleted materials are given in Table 1.

Preparation of K⁺-depleted micas

Displacement with DA⁺. Two gram samples of each mica were treated with 1.1 of a solution of dodecylammonium chloride (0.04N) at 70°C. The suspensions were shaken periodically, and at weekly intervals the supernatant solution was removed and replaced with fresh DAC solution. In this way the concentration of potassium in the solution was maintained at a low level. For the trioctahedral minerals, 2 or 3 successive treatments normally reduced the potassium content of the samples to less than 10 me K⁺/100 g. For the muscovites, continued treatment for 4 months reduced the potassium content to approximately 30% of the initial level in one case and only 60% in another.

Formation of Na⁺- or Ca²⁺-micas. The affinity of alkylammonium cations for the charge site of the silicate is large, increasing with length of the alkyl chain (Cowan and White, 1958). For the dodecylammonium cation, adsorption also occurs in excess of the exchange capacity and the silicate surface is rendered hydrophobic so that complete
replacement of the organic cation by simple exchange reactions in aqueous solution is extremely difficult. However, by reacting the $\text{DA}^+$-mica with a metal alkoxide as suggested by Weiss and Thamerus (1962) complete conversion of the $\text{DA}^+$-saturated mica to a metal ion saturated form can be accomplished. The reaction which occurs within the interlayer region can be expressed by the following unbalanced equation,

$$\text{C}_{12}\text{H}_{25}\text{NH}^+\text{-mica} + M(O\text{CH}_3)_n \rightarrow \text{C}_{12}\text{H}_{25}\text{NH}_2 + M\text{-mica} + n\text{CH}_3\text{OH},$$

where $M$ is a metal ion of valence $n$.

By this reaction the original alkylammonium cation associated with a charge site of the silicate surface forms an uncharged amine molecule and its place is taken by the metal cation produced in situ from the appropriate methoxide.

Solutions of methoxides were prepared by reacting the clean dry metal (AR grade) with an excess of dry AR methanol. The reaction between sodium and methanol was vigorous and even at room temperature proceeded rapidly to completion. Gentle heating was necessary to initiate the reaction between calcium and methanol which then continued spontaneously. To prevent hydrolysis and resulting high pH, it was essential to exclude water both during the preparation and storage of the methoxide solutions.

For efficient reaction, excess DAC solution and free amine were removed from within the interlayer by preliminary washings with aqueous methanol and finally at least twice with dry AR methanol. The samples were shaken in 200 ml of freshly prepared methoxide at room temperature for 4–5 hr to allow uniform distribution of the methoxide within the interlayer region. On heating the suspension to 70°C the free amine was produced and gradually released into the methanol solution. The progress of the reaction was followed by X-ray diffraction, which showed a decrease in the amount of residual $36\,\AA$ phase with time and the appearance of peaks at 14-3–15 $\AA$ or 12-0–12-6 $\AA$ for the Ca or Na products, respectively. Removal of the liberated amine was normally complete within 3–4 weeks. Periodic changes of solution increased the rate of removal. When the X-ray patterns indicated an absence of interstratified material the samples were washed with hot methanol, then 4 times with hot 50% methanol and finally 4 times with double-distilled water.

All samples were dried overnight at 70°C and then stored in a desiccator over a saturated solution of NaNO$_2$ (66% RH).

**Analytical methods**

*Elemental analysis.* The original micas and the sodium form of the altered products were analysed for elements down to magnesium by X-ray fluorescence spectrography using a Philips 1010 generator and 1050 vacuum spectrograph. The samples were prepared as recommended by Norrish and Chappell (1967). After removal of all water by ignition to 1000°C, approximately 280 mg (accurately weighed) of each sample was fused in a lanthanum oxide–lithium borate mix and cooled to form a glass disc. The nominal percentages obtained were corrected for matrix effects by using the mass absorption coefficients and equations given by Norrish and Chappell (1967).

Total sodium contents were determined by flame photometry following dissolution in HF. Some of the digests were also analysed for potassium by flame photometry for comparison with the normal determination by X-ray fluorescence.

Ferrous iron was determined by the procedure of Reichen and Fahey (1962) but dissolution was carried out at 20°C rather than 70°C to avoid possible interference from organic compounds contained in some of the altered samples.

