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EXCHANGE OF INTERLAYER CATIONS IN MICACEOUS MINERALS

Progress Report

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ABSTRACT

The sorption and exchange of cations on interlayer sites of micaceous minerals has been studied in terms of six distinct subdivisions. 1. Comparisons of Cs sorption by degraded micas in acetone or boiling solutions have shown the interlayer cation population can be variable and a factor governing the exchangeability of added Cs. Ways of producing Na-degraded mica with negligible K for controlled Cs sorption experiments have been developed. 2. Determinations of maximum levels of indigenous Cs, Rb and K exchange in lepidolite support the idea that these cations occur in a random distribution throughout each interlayer space. 3. A look at interlayer cation exchange with solutions that have a composition comparable to real radioactive wastes has been initiated with emphasis on the effects of Al. 4. As much as 80% of the octahedral Fe^{++} in mica has been oxidized by $\text{Br}_2\text{-NaCl}$ solutions, whereas lesser amounts of oxidation occurred when expansion was controlled by K. 5. Detailed exchange studies with heated micas have identified a retardation effect of heat on dehydroxylated muscovite and correlation with Fe^{++} oxidation in lepidomalane. 6. The elimination of small particle effects with large mica-solution ratios has been re-examined.

DETAILED REPORT

While the experimental work carried out in this project during the past year has been as extensive as in the past and has continued to entail a detailed study of several diverse aspects of interlayer cation exchange, an attempt has been made to present a more abbreviated progress report than heretofore. To do so, less background material and a minimum of illustrative data have been included. However, the following subdivision of our activities should help delineate the areas of major emphasis and identify our general accomplishments.

Sorption and Exchange of Added Interlayer Cs

In contrast to the numerous investigations and reports dealing with Cs sorption and exchange on the peripherally exposed sites of micaceous minerals, the experimental work carried out in this project pertains to the interaction of Cs with interlayer exchange sites of layer silicates that tend to be contracted by the presence of interlayer Cs, Rb, K or NH_4 . Consequently, the conditions governing the accessibility of the exchange sites as well as the simple aspects of ion competition and Cs retention forces have demanded attention. Moreover, our intention has been to delineate and characterize the factors governing both the sorption of added Cs by these sites and the subsequent exchangeability of this sorbed Cs.

Previous reports (document OOO-1680-19) have described our initial approach of adding Cs to NaCl-NaTPB-degraded mica mixtures to prepare micaceous mineral samples with interlayer added Cs and some of the results we have obtained in subsequent determinations of the exchange of this Cs. This approach has been continued while a more systematic attack on the preparation of M degraded mica (where M is a specified population of sorbed cations), the controlled exchange of Cs for M and then the exchange of the sorbed Cs has been initiated. Some of the ramifications encountered and the progress attained with both approaches can be outlined as follows.

After Cs is added to NaCl-NaTPB-mica mixtures, the mineral must be freed of Cl^- and TPB^- salts. To do so, acetone has been added to dissolve TPB-precipitates or boiling procedures have been used to decompose the TPB^- ion. The mineral samples produced by these means have varied in many respects. Differences in regard to cation population (less Cs versus Na in acetone treated samples), cation distribution in various interlayers and even the mineral layer charge have been observed. In addition, the relative effect of the two methods of removing TPB^- salts has varied with the mineral, the concentration of Cs in solution and the size of the mineral sample involved. A lack of Cs sorption by acetone treated samples has prompted greater emphasis on the use of boiled samples for Cs exchange work but limitations on the size of the sample that can be prepared by boiling procedures have been encountered. Procedure modifications that will circumvent these difficulties and capitalize on their differences are being given further consideration.

