EXCHANGE OF INTERLAYER CATIONS IN MICACEOUS MINERALS

Progress Report

by
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ABSTRACT

A basis for studying indigenous interlayer Cs exchange was established by surveying the Cs content of micas and modifying the exchange procedures. Various size-fractions of lepidolite were then degraded and the percentage Cs, Rb and K exchanged in specified periods were shown to be the same. Moreover, the Cs exchange data reflected the effects of particle size already established with K. An exchange of Cs for Na in degraded samples of the same lepidolite size-fractions was carried out and the exchangeability of this added Cs was determined. Major differences in the exchange data for indigenous and added Cs, dried or heated samples, and lepidolite or lepidomelane fractions were observed.

Detailed studies of the changes in interlayer K exchangeability that are induced by preheating coarse-grained muscovite at different temperatures and for different periods established a close relationship between the rate of K exchange and the weight lost by dehydroxylation. Additions of H_2O_2 to solutions employed in the exchange of Na for interlayer cations in lepidomelane produced a major increase in the rate of exchange that could not be related to Fe oxidation in the mica core or exfoliation by evolved oxygen.

DETAILED REPORT

A substantive summary of the activities and accomplishments of the past three years of this project has been prepared this year (Document GCO-1680-19). Thus, a detailed account of our progress for the past year would be unduly repetitive. A brief statement identifying the contributions from just the one year will be presented instead.

1. Indigenous Cs: A survey of the Cs content of available mica samples was continued but failed to produce a mineral with more interlayer Cs and Rb than the lepidolite selected initially for a study of interlayer Cs exchange. A sample of this lepidolite was dry ground in a Shatterbox and several size fractions were separated and characterized in terms of total and NaTPB-extractable Cs, Rb and K. To do so, further work on methods of analyzing solutions of the three cations, and techniques for small amounts of exchange had to be carried out. Some of the coarse size-fractions are still undergoing treatment because this mineral releases its interlayer cations very slowly. However, the exchange data for 2- μ and <0.2 μ fractions show the distribution of Cs, Rb and K in the particles and the exchangeability of these cations are essentially the same.

2. Added Cs: Having used lepidomelane and muscovite samples in an exploration of ways of sorbing interlayer Cs, a shift was made to lepidolite size-fractions once K-depleted samples became available. This was done to obtain a comparison of interlayer and added Cs exchange in the same sample. By terminating the NaTPB-degradation of the lepidolite with boiling 1N CsCl, a sample with 140 mg Cs/100g was obtained. Portions of this Cs-degraded lepidolite were air dried or oven dried for 24 hours at 110°C or 450°C. Heating the sample at 110°C had little effect in the subsequent exchange of Cs by Na, but the 450°C treatment reduced the rate of exchange. As with K, added interlayer Cs was easier to replace than indigenous Cs. The role of other cations in the interlayers and the method of adding the Cs remains to be determined.

3. Heated micaceous minerals: The use of heat treatments to induce changes in interlayer K exchange was continued with a variety of ground and naturally fine-

grained minerals. With this approach, general relationships between K exchangeability and other mineral characteristics were established. At the same time, detailed studies of the effects of heat treatments on muscovite (dioctahedral), phlogopite (low Fe, trioctahedral) and lepidomelane (high Fe, trioctahedral) samples were initiated. By using weight loss as evidence of dehydroxylation in heated samples, a close association between the K exchangeability and hydroxyl status of muscovite was established. Phlogopite was not dehydroxylated and not altered in terms of K exchangeability by temperatures up to 800°C. The lepidomelane samples, however, exhibited a major reduction in rate of K exchange when they were deprotonated by heat induced Fe^{++} oxidation. Crystallographic changes in heated samples of these three micas have been determined and related to the incidence of weight loss, Fe oxidation and variations in interlayer K exchangeability.

4. Redox conditions: While the literature continues to emphasize the possibility of altering the exchangeability of interlayer cations by changing the redox status of the structural Fe in micaceous minerals, this project has verified that Fe^{++} oxidation in contracted minerals does not occur when H_2O_2 is added to the solution. Instead, we find only the Fe^{++} in the weathered periphery of particles is oxidized and the rate of K exchange is increased, not decreased, by the presence of H_2O_2 . This observation has been studied in some detail during the past year. Comparisons of minerals with different Fe^{++} content suggest the effects of H_2O_2 are mainly due to the Fe^{++} but some exceptions have been observed. Exfoliation due to the evolution of O_2 gas by H_2O_2 between the layers of the weathered edges of the minerals has also been ruled out as an explanation for the increased rate of K exchange. Instead, the rate of edge weathering by diffusion is enhanced by the presence of H_2O_2 in the solution. Instability of the TPB ion in H_2O_2 solutions has complicated this investigation.

5. Procedures: Most of the interlayer cation exchange experiments encountered in this project involve enough of the cation to circumvent analytical problems. When the sample size is very small (as in mineral/solution experiments) or does not contain much of the cation under question (e.g. indigenous Cs or reverted K in Cs degraded minerals) some modification in the experimental procedure is essential. Various ways of minimizing the final volume of the solution with the replaced cation but still provide a complete removal of TPB and mineral have been examined this year. Considerable success has been achieved with a procedure involving the removal of excess TPB by filtration and the use of Cu instead of Hg for the decomposition of the remaining TPB. Other procedures under study this year have been those providing controlled levels of Cs addition to interlayer surfaces of micaceous minerals.

FOREIGN TRAVEL

A paper on results from this project was presented at the 1972 International Clay Conference, Madrid, Spain. Further details regarding the purpose and accomplishments of this trip are described in Form 445 and the trip report submitted on August 4, 1972.

PUBLICATIONS

COO-1680-14: Extractable potassium in Grunite illite: II. Effects of particle-size and grinding. S. J. Smith and A. D. Scott. Soil Sci. in press (1973).

COO-1680-15: Changes in interlayer potassium exchangeability induced by heating

micas. A. D. Scott, F. T. Ismail, and R. R. Locatis. Proc. Int. Clay Conf. Madrid, in press (1973).

COO-1680-17: Exchangeability of potassium in heated fine-grained micaceous minerals. S. J. Smith and A. D. Scott. Clays and Clay Minerals, Submitted for publication (1973).

TIME ON PROJECT

A. D. Scott, Principal Investigator.

February 1, 1972 - April 30, 1973 - - - - - 30%

May 1, 1973 - July 31, 1973 - - - - - 30% anticipated

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