*Water loss.* Samples previously equilibrated at 66% RH were pressed into pellets (8 mm dia.) under a pressure of 200 lbs/in.$^2$ and re-equilibrated at 66% RH for a further period of at least 4 weeks.

The total water content of each sample was determined by heating in a stream of dry air in a tube furnace held at 1000°C (the maximum temperature obtainable), the water vapour so formed being adsorbed on magnesium perchlorate and determined by weighing.

Adsorbed water ($\text{H}_2\text{O}^-$) was assessed for the original samples as being the loss of weight on heating to 110°C. For the altered samples the loss of water on heating to 400°C was used.

Structural water ($\text{H}_2\text{O}^+$) was calculated as the difference between the total water loss (at 1000°C) and the adsorbed water as determined above.

**RESULTS**

The total chemical analyses of the original and the altered micas are given in Table 1. The amount of adsorbed water associated with the interlayer cation was much greater for the altered samples than for the original micas. Consequently, the analyses for the altered samples have been calculated on the basis of the weight after heating to
Table 1. Total chemical analysis of the original and altered micas

<table>
<thead>
<tr>
<th></th>
<th>Biotite Harts Range</th>
<th>Biotite Ontario</th>
<th>Lepidomelane Original</th>
<th>Phlogopite Ontario Original</th>
<th>Phlogopite Altered</th>
<th>Phlogopite Harts Range Original</th>
<th>Phlogopite Quebec Original</th>
<th>Muscovite Ontario Original</th>
<th>Muscovite Altered</th>
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<td>SiO₂</td>
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<td>35.61</td>
<td>37.20</td>
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<td>35.34</td>
<td>35.04</td>
<td>41.76</td>
<td>42.64</td>
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<td>19.82</td>
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<td>15.22</td>
<td>15.22</td>
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<tr>
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<td>3.47</td>
<td>7.62</td>
<td>3.24</td>
<td>16.83</td>
<td>0.03</td>
<td>0.88</td>
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<td>16.74</td>
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<td>22.30</td>
<td>10.92</td>
<td>1.57</td>
<td>1.27</td>
<td>1.00</td>
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<td>0.56</td>
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<td>0.09</td>
<td>0.08</td>
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<td>9.39</td>
<td>9.43</td>
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<td>9.64</td>
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<td>0.60</td>
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<td>3.85</td>
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<td>0.16</td>
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<td>0.02</td>
<td>0.02</td>
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<td></td>
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<td>0.61</td>
<td>0.99</td>
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<tr>
<td></td>
<td>0.99</td>
<td>99.46</td>
<td>100.26</td>
<td>99.09</td>
<td>98.85</td>
<td>99.16</td>
<td>100.49</td>
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</tr>
</tbody>
</table>

*For original samples = Total H₂O (100°C) minus H₂O (110°C).  **For original samples = loss of water to 110°C
For altered samples = Total H₂O (100°C) minus H₂O (40°C).  For altered samples = loss of water to 40°C.
For phlogopites H₂O⁺⁺ may be underestimated due to incomplete dehydroxylation at 100°C.  n.d. = not determined, - = not detectable.
400°C, the temperature below which it was anticipated that all adsorbed water would be lost. For the original samples the weight after heating to 110°C was used as reference.

Table 2 shows the individual ions occurring within the interlayer and the total charge, expressed as milli-equivalents of cation per 100 g of ignited sample (1000°C); the change in charge as a result of removal of K⁺ is also given. Table 2 also shows the content of Fe²⁺ in the various samples, expressed as millimoles of FeO per 100 g ignited sample. The differences in FeO content between the altered and the original materials are also shown.

The losses in weight on heating the altered samples under vacuum from 20-450°C are given in Fig. 1 for the ferruginous micas and in Fig. 2 for the phlogopites and a muscovite. A comparison of the dehydration characteristics of the altered Quebec biotite, as determined by thermal gravimetric analysis (TGA) and using the silica spiral balance with extended equilibration times, is given in Fig. 3.

Table 3 gives data for the carbon contents of the altered materials, in relation to the composition of the methoxide used to remove the DA⁺, showing that removal of residual organic molecules was more complete following the sodium methoxide treatment.

Table 4 contains data on various oxide ratios calculated for the original and altered samples from the chemical analyses reported in Table 1.