Cs exchange by Na has been investigated with a few grams of Cs degraded micas that were prepared by boiling NaTPB-degraded mica mixtures with CsCl . Earlier ob-

servations of a decrease in Cs exchangeability in heated lepidomelane samples (document COO-1680-13) was attributed to Fe^{++} oxidation. As shown in Figure 1, however, the exchange of added Cs in a lepidolite sample, that exhibits little effect of heat on indigenous interlayer cation exchange (due to a lack of Fe^{++} oxidation or dehydroxylation), is also greatly retarded by 450°C heat treatments. The role of cation dehydration and interlayer spacing in the Cs exchange behavior of these minerals remains to be seen, but the data in Figure 2 make it clear that the population and distribution of other cations in the interlayers can be involved. The Cs-degraded samples of lepidomelane and lepidolite contained essentially the same amount of K (about 11 me/100 g) but a comparison of the Cs and K exchange data obtained with each sample shows the K was interspersed with the interlayer Cs in the lepidomelane but was largely confined to the inner core of the lepidolite particles. Without such information, the interpretation of interlayer Cs exchange data is questionable.

Most comparisons of the exchangeability of Cs and K on micaceous minerals have been reported in the literature as showing the Cs is the more difficult cation to replace. This conclusion applies to peripherally held cations and to those fixed between the layers of natural vermiculites. Thus, it was anticipated that interlayer added Cs in degraded micas would be less susceptible to exchange than K (i.e. less replaced by an equilibrium exchange) but we are finding (Figure 3) that the Cs is replaced at a slower rate than K even when the system maximizes the diffusion gradient by the precipitation of replaced Cs or K. Such distinctions will help us sort out the relative effects of mineral-cation interactions in the expanded edges versus the contracted weathering front.

The ill-defined effects of varying amounts and distributions of Na and read-sorbed K on the exchange of interlayer Cs in mineral samples that have been prepared by mixing CsCl with NaCl-NaTPB-mica have emphasized the need to approach the problem by the preparation of M degraded mica instead. Moreover, it is only with M degraded micas that we can study the process of Cs sorption under well defined and controlled conditions. Despite our many efforts to follow this approach, however, we have been continually hampered by the occurrence of K read-sorption. The degree of this difficulty is illustrated by Table 1 which shows a completely degraded 0.5 g sample of lepidomelane in 10 ml 1N NaCl-0.2 M NaTPB solution will readsorb 85 me K/100 g if the KTPB is dissolved in its presence. Various modifications in the procedure, e.g. the use of acetone or dioxane to decrease the disassociation of KTPB, drying the mineral to contract the layers before they were exposed to K, etc., proved ineffective but the beneficial effects attained by washing a filtered sample with NaCl-acetone gave us a solution to our problem.

Table 1. Effect of KTPB removal procedures on the readsorption of K by degraded lepidomelane samples

Sample Treatment	KTPB Removal	Sorbed Cations	
		K -- me/100 g --	Na
Not filtered	1N NaCl - 60% acetone	85.0	145
Filtered	1N NaCl - 60% acetone	32.5	203
Filtered - air dried	1N NaCl - 60% acetone	67.3	169
Filtered	100% acetone	88.0	136
Filtered	100% dioxane	69.5	171

For other aspects of this project, especially the study of mineral-solution ratio effects and the exchange of small amounts of indigenous interlayer Cs, it was necessary to establish procedures whereby NaCl-NaTPB-degraded mica mixtures could be freed of excess NaTPB before the degradation process was terminated by NH_4Cl additions. In doing so, it was shown that no readsorption of K by the mineral occurred if the mixture was simply filtered. Thus, this filtration procedure was extended to the preparation of M degraded mica by washing the filtered residue with NaCl-acetone and by saving the NaCl-NaTPB filtrate for successive treatments of the mica. Even though the rate of NaCl-acetone addition was geared to the filtration rate to minimize dissolved K-mica contacts, we were unable at first to reduce the readsorbed K to less than 8 me/100 g. As shown by the data in Table 2, however, we have been able to further modify our procedure to obtain degraded mica with no more than 1 me K/100 g.

