CHANGES IN INTERLAYER POTASSIUM EXCHANGEABILITY
INDUCED BY HEATING MICAS

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ABSTRACT

Samples of several natural micas and a synthetic fluorphlogopite were heated at temperatures up to 850°C and then placed in NaCl-NaTPB solutions at 25°C to determine the effect of various heat treatments on the exchangeability of their interlayer K. The maximum degree of K exchange was generally unaltered when the samples were heated but major changes in the rate of exchange occurred. The K in muscovite was released much faster if the samples were preheated at temperatures above 350°C and even faster if the temperature were raised to 725°C or the time of heating were increased. As a result, nearly complete exchange of K in <50 μ muscovite particles was achieved in 1 week instead of 2 years. On the other hand, the release of K by biotite and lepidomelane was retarded by similar heat treatments. Lepidomelane was affected by temperatures as low as 250°C and to such an extent that samples heated at 450°C for 24 hours released only 65% of its K in 2 years instead of all its K in 1 week. Phlogopite was relatively unaffected by temperatures up to 650°C whereas fluorphlogopite exhibited a decrease in rate and degree of K exchange when heated at 450°C.

The K release behavior of the heated mica samples was evaluated in terms of Fe⁺⁺ oxidation, dehydroxylation and structural adjustments in heated micas. The significance of dehydroxylation was not clearly defined but a relationship with Fe⁺⁺ oxidation was observed. Fluorphlogopite (no Fe⁺⁺ or OH⁻) was altered by heat; hydrobiotites that contained Fe⁺⁺ were not. Structural adjustments seem to be a major factor.

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INTRODUCTION

The interlayer K in micas is subject to exchange by other cations if the extraction procedure provides enough control over the blocking effects of fixable cations (Hanway et al., 1957; Scott and Smith, 1966) and the mica particles are not too small (Scott, 1968). Even under these conditions the micas exhibit marked differences in their resistance to K depletion. To delineate the reasons for these differences, several comparisons of different micas have been made (Rausell-Colom et al., 1965; Newman, 1970; Mackintosh et al., 1971). Another approach lies in the possibility of using some means of changing the K release behavior of individual micas. To this end the effects of heating micas have been determined.

The fact that micaceous minerals can be heated to change their K release behavior was established some time ago when samples of Grindite illite were heated to eliminate interferences from nitrogen compounds that were present (Smith and Scott, 1963). By heating the illite at 450°C for 24 hours the maximum extractable K (by NaCl-NaTPB solutions) was increased from 68% to 93% even though it is now known that the exchange of K in this mineral is limited by the size of the particles, not by nitrogen compounds. Further evidence that the extraction of K from micas can be modified by preheating the mineral has been provided by Robert (1971) in that less K was shown to be extracted by sodium cobaltinitrite when biotite was heated to oxidize Fe^{++} in the mineral.

Interest in the effects of heat treatments on micaceous minerals also stems from the observation of Tamura and Jacobs (1961) that the selectivity of montmorillonites for Cs can be enhanced by heating the mineral at temperatures ranging from 600° to 700°C. Since cation sorption by micaceous minerals constitutes one means of disposing of radioactive Cs wastes, changing the exchangeability of interlayer cations in micaceous minerals by heat treatments has practical significance.

EXPERIMENTAL

Sheets of muscovite (Effingham Township), biotite (Bancroft), phlogopite (North Burgess) and lepidomelane (Faraday Township) from Ontario, Canada, a synthetic fluorophlogopite supplied by the Mycalex Corporation of America and a coarse-grained hydrobiotite (regularly interstratified vermiculite-biotite) from South Carolina were crushed in a hammer mill and separated into size-fractions. Only samples that did not exhibit limited interlayer K exchange because of small particles were used in this study.