**DISCUSSION**

**Nomenclature of the altered products**

In many cases after potassium removal the altered products have many properties more akin to natural vermiculites than to the original mica. However, to avoid confusion in terminology, the name of the original mica, prefixed by the Table 2. The amounts of interlayer cations and FeO in the 53–75μ fraction of original and altered micas

<table>
<thead>
<tr>
<th>Sample</th>
<th>Condition</th>
<th>K (me/100 g ignited weight)</th>
<th>Na (me/100 g ignited weight)</th>
<th>Ca (me/100 g ignited weight)</th>
<th>Ba (me/100 g ignited weight)</th>
<th>Total (me/100 g ignited weight)</th>
<th>Change in charge†</th>
<th>FeO oxidized mmoles/100 g</th>
<th>FeO oxidized mmoles/100 g</th>
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<tr>
<td>Biotite</td>
<td>original**</td>
<td>204</td>
<td>20</td>
<td>4</td>
<td>—</td>
<td>228</td>
<td>76</td>
<td>233</td>
<td>63</td>
</tr>
<tr>
<td>Ontario†</td>
<td>altered***</td>
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<td>136</td>
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<td>—</td>
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<td>7</td>
<td>3</td>
<td>—</td>
<td>214</td>
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<td>257</td>
<td>70</td>
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<td>—</td>
<td>175</td>
<td>—</td>
<td>187</td>
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<td>—</td>
<td>244</td>
<td>—</td>
<td>—</td>
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<tr>
<td>Muscovite</td>
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<td>118</td>
<td>—</td>
<td>—</td>
<td>247</td>
<td>—</td>
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</tr>
</tbody>
</table>

*Expressed as me/100 g ignited weight assuming the total interlayer cations equal to K + Na + Ca + Ba.

**All values for original material calculated on the basis of weight after heating to 110°C.

***All values for altered material calculated on the basis of weight after heating to 400°C.

†Difference in total interlayer cations before and after treatment with DAC and NaOCH₃.
Fig. 2. Water loss from altered phlogopites and muscovite. 
●—Ontario Na-phlogopite; ■—Harts Range Na-phlogopite; ▼—Quebec Na-phlogopite; ▲—Ontario Na-muscovite.

Table 3. Carbon contents of altered micas*

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<tr>
<th>Sample</th>
<th>Methoxide</th>
<th>%C</th>
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<tr>
<td>Biotite, Ontario Ca</td>
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<td>Biotite, Ontario Na</td>
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<tr>
<td>Biotite, Ontario Na</td>
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</tr>
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<td>Biotite, Harts Range Ca</td>
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<td>Lepidomelane Ca</td>
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<tr>
<td>Phlogopite, Harts Range Ca</td>
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<td></td>
</tr>
<tr>
<td>Phlogopite, Ontario Ca</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>Phlogopite, Quebec Na</td>
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</tr>
<tr>
<td>Muscovite, Ontario Na</td>
<td>0.06</td>
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*Analysis by Australian Microanalytical Service, Division of Applied Chemistry, CSIRO, Melbourne. 
**After heating to 400°C under a vacuum of 10^-4 mm Hg.

Fig. 3. Water loss from Quebec Na-biotite. (a) Using silica spiral spring balance and prolonged temperature equilibration. (b) Determined by TGA with relatively rapid, continuous temperature changes.

introduced cation will be used for the altered product; e.g. Harts Range Na-phlogopite describes the Harts Range phlogopite which has been depleted of K⁺ by treatment with DAC and subsequently the DA⁺ replaced by Na⁺.

Calculation of changes in composition

In Table 2, the charge associated with the silicate is expressed as milli-equivalents of cation per 100 g of ignited sample. Although this is not a direct measure, surface charge density can be calculated from this if the unit cell dimensions and the formula weight are known. For most purposes this is not essential and the charges per unit weight of original and altered samples can be compared directly to determine the changes which may have accompanied displacement of potassium.

Other workers have tried to assess changes in composition from changes in calculated structural

<table>
<thead>
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<th>Table 4. Oxide ratios for the original and altered micas</th>
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<td>Interlayer cation</td>
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<td>Muscovite, Ontario K</td>
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</table>
formulae, for the determination of which precise analyses of structural water and fluorine content are required. The data in Figs. 1 and 2 indicate that accurate distinction between structural water \((\text{H}_2\text{O}^+)\) and adsorbed water \((\text{H}_2\text{O}^-)\) is not possible for the altered samples so the arduous calculation of structural formulae does not seem to be warranted.