Table 2. Effect of successive NaCl-NaTPB, filtration and NaCl-acetone treatments on the K content and layer charge of degraded lepidomelane

Sample Treatment	Sorbed Cations		Layer Charge
	K ----- me/100 g -----	Na	
Na saturated original mica	194	26	220
Mica in NaCl-NaTPB solution 2 mon., filtered, 1N NaCl-60% acetone washed	40.0	167	207
Residue in NaCl-NaTPB solution 30 min., filtered, 1N NaCl-60% acetone washed	14.4	199	213
Residue in NaCl-NaTPB solution 30 min., filtered, 1N NaCl-60% acetone washed	3.7	203	207
Residue in NaCl-NaTPB solution 30 min., filtered, 1N NaCl-60% acetone washed	1.2	203	204
Residue in NaCl-NaTPB solution 30 min., filtered, 1N NaCl-60% acetone washed	1.1	202	203
Residue in NaCl-NaTPB solution 30 min., filtered, 1N NaCl-60% acetone washed	1.1	206	207

The results in Table 2 were obtained with samples of lepidomelane which usually loses much of its layer charge when K depleted. The loss in layer charge reported in Table 2 was no more than 17 me/100 g and thus constitutes a further benefit of this procedure and an indication of new approaches to a study of the role of layer charge on the exchange of interlayer cations. When the layer charge of biotites remains high they present problems similar to those encountered with the dioctahedral minerals. Using the above procedure to prepare Na degraded lepidolite the question soon arose as to how this Na mica should be handled to avoid contraction before Cs exchange experiments could be made. We now find that even air drying at a relative humidity of about 40% can cause an irreversible collapse of the Na degraded lepidolite. Thus, we are not yet in the position of initiating the Cs sorption studies we would like made with well defined M degraded micas.

Exchange of Indigenous Interlayer Cs

The exchange of indigenous interlayer Cs (as well as the coexisting interlayer K and Rb) in seven lepidolite fractions ranging from 10-20 μ to <0.2 μ in particle size was continued throughout the past year. Previous reports on this subject have been limited to extraction periods of under one year which did not achieve all the exchange that is possible with the coarser fractions. Thus, the main intent of our continuing these determinations has been the attainment of maximum levels of exchange but some of the work was designed to verify and improve previous data.

Lepidolite has proved to be one of the slowest releasers of interlayer cations. While this may be explained by the presence of Cs and Rb which are supposedly bonded more strongly than K, similar behavior of lepidolite with added interlayer cations is indicating that it is a mineral related situation. In either event, after 150 weeks the 10-20 μ fraction is finally approaching its maximum interlayer cation release. At this stage, the release of Cs, Rb, and K seems to be nearly equivalent in that 98, 97 and 95%, respectively, was replaced. Even better comparisons of the maximum degrees of Cs, Rb and K exchange can be made with the 2-5 μ and the <0.2 μ fractions because even the 100 week contact periods achieved this year were more than adequate to ensure maximum release. With the 2-5 μ particles, the maximum exchange of Cs, Rb and K amounted to 93, 92 and 92% whereas the <2.0 μ particles released 75, 74 and 75%, respectively. Not only did the lepidolite particles release equivalent amounts of the 3 cations, but the limitations of particle size on the degree of exchange was the same for all. From all this data and the earlier reported kinetics for these systems, we can conclude that the 3 cations coexist in each interlayer space and are randomly distributed in proportion to the total amount of each cation in the mineral. Such a conclusion raises many new questions; e.g. why does the presence of so much Rb (39 me/100 g) and Cs (2.6 me/100 g) in each interlayer space not increase the 001 spacing of the mineral over that expected for just the smaller interlayer K ion. However, the results we have already obtained with these indigenous interlayer cations is providing a useful basis for comparisons with the exchange behavior of added cations.