To extract K from the micas, 0.5 g samples were placed in 10 ml 1N NaCl-0.2N NaTPB-0.01M EDTA solutions at 25°C for different periods. The exchange of K by Na was terminated by adding NH_4 , the TPB ions were decomposed by adding HgCl_2 and boiling the solution, and the K in the filtrate from this mixture was determined by flame emission. With this procedure, nearly all the K in coarse particles of dioctahedral as well as trioctahedral micas can be replaced (Scott and Smith, 1966). Many of the 0.5 g samples were heated in a furnace before they were placed in the NaTPB solution to determine the changes in K exchangeability induced by various preheating temperatures and periods. Pyrex erlenmeyers were used with samples heated to 400°C, platinum crucibles for higher temperatures. All samples were placed on a raised platform in a ventilated furnace that was controlled within $\pm 10^\circ$ of the specified temperature and cooled in a dry desiccator.

The method described by Peters (1968) was used to determine the Fe^{++} content of the mica samples. Total Fe and K determinations were made by digesting samples in HF and analyzing the solutions by atomic absorption. Each mica sample was weighed prior to heating and all results are reported in terms of their 110°C-24 hour oven-dry weight.

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RESULTS AND DISCUSSION

K Extraction Curves for Heated Micas

Curves describing the release of K from $<5\mu$ -muscovite and $<50\mu$ -biotite samples that were placed in NaTPB solutions for different periods are shown in Figs. 1 and 2. A comparison of the curves obtained with unheated samples of both micas and then with samples that were heated at 450°C or 600°C for 24 hours brings out the differences in K release behavior of the micas and the effects of preheat treatments on each of them. Essentially all the K ($>95\%$) in the unheated samples of both micas was extracted by this procedure, as would be expected when the particles are this large. However, the times required for a complete exchange of K in the two micas were quite different--about 6 weeks being needed for muscovite, only 1 week for biotite. Considering the difference in maximum size of the muscovite and biotite particles, these results emphasize once more that K in muscovite is much less susceptible to exchange than the K in biotite even when the blocking effects of K in solution are minimized (Scott and Smith, 1966). By preheating the micas, this difference in K release behavior was reversed.

When the muscovite samples were heated before they were placed in the NaTPB solutions, an increase in the rate of K release was observed, whereas heated biotite released K at a slower rate. With both micas, the changes in K exchange rate induced by a preheat temperature of 450°C were further enhanced if the samples were heated at 600°C instead. The maximum degree of exchange attained with all the samples, however, remained essentially unchanged. Thus, the magnitude of the effect of preheating the micas is best reflected in the changes in time required for complete K exchange--a reduction to only 2 days for muscovite, an increase to 20 weeks for biotite.

Comparisons of the data in Figs. 1 and 2 with previous observations that have been made with heated micaceous minerals show the K in muscovite becomes

more susceptible to exchange as did the K in heated Grundite illite (Smith and Scott, 1963) and the resistance of biotite to K depletion was enhanced by heat treatments as reported by Robert (1971). Unlike the results presented by Robert, however, the degree of K exchange attained with biotite in NaTPB solutions was not reduced by prior heating; only the rate of exchange was impaired. This difference in results is presumably due to the maintenance of a lower level of K in solutions that contain NaTPB rather than sodium cobaltinitrite (solubility of potassium tetraphenylboron and potassium cobaltinitrite in water being 1.8×10^{-4} and 2×10^{-3} mole/l, respectively). Upon heating, the selectivity of biotite for K is enhanced and the concentration of K in the extracting solution must be reduced to levels approaching those required by muscovite if complete exchange of the interlayer K is desired. Whereas Robert (1971) extracted little more than 20% of the K in muscovite by sodium cobaltinitrite solutions, no unheated mica particles of comparable size have yet been found that do not release essentially all their K to NaTPB solutions.