By calculating the amounts of interlayer cations on the basis of ignited weights, any error that may be introduced due to incorrect distinction between \(\text{H}_2\text{O}^+\) and \(\text{H}_2\text{O}^-\) is excluded. However, other sources of error are possible, e.g.

1. Changes produced in the formula weight of the altered sample by introducing a lighter element, sodium, for potassium,
2. Oxidation of ferrous iron,
3. The possible formation of hydroxy species of Fe and Al which could block interlayer exchange sites, and
4. Loss of fluorine on ignition.

Assuming no other change in chemical composition, the introduction of \(\text{Na}^+\) for \(\text{K}^+\) leads to estimates of charge density which are high by about 3-4%. By contrast, oxidation of iron (II), particularly for the ferruginous micas would give low values. For the phlogopite micas, the errors caused by replacing \(\text{K}^+\) with \(\text{Na}^+\) and by the oxidation of ferrous iron would tend to offset one another. For the ferruginous micas, oxidation of \(\text{Fe}^{2+}\) would tend to dominate the change, giving rise to low values.

The extent to which blockage of exchange sites by hydroxy species contributes to low results is uncertain but the data obtained by X-ray diffraction suggest it is small. After heating the Na-phlogopites or Na-biotites at 400°C, X-ray patterns revealed very sharp peaks near 10 Å with no indication of any interlayer contamination.

Possibly the greatest error associated with the use of ignited weights as reference is that due to loss of fluorine on ignition. Rimsaite (1967) showed that temperatures of 1100°C to 1200°C are necessary to ensure complete dehydroxylation of phlogopites. However, Newman (1967) and Besson et al. (1968) have shown that if phlogopites depleted of potassium are heated to these temperatures, appreciable loss of fluorine occurs. Unfortunately, in the present work, the fluorine contents of the altered samples could not be determined due to the limited amounts available; a loss of fluorine on ignition could thus not be confirmed.

Changes in negative charge

Based on the results shown in Table 2, the displacement of potassium from micas by DAC has led to an appreciable decrease in surface charge density of biotites and phlogopites. This is consistent with the findings of Rausell-Colom et al. (1964), Scott and Smith (1966) and Newman and Brown (1966) for ferruginous micas. The largest decrease in charge following DAC treatment was 76 me/100 g, recorded for the Ontario biotite. This exceeds by approximately 14 me/100 g the loss recorded by Newman and Brown (1966) for the same biotite following treatment with sodium tetraphenylboron (Na-TPB). The calculated total content of interlayer cations for the Ontario-Na-biotite was 152 me/100 g which is comparable to a low charge vermiculite. The validity of this low value was supported by XRD data since the Ontario-Ca-biotite expanded to 17.36 Å on treatment with glycerol. According to Walker (1958), this is characteristic only of smectites and very low charged vermiculites. The remaining altered samples had higher charge densities and did not expand following treatment with glycerol.

For the phlogopites, the charge loss was smaller than for the ferruginous micas, decreases of only 15-39 me/100 g being observed. The smallest loss of charge (15 me/100 g) was noted for the Quebec phlogopite but appreciable potassium (41 me/100 g) still remained in the altered sample; a greater loss of charge may have occurred if all of the potassium had been displaced. In spite of the significant decreases in charge, the charge densities of the altered phlogopites still remained high, just less than 200 me/100 g. The data given by Newman and Brown (1966) show decreases in charge for low iron (II) phlogopites when expressed as extent of interlayer cations but the authors based their conclusions on the differences in calculated structural formulae, as did Robert and Pedro (1966).

Although the muscovites were not totally depleted of potassium as a result of DAC treatment, no change in their charge characteristics could be detected. This is consistent with data previously reported by Cook and Rich (1963) and Scott and Smith (1966) although Leonard and Weed (1967) have claimed appreciable charge loss for muscovites under certain conditions.