Solution Composition and Procedures for Cs Exchange

When this project was initiated a considerable amount of information about

the effects of procedure and solution composition on the exchangeability of inter-layer cations was already available. However, this subject has continued to be a major facet of our project and has prompted our looking at the effects of various counter cations, salt concentrations, etc. Most of our attention has been deliberately concentrated on the achievement of maximum replacement or sorption of the cations (K, Rb, Cs, NH_4) that contract the layers of highly charged micaceous minerals because we would like to sort out the processes and factors governing the exchange of cations on interlayer sites. When it comes to a specific situation where radioactive Cs in a waste solution of particular composition is to be separated by ion exchange, our results have useful predictive value. Still, a look at the exchangeability of fixable cations with solutions that simulate the composition of real wastes has been undertaken.

We initiated this work by a research for a typical waste composition to emulate but have found the non-radioactive portion of the wastes is frequently not defined and when it is the variations from one location to another can be quite extreme. The high concentrations of NaNO_3 encountered in many of these solutions offer little difficulty because Na-Cs interactions are relatively well known. Likewise the effects of H in solutions that vary widely in pH can be predicted but the associated question of the Al in these solutions is another matter. Many of the wastes contain high levels of Al which will range in form from Al^{+++} to aluminate ions as the pH is varied and may pose additional problems through hydroxy-Al interactions with layer silicates. Consequently, experiments on the role of Al have been started. So far, we have worked with a commercial hydroxy-Al solution (6.2M Al) that is used for clay stabilization in the oil industry but have not encountered any unusual results.

Role of Structural Iron

Since the reasons for our interest in the effects of structural Fe on inter-layer cation exchange, the changes in Fe redox status achieved by others and our own success in changing the exchangeability of interlayer cation by oxidizing the Fe in lepidomelane with H_2O_2 have been discussed in previous reports (e.g. documents COO-1680-13 and COO-1680-19), no repetition of this background material is needed here. Suffice it to say that we found H_2O_2 treatments did not oxidize Fe in lepidomelane particles until the Fe was exposed by an expansion of K depleted zones of the mica. Consequently, we were skeptical that changes in the exchangeability of the interlayer cations in contracted micas could be achieved by wet chemical methods of oxidizing or reducing Fe in the mineral. Subsequent experiments with Br_2 treated lepidomelane samples, however, have reopened the question and have led to a very intensive study of the effects of Br_2 treatments during the past year.

After preliminary experiments with lepidomelane samples in Br_2 saturated H_2O , 1N NaCl or 1N KCl produced more Fe oxidation than expected, numerous experiments were initiated to determine the conditions required for this oxidation and the extent to which the Fe can be oxidized. The variables included different temperatures (25° , 90° , and 160°C), particle size (50-60 μ , 10-20 μ and 2-5 μ); solution volume (10 to 9000 ml), salt solution (NaCl, KCl or none), KCl concentration (1N to saturated) etc. Obviously, it is not possible to include much of the data from such

a variety of experiments in a short report. Moreover many of the experiments are still underway even though they have been in progress for more than 30 weeks and could be misleading if judged prematurely. Still, the fact that Br_2 oxidation of Fe^{++} was achieved in mica particles that were surrounded by enough KCl to presumably keep the mineral contracted is significant enough to warrant our immediate attention.

The oxidation of Fe in micas has been reported by several other people, but Br_2 saturated H_2O or salt solutions permitting K release have been invariably used. As shown in Figure 4 such conditions do cause a considerable amount of oxidation. These data were obtained with 0.5 g mica sealed in a glass ampule with 10 ml Br_2 saturated solution. Placing this much mica in such a small volume of solution should have kept the release of K even in 1N NaCl to a very low level--certainly not enough to expose 75% of the Fe to oxidation by layer expansion. Yet the difference in K release expected with NaCl versus H_2O does show up in more Fe oxidation. Whether K release and Fe oxidation continue as associated processes remains to be seen but it is clear that K additions do retard Fe oxidation and that the concentration of K is important. Such data suggests that most samples of mica that have been treated with Br_2 to oxidize structural Fe are probably no longer fully contracted and that the subsequent K release data should not be interpreted in terms of Fe oxidation alone.