Mica Response to Different Temperatures

To characterize completely the effects of a particular heat pretreatment on the exchangeability of K in mica samples it is necessary to show the entire K extraction curves as was done in Figs. 1 and 2. However, to show the range of effects that can be achieved with different temperatures and to compare micas in terms of their response to preheating, the amount of K extracted in selected contact periods with NaTPB solutions can be used. This procedure has been used in Fig. 3 to show the changes in K exchange induced in $<50\mu$ samples of muscovite and three trioctahedral micas by 24-hour treatments with a range of temperatures. The lepidomelane curve shows the amounts of K extracted in 1 day whereas the other mica curves were determined with 1-week extraction periods. The selection of these extraction periods was based on the observation that these points on the K extraction curves for the respective micas were particularly responsive

to the changes induced by preheating. In 1 week, edge weathering was just beginning in the muscovite sample, whereas, the exchange of K was essentially complete in 1 day for lepidomelane and in 1 week for the biotite and phlogopite samples. It must be emphasized that the curves in Fig. 3 reflect the changes in K exchange rate that were produced by preheating, not the maximum degree of exchange achieved.

Preheating the muscovite sample at temperatures up to 350°C produced a small decrease in the amount of K released in 1 week. As the preheat temperature was increased further, however, the rate of K release increased rapidly to a maximum in the samples that were heated at 725°C. At this maximum rate of K release, 95% of the K in the $<50\mu$ muscovite particles was replaced in 1 week instead of the 2 years required with unheated samples.

As shown in Fig. 1, preheating the biotite samples reduced the rate of K exchange but the curve in Fig. 3 shows this change is negligible until the temperature exceeds 350°C. Moreover, additional reductions in K release rate were observed with temperatures above 600°C. By comparison, the phlogopite was little affected by preheat temperatures up to 650°C, while the lepidomelane was altered by temperatures as low as 250°C and to a greater degree by all comparable temperatures. The difference between biotite and lepidomelane is evident in their response to preheating at 450°C, but the difference is even more striking if data for longer contact periods with NaTPB are considered. For instance, the 450°C-24 hour treatment prolonged the period for complete K exchange in biotite to 6 weeks whereas samples of the lepidomelane that released all their K in 1 week if unheated released only 65% of their K in a 2-year period following the same heat pretreatment. At this rate of K release, several more years will have to elapse before it is known if complete K exchange will occur in this heated lepidomelane. K extraction data that were obtained with contact periods under 1 week show the phlogopite is not entirely immune to the effects

of preheating. A small decrease in the rate of K release was observed in phlogopite samples that were heated at 600°C but the change was too small to prevent complete exchange within a week.

Considering the data for all the micas in Fig. 3, it is evident that differences in the response of micas to preheating exist, not only between dioctahedral and trioctahedral mica groups, but among the trioctahedral micas as well. Much of this response can be achieved with temperatures between 300°C and 650°C. With temperatures exceeding 750°C appreciable reductions in K exchange rates occurred with muscovite and phlogopite. The biotite and lepidomelane samples released K so slowly after being heated at 750°C additional effects from higher temperatures were not discernible.

Effect of Heating Period on Micas

Since the muscovite and lepidomelane samples exhibited major changes in K exchangeability upon heating, these minerals were selected for a determination of the rate with which the heating effect occurs. Samples of <5 μ muscovite and <50 μ lepidomelane were heated at 300°C, 450°C and 600°C for different periods, cooled and then placed in NaTPB solutions for 1 day. The curves in Fig. 4 depict the changes in K exchange that were induced.

Muscovite was unaffected by even long periods of heating at 300°C but was progressively more altered as the time of heating at 450°C and 600°C were increased. Apparently, there is a minimum temperature between 300°C and 450°C that is needed to initiate a change in K exchangeability in this mineral, but the existence of a time-temperature interaction complicates further delineation of this minimum temperature. Indeed, the 2-hour lag in the muscovite response to heating at 450°C suggests the initial alterations of the mica may be complex. With lepidomelane, the minimum temperature for changes in K exchangeability was lower (<300°C) and the rate with which these changes occurred with heating were greater than those observed with muscovite. With both micas the higher tempera-

tures provided the most effective means of changing the exchangeability of K but it is obvious that longer heat periods can be substituted for higher temperatures to attain much of the changes. Since a large segment of each curve in Fig. 4 has a logarithmic form, the preheat time required for maximum change in K exchange could be quite long at low temperatures, but, with any temperature, it is necessary to specify both the time and the temperature when the degree or cause of the changes in K exchangeability is considered.