Chemical alterations

Water loss. By using a silica spiral spring thermobalance and stepwise temperature increases with a prolonged period for equilibration rather than thermal gravimetric techniques with a relatively rapid continuous temperature rise, it was anticipated that a plateau might be obtained over a temperature range which would allow a distinction to be made between \(\text{H}_2\text{O}^+\) and \(\text{H}_2\text{O}^-\) (Thomp-
son et al., 1967). However, Fig. 3 shows a close agreement between both methods. Figures 1 and 2 show that water loss above 150°C occurs as a continuum, precluding accurate distinction between removal of adsorbed water and commencement of dehydroxylation.

Water lost in the vicinity of 300–450°C is proportionately greater for the altered ferruginous micas than for phlogopites. Of the water remaining in the samples after heating to 110°C, almost half was lost from the ferruginous micas on heating to 450°C, whereas only about a third was lost from the phlogopites. According to Farmer et al. (1968), dehydroxylation of altered biotites should commence at temperatures below 400°C. This is not so for phlogopites, since the water associated with octahedrally coordinated Mg is held tenaciously and dehydroxylation probably does not occur below 400°C.

The content of water not removed from the altered samples by heating to 400°C suggests that, associated with the removal of K⁺, there has been an increase in the actual H₂O⁻ content of the mica structures.

The loss of weight on heating under vacuum to temperatures near 400°C may also be influenced slightly by the residual carbon content of the altered samples. Data given in Table 3 show that the Ontario Na-biotite had its carbon content reduced on heating under vacuum to 400°C. However, the weight loss from this source would be small (about 0.2%) compared with the loss of adsorbed water over the range 150–450°C.

When calculating the total water derived from the silicate mineral, a correction was applied to allow for the water produced by oxidation of organic compounds on heating to 1000°C. The maximum error would occur if all the carbon in the altered materials were present as methanol, which would be oxidized as follows:

\[
\text{CH}_3\text{OH} \xrightarrow{\text{O}_2, 1000^\circ\text{C}} \text{CO}_2 + 2\text{H}_2\text{O}
\]

i.e. 1 mg carbon produces 3 mg water. This correction has been applied to the data given in Table 1. The absolute error can be minimized by using sodium methoxide to react with the DA⁺ since the residual carbon content of the altered material is then reduced to an almost negligible level. Similar problems involving organic compounds can be encountered when Na–TPB is used. Although Na–TPB efficiently displaces potassium from micas, it is uncertain how much precipitated KTPB remains in the interlayer regions. Neither Scott and Smith (1966) nor Newman (1967) has reported the residual carbon contents of the altered minerals.

This is unfortunate since the residual carbon in the altered material can be a crucial factor which must be known when studying water relationships.

**Loss of metal cations.** Evidence for the loss of metal cations during K depletion can be obtained by deriving ratios of the elemental percentages; these ratios are presented in Table 4. This approach is valid since errors introduced within a particular sample by the incorrect assignment of structural water or oxidation of iron are relative and affect each value proportionately.

The precision achieved in elemental analysis by the X-ray fluorescence technique was determined as 1% for SiO₂ and Al₂O₃ and 2% for MgO. If a maximum error of 2% is assumed for all analyses then differences in the ratios SiO₂/Al₂O₃, SiO₂/MgO and Al₂O₃/MgO greater than 0.07, 0.18 and 0.09 respectively were considered to be significant, being outside the limits of experimental error. The data given in Table 4 indicate that the Na-lepidomelane and Ontario Na-biotite lost a significant amount of Al₂O₃ relative to SiO₂. Similarly, MgO was lost relative to both SiO₂ and Al₂O₃ in the Harts Range Na–biotite and to SiO₂ in Na–lepidomelane.

Although the changes in the ratios are small, those mentioned are outside the calculated experimental error, suggesting that some loss of cations, principally Mg, occurred during the treatment. However, for the Ontario biotite the changes in ratio were not as great as those calculated from the analytical data given by Newman and Brown (1966). Their data indicate considerable loss of MgO, the changes in ratio being approx. 7–8 times greater than the changes in Table 4.

**Oxidation of Fe²⁺.** Reference to Tables 1 and 2 shows that during the displacement of potassium considerable amounts of ferrous iron are oxidized. The amounts range from 4 m-moles of FeO per 100 g for Ontario Na-phlogopite to a maximum of 158 m-moles of FeO per 100 g for the Na-lepidomelane. However, the oxidation of ferrous iron does not necessarily relate to the change in layer charge (see Table 2). During the displacement of potassium from the lepidomelane, 158 m-mole FeO/100 g was oxidized to the ferric form, whereas the loss in charge amounted to 49 me/100 g. Similarly, the amounts of iron (II) oxidized exceeded the decrease in charge for the Harts Range biotite.