Having shown that solution K inhibits Fe oxidation by Br_2 , it is quite surprising that the oxidation process cannot be stopped entirely by even saturated KCl solutions. However, it is probably the saturated KCl systems that will help us learn why Fe oxidation continues when lesser amounts of K are released to water.

While the emphasis during the past year has been on the Fe oxidation process itself, some determinations of K release from samples with different Fe^{++} levels have been made. So far these results confirm published reports of reduced K exchangeability in oxidized samples. Much more work is needed, however, before these results can be related to the status of the mineral and the oxidation procedure employed.

Heated Micaceous Minerals

While the effects of heat treatments on the exchangeability of interlayer cations in micaceous minerals has been given major and long time attention in this project the subject continues to be one of the most fascinating approaches to a delineation of mineral characteristics governing interlayer cation exchange. Initially it seemed as though we had a situation where heat treatments simply enhanced the exchangeability of interlayer cations in dioctahedral micas and inhibited exchange in trioctahedral. A survey of these effects with coarse mica samples (document C00-1680-15) and with naturally-occurring, fine-grained micaceous minerals (document C00-1680-17) made it clear, however, that the subject is very complex and fraught with inconsistencies as to the role of the mineral. Thus, detailed studies were initiated with muscovite (dioctahedral) and lepidomelane (trioctahedral) samples to determine how these heat induced changes occur.

Using the amount of K extracted by 1 week contact periods with NaCl-NaTPB solutions as an index of the changes in K exchangeability in heated muscovite, we established a close relationship between this change and the degree of dehydroxylation in the mica. Heating temperatures up to 700°C and a wide range of heating periods gave results that were consistent with this observation but combinations of higher temperatures and even short heating periods produced either no increase in K release or a decrease in release. Since this change in the response of the mica to heat occurred when maximum dehydroxylation was approached, it was concluded that recrystallization of the mica must be rendering part of the K nonexchangeable. The data in Figure 5 shows this is not the case.

Complete K extraction curves were obtained with <50 μ muscovite samples that were heated at different temperatures and for different periods. Some of the curves obtained with samples heated 24 hours at selected temperatures are given in Figure 5. As the heating temperature was increased from 25°C to 600°C the rate of initial K release was increased but much of the K was still released at a slow rate. Higher temperatures were needed to make more of the K susceptible to faster release. Such results can be explained by the development of a peripheral zone of dehydroxylation in the heated mica particles and an enhancement of K release rate from only the dehydroxylated zone. However, before all the mica is dehydroxylated and all the K is made more susceptible to exchange, a delay in the initiation of K release by heated micas sets in. This delay was evident with samples heated at only 650°C and becomes more marked as the temperature was increased to 800°C and then to 900°C. It is this initial time lag in K release that is responsible for the reduction in 1 week K release values reported earlier in connection with our dehydroxylation studies--not a decrease in exchangeable K through recrystallization.

While the data we have obtained with muscovite and illustrated by Figure 5 is consistent with our previous conclusions that dehydroxylation accounts for the enhanced K release in dioctahedral micas, we now find the dehydroxylated mica is exhibiting heat induced changes in K exchangeability that are comparable to trioctahedral micas. This behavior of dioctahedral micas cannot be attributed to Fe^{++} oxidation as has been done with some trioctahedral micas, yet trioctahedral micas with little Fe^{++} but no potential for dehydroxylation do not show this behavior. Thus, many aspects of these changes in K exchangeability that can be induced by heat treatments continue to be unresolved and the subject of our ongoing investigation.

Detailed studies with heated lepidomelane samples have concentrated on the role of Fe oxidation and the changes in whole K release curves by a variety of heat treatments. Only the Fe oxidation data will be presented to illustrate the nature of our work and results.

Individual 0.5 g samples of 5-10 μ lepidomelane were heated at temperatures ranging from 300°C to 900°C and for different periods and then analyzed for Fe^{++} or degraded in NaCl-NaTPB for 3 days. The 3 day K release values were used as an index of the heat induced effects and were correlated with the degree of Fe oxidation achieved by the same heat treatments. Some of the results are presented in Figure 6. It is evident that the heat induced changes in K release and Fe oxidation are closely related. Such a good relationship prompts us to conclude that

the redox status of Fe in micas has a major influence on interlayer K exchangeability.