Relation to Mineral Characteristics

The changes in K exchangeability that occurred when micas were heated are in accord with the potential effects of changes in $d(001)$ that have been observed or anticipated for heated micas. Since muscovite has been shown to expand in the c direction when heated (Cole, 1969; Vedder and Wilkins, 1969), there could be more space between the layers that would allow easier release of K in heated samples. On the other hand, Drits (1969) has pointed out that a loss of OH groups in trioctahedral micas leads to a decrease in $d(001)$. Heating the trioctahedral micas, therefore, could reduce the interlayer separation and make the interlayer K more difficult to replace. Measurements of the $d(001)$ of heated and unheated samples of the micas characterized in Fig. 3 verified that such changes in basal spacing did occur in these micas, but the magnitude of the changes (based on 5 to 7 orders) were too small to be more than indicative of whether an increase or decrease in K exchangeability could be expected. Also, the validity of this conclusion is limited by the degree to which the changes in $d(001)$ are due to variations in layer thickness.

Details regarding the orientation of OH^- ions in various micas, the changes in orientation or loss of OH^- ions through oxidation, dehydroxylation or deprotonation processes, and the impact of the interactions between interlayer K and OH^- , O^{2-} or F^- ions on the alteration of micas by K depletion have been amply described (Serratosa and Bradley, 1958; Bassett, 1960; Vedder and McDonald, 1963;

Barshad and Kishk, 1968; Vedder and Wilkins, 1969; Juo and White, 1969; Rimsaite, 1970; Robert, 1971). Attention to these mineral characteristics should be useful in an interpretation of the K release data that depict different responses of micas to heating.

The fact that interlayer K in muscovite is less susceptible to exchange than the K in biotite or phlogopite is well known (compare the unheated mica curves in Figs. 1 and 2) and is often attributed to the orientation of the OH^- ions in muscovite being less perpendicular to the cleavage plane (Bassett, 1960). Now we find the K in heated muscovite is as easily replaced as that in unheated biotite even though no changes in the orientation of the OH^- ions are believed to occur when muscovite is heated (Fripiat et al., 1966). Furthermore, any effects the OH dipoles might have on interlayer K in muscovite should have been reduced by dehydroxylation and identified by a decrease in K exchange in the heated samples. Since this did not happen, there seems to be a good possibility that OH^- ions have little significance on the exchange of K in muscovite.

The onset of the changes in K exchangeability in heated muscovite occurred near the temperature (350°C) at which exothermic peaks appear in DTA curves from a release of strain in the mineral structure (Mackenzie, 1970) and Hutchison (1966) observed peaks in the decrepitation curves for this mica. Coupled with the observation that the b and c dimensions of muscovite are increased by heating and increased tilting of the tetrahedra occurs in dehydroxylated mica (Vedder and Wilkins, 1969), these relationships suggest that the K in muscovite is made more susceptible to exchange by spatial adjustments in the structure. To have a time dependent change in K exchangeability (Fig. 4) some process like dehydroxylation must be contributing to this structural rearrangement.

The changes in K exchangeability that were observed with heated triocta-

hedral micas were consistent with the effects anticipated from a loss of protons by dehydroxylation and Fe^{++} oxidation during the heat treatment. That is, the loss of protons would leave the K in a more negative environment and thereby make the K less easily replaced. To delineate the relative contribution of the two processes, however, it was necessary to determine the amount of Fe in each mica and the degree of Fe^{++} oxidation attained by heating. The phlogopite, biotite and lepidomelane contained 25.2, 226 and 283 m moles total Fe per 100g and 24.5, 214 and 276 m moles Fe^{++} per 100g, respectively. The extent to which the Fe^{++} in lepidomelane was oxidized by heating samples for 24 hours at different temperatures and the effect of these heat treatments on the amount of K extracted in 24 hours by NaTPB solutions are shown in Fig. 5. Obviously, the Fe^{++} was oxidized and the changes in K exchange were inversely related to the degree of oxidation. By comparison, the phlogopite data (Fig. 3) show the changes in K exchange were small when there was little Fe^{++} in the mineral for oxidation.