It is also clear from the data in Table 2 that the reduction in charge for the Harts Range and Ontario phlogopites and Ontario biotite cannot be explained solely by the oxidation of iron (II) and that another mechanism must be partly responsible for the observed changes.
Protonation. Evidence obtained in the present study for an increase in structural water in the altered materials suggests that incorporation of protons into the silicate structure may be responsible. This agrees with observations made by other workers (Jorgensen and Rosenquist, 1963; Newman and Brown, 1966; Raman and Jackson, 1966; Newman, 1967).

The most plausible sites for protonation of the silicate structure are:

1. the apical oxygen shared between the octahedron and tetrahedron (Jorgensen and Rosenquist, 1963),
2. the oxygen associated with vacancies in the octahedral layer arising from ejection of Mg or Fe(III) during the weathering process (Farmer et al., 1968), or
3. the Si—O—Al bond in the tetrahedral layer (Szymanski et al., 1960).

The structural hydroxyls produced by protonation at any one of these sites would have characteristics different from the normal octahedral OH and so are likely to be lost at temperatures lower than normal. If more than one type of protonation is possible it is probable that water loss would occur at different temperatures in each case and a continuous weight loss with temperature would result as indicated in Figs. 1 and 2.

For the ferruginous micas the decrease in charge as shown in Table 2 was greater than that reported by Newman and Brown (1966) for similar specimens treated with Na–TPB. One reason for the difference may be in the pH conditions during the reaction. Displacement of potassium by DA⁺ was accomplished under mildly acid conditions (pH 5.2–5.8). Depletion with Na–TPB in the absence of EDTA, the technique used by Newman (1967), can result in a final pH as high as 9 (Scott, personal communication). Under the more acid environment of the DAC extraction the protonation reaction may assume a more significant role.

CONCLUSIONS

Dodecylammonium micas react readily with sodium and calcium methoxides to form altered micas in which sodium or calcium ions are the dominant ions in the interlayer positions. These products show interlamellar expansion in water similar to that of vermiculites. Their composition is in accord with the fact that the layer charge density has been reduced, in the course of the exchange reaction and displacement of the amine, to values corresponding to those of vermiculites. The reduction of charge density is apparently associated with oxidation of ferrous to ferric ions, and the entry of protons into the lattice. Changes in the relative contents of Si, Al and Mg indicate that other minor changes have also occurred. Because of this, and because of the difficulty involved in distinguishing structural and adsorbed water and the precise changes due to losses of fluoride on heating and residual amounts of organic materials, detailed structural description of the reaction products is not possible. Similar criticisms may be made of other investigations of reaction products of micas, and attempts to describe their structure in detail must be treated with caution.

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Résumé — On a extrait le potassium interfeuillet de toute une gamme de micas par traitement avec des
solutions diluées de chlorure de n-dodécylammonium. Dans une réaction ultérieure avec le méthylate
du métal approprié, on a produit la forme Na ou Ca du mica altéré. Les propriétés de l'échantillon
d'origine et de l'échantillon saturé par le sodium ont été comparées afin d'évaluer les variations de
teneur en eau, de densité de charge et de composition chimique (en particulier fer ferreux) qui résultent
du déplacement du potassium.

On n'a pas essayé de calculer les formules structurales car il a été établi qu'on ne pouvait faire
une distinction précise entre l'eau adsorbée et l'eau de constitution dans les échantillons altérés. Les
variations de charge du feuillet sont donc exprimées sur la base des échantillons calcinés à 1000°C.
Des diminutions de charge allant jusqu'à 76 me/100 g ont été enregistrées avec les biotites, des
diminutions plus petites ont été notées avec les phlogopites, et aucune réduction n'a été observée
avec deux muscovites étudiées.

L'oxydation du fer ferreux existe avec tous les échantillons trioccaédriques, l'oxydation la plus
grande concernant les échantillons initialement riches en fer. On n'a pas trouvé de relation nette entre
la quantité de fer oxydé et la diminution de la charge du feuillet.