Our other experiments on K release curves are showing us that the role of Fe is not as simple as Figure 5 might suggest. They are also making it clear that the release of K from heated lepidomelane can be extremely slow--contact periods much longer than our current 40 week periods being needed for samples that would release all their K in 3 days if unheated. This slowness in K release will delay further conclusions about the role of structural Fe because some particularly pertinent changes in K release behavior are showing up in the very long degradation periods.

Now that we have been successful in oxidizing Fe in mica samples by wet chemical methods (Br_2) it will be possible for us to compare the effects of comparable degrees of Fe oxidation that have been achieved by heat or Br_2 treatment. Such experiments are already underway.

Small Particle Effects

The limitations imposed by particle size on the degree of interlayer cation exchange that is attainable with small particles has been a persistent problem throughout the life of this project. Moreover, as Norrish pointed out in his review at the 1972 International Clay Conference (citation in project proposal) this particle-size effect is of major concern to everyone dealing with mica weathering. The very persistence of fine grained micaceous minerals in soils attests to the lack of interlayer cation release by small particles. Consequently, we have continually sought an explanation for this small particle-size effect and to this end we have looked for ways to replace the interlayer cations in even small particles.

One of our approaches that seems to provide more exchange in fine material is that of using small mica samples in large volumes of solution (large mica/solution ratios). Despite our earlier reports that most of the K in samples of natural illites and finely ground micas may be replaced by wide enough mica/solution ratios, further work in the past year has raised questions about the quantitative aspects of these results. The problem involves the magnitude of the blank K values that can be encountered with very large volumes of NaCl-NaTPB solution. When the mica sample is also reduced to obtain adequately large mica/solution ratios, the blank K values can be too large a part of the total K determination to allow much confidence in the extracted K values. Consequently various ways of reducing the blank K values by filtering NaCl-NaTPB-mica mixtures and re-using the filtrate with new mica samples, determining the accuracy with which corrections for the blank can be made and using large mica samples despite the excessive cost of correspondingly large amounts of NaTPB have been explored. The results have been disappointing but this line of work has not yet been abandoned because the existence of some effect of mica/solution ratios is well established.

Another approach we have been using in our study of small particle effects is based on the concept that the opening of some layers makes the cations in adjacent interlayers more resistant to exchange. Presumably, all the interlayer cations would be replaceable if all layer weathering is avoided and the exchange process occurs by edge weathering only. So far, however, our experimental results have

not matched this expectation.

PUBLICATIONS

Oral presentation: Exchangeability of potassium in heated muscovite.
L. M. Kozak and A. D. Scott. 1973 Clay Minerals Conf. (Banff) 1973.

TIME ON PROJECT

A. D. Scott, Principal Investigator

August 1, 1973 - April 30, 1974 ----- 30%
May 1, 1974 - July 31, 1974 ----- 30% anticipated

PREPARED BY

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Fig. 1 - Amounts of indigenous Cs in original mica and added Cs in air dry and heated degraded mica extracted by NaCl-NaTPB solutions.

Fig. 2 - Comparison of residual K and added Cs extracted from degraded mica samples in NaCl-NaTPB solutions.

Fig. 3 - Exchange of K in K-degraded and of Cs in Cs-degraded lepidomelane by contact with NaCl-NaTPB solutions.

Fig. 4 - Degree of Fe^{++} oxidation due to Br_2 treatments of lepidomelane at $90^\circ C$.

Fig. 5 - Amounts of K extracted from muscovite by NaCl-NaTPB solutions after samples were heated at different temperatures for 24 hours.

Fig. 6 - Effect of heat induced Fe^{++} oxidation on the amount of K extracted in 3 days by NaCl-NaTPB solutions.