By means of TGA curves, it was established that all the micas characterized in Fig. 3 gradually lost weight ($<1\%$) when they were heated from 300° to 700°C . The samples heated for 24 hours at specified temperatures would have no doubt lost even more weight (Roy, 1949) and presumably the weight reduction means the micas suffered some loss of protons by dehydroxylation. The effect of this dehydroxylation on the K exchange behavior of trioctahedral micas seems to be small (phlogopite data) relative to the changes involving Fe^{++} oxidation. Fe^{++} oxidation without a loss of protons would reduce the exchangeability of K by changing the orientation of OH^- ions but this possibility is remote in heated micas. The relative effects of Fe^{++} oxidation and dehydroxylation are more likely due to differences in the number of protons lost and the number of O^- left by the two processes. The sharp decrease in K exchangeability in phlogopite at temperatures $>750^\circ\text{C}$ could very well be due to a major increase in dehydroxylation.

At the same time, the relationship between K exchange and Fe^{++} oxidation is not as close as expected, in that the changes in K exchange started at a lower temperature, developed faster, and ended at a lower temperature than the Fe^{++} oxidation.

Explanations for the changes in K exchangeability in heated micaceous minerals have had to contend with more and more complexities as a wider variety of minerals have been tested for their response to heat. This point is illustrated by the results that were obtained with 2-5 μ fluorophlogopite and <50 μ hydrobiotite samples (Fig. 6). Even though the synthetic fluorophlogopite contained no hydroxyls or Fe^{++} , the rate of K exchange was reduced by heating samples at 450°C for 24 hours. In this respect, the synthetic mica behaved like the natural trioctahedral micas but showed the decrease in K exchange does not need to entail the processes of dehydroxylation or Fe^{++} oxidation. The synthetic fluorophlogopite was also distinctive in that the maximum degree of K exchange was reduced by the heat treatment. When the hydrobiotite samples were heated, exfoliation occurred and caused a marked increase in the initial amount of K extracted. This effect of exfoliation can arise even with micas but is usually not significant unless the particles are large (Gaines and Vedder, 1964) and was not a problem with the other mica samples used in this study. After the initial release of K by exfoliation, the rate of K release was not appreciably different in the heated and unheated samples of hydrobiotite. Similar results have been obtained with other hydrobiotites even though the amount of Fe^{++} in all samples ranged from 18 to 90 m moles per 100g. With these minerals, dehydroxylation and Fe^{++} oxidation by heat treatments seems to have little effect on the process of K exchange.

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FIGURE LEGENDS

FIG. 1. K extracted from $<5\mu$ muscovite by different contact periods with NaTPB solutions after 24-hour periods of heating at different temperatures

FIG. 2. K extracted from $<50\mu$ biotite by different contact periods with NaTPB solutions after 24-hour periods of heating at different temperatures

FIG. 3. K extracted from $<50\mu$ micas by contact with NaTPB solutions for 1 day (lepidomelane) or 1 week (other micas) after 24-hour periods of heating at different temperatures

FIG. 4. Effect of time of heating $<5\mu$ muscovite and $<50\mu$ lepidomelane at different temperatures on K extracted in 1 day by NaTPB solutions

FIG. 5. Fe^{++} oxidized by heating $<50\mu$ lepidomelane for 24 hours at different temperatures and associated change in K extracted in 1 day by NaTPB solutions (unheated mica: 276 m moles Fe^{++} per 100g; 178 me K per 100g)

FIG. 6. K extracted from $<50\mu$ hydrobiotite and 2-5 μ fluorophlogopite by different contact periods with NaTPB solutions after 24-hour periods of heating at different temperatures