Tous les échantillons altérés contenaient des quantités de H\textsubscript{2}O\textsuperscript{+} plus élevées que les matériaux
d'origine, ce qui suggère qu'une protonation des atomes d'oxygène du réseau s'est passée pendant ou
après l'extraction du potassium.

On en conclut que l'altération des micas par des cations organiques est un processus complexe,
qui change dans le détail d'un mica à l'autre et qui se développe d'une manière similaire à ce que l'on
observe dans l'altération par des sels minéraux.

Kurzreferat — Zwischenschichtkalium wurde aus einem weiten Bereich von Glimmermineralen durch
Behandlung mit verdünnten Lösungen von n-Dodecyammoniumchlorid entfernt. In der nachfolgenden
Reaktion mit dem entsprechenden Metallmethoxyd wurde die Na\textsuperscript{+} oder Ca\textsuperscript{2+} Form des veränderten
Glimmers erzeugt. Die Eigenschaften der ursprünglichen und der mit Natrium gesättigten Proben
wurden verglichen um die Anderungen im Wassergehalt, der Ladedichte und der chemischen
Zusammensetzung (insbesonders an Ferro-Eisen), die sich aus der Verdrängung des Kaliums ergaben,
zur beurteilen.

Eine Berechnung der Strukturformeln wurde unterlassen, da es sich herausstellte, dass für
die veränderten Proben keine genaue Unterscheidung zwischen adsorbiertem Wasser und struk-
turellem Wasser gemacht werden konnte. Änderungen in der Schichtenladeung werden daher auf der
Grundlage von auf 1000°C gegliederten Proben zum Ausdruck gebracht. Für Biotite wurden Ladungs-
verluste von bis zu 76 me/100 g verzeichnet, während für Phlogopite kleinere Verluste und für
die beiden zur Untersuchung gelangenden Muskovite überhaupt keine Verluste festgestellt wurden.

Oxydation von Ferro-Eisen ergab sich bei allen triokaedrischen Proben, wobei die weitgehendste
Oxydation in den Proben mit hohem Anfängsgewicht an Eisen stattfand. Es konnte keine konsequente
Beziehung zwischen der oxydierten Eisenmenge und dem Verlust an Schichtenladung erkannt werden.

Alle veränderten Proben enthielten grössere Mengen von H\textsubscript{2}O\textsuperscript{+} als die ursprünglichen Stoffe, was
darauf hin deutet, dass während oder nach der Entfernung des Kaliums Protonisierung des strukturellen
Sauerstoffs stattfand. Es wird gefolgert, dass die Änderung von Glimmern durch Reaktion mit organischen Kationen ein
komplizierter Vorgang ist, der sich in Einzelheiten von Glimmer zu Glimmer unterscheidet und
einem ähnlichen Gang wie die Änderung durch Reaktion mit anorganischen Salzen folgt.

Резюме — Из широкого ряда минералов слюды был удален промежуточный калий обработкой
разведенными растворами хлорида n-додециламмония. Последующей реакцией с метилатом
соответствующего металла получались ионы Na\textsuperscript{+} или Ca\textsuperscript{2+} слюды. Свойства первоначальных
или пропитанных натрием образцов сравнивались для определения изменений количеств
воды, плотности заряда и химического состава (в частности содержания двухвалентного
железа), происходящих вследствие смешения калия.

Расчеты структурных формул не производились, т.к. было установлено, что для измененных
образцов нельзя было точно определить разницу между адсорбированной и структурной
водой. Изменения заряда слоя выражены на основе образцов воспламеняемых до 1000°C. Потери заряда до 76 мк/100 гр были зарегистрированы для биотитов, отмечены уменьшения зарядов для флогопитов и не было замечено никаких потерь для двух исследуемых мусковитов.

Окисление двухвалентного железа наблюдалось во всех триоктаэдрических образцах, причем наибольшее окисление оказалось в образцах, имевших вначале большое содержание железа. Постоянного взаимоотношения между количеством окисленного железа и потерей заряда слоя не наблюдалось.

Все измененные образцы содержали больше H₂O⁺, чем первоначальные материалы; это наводит на мысль, что образование протонов структурного кислорода происходило во время или после удаления калия.

Заключение: изменение слюд реакцией с органическими катионами является сложным процессом, отличающимся в деталях для различных слюд и проходящим подобным же путем при изменениях реакции с неорганическими солями.