EXCHANGE OF INTERLAYER CATIONS IN MICACEOUS MINERALS

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ABSTRACT

Laboratory experiments were carried out to establish a comprehensive understanding of the processes and factors governing the sorption and release of interlayer cations in micaceous minerals. A diverse approach with several lines of work was used to delineate the effects of different procedures, solution compositions and mineral properties. It was soon clear that the major factors controlling the exchange of interlayer cations are the blocking effects of dissolved fixable cations and the limiting effects of small particles. By using sodium tetraphenylboron to reduce the blocking effects and by excluding particles that were smaller than 2 μm , however, the subtle effects of many other factors were brought out. The redox status of structural iron, the hydroxyl groups, the interlayer spacing and the layer charge of the minerals are indicative of the type of factors involved and the fact that they are mainly interactive in nature. One conclusion from this work is that most experimental results for interlayer cation exchange are bound to reflect some combination of the controlling factors. More important, however, was the observation that proper management of interlayer cation exchange can make micaceous minerals a good sink for cesium and source of potassium.

INTRODUCTION

The development and application of concepts about the sorption of cations on interlayer surfaces of soils and layer silicates and the release of both indigenous and sorbed interlayer cations from these materials to their surroundings have been the major goals of this project. To achieve these goals many cations, mineral properties, reaction conditions and processes had to be considered and a highly diversified approach with many lines of investigation had to be developed. Indeed, the investigation had to be ramified enough to cope with the wide ranging relevance of interlayer cation exchange to the management of radionuclide wastes, the tracing of water and airborne particulate matter, the weathering and transformation of minerals and soils, the fertility of soils and the characterization and behavior of clay minerals. Thus, a comprehensive report of all aspects of this project would be unduly excessive. Such details will be relegated to the numerous technical publications that exist or are being prepared. This report will be confined to an outline of the lines of investigation (to summarize the project activities) and a discussion of the progress that has been made.

For clarity in this report, the terminology initiated in the third progress report (document C00-1680-7) and used thereafter will still apply. Only the original, contracted mica with its indigenous interlayer cations will be called mica. Once the mica samples have been K depleted and expanded, they will be called degraded micas to distinguish them from naturally occurring vermiculites. The cations satisfying a major portion of the layer charge will be specified as needed (e.g. Ca degraded biotite or in general M degraded biotite). Cations like K, Rb, Cs and NH_4 that contract highly charged layer silicates when they are sorbed on interlayer sites will be referred to as fixable cations. Other cations like Na that are caught between the layers by the mineral contraction imposed by

fixable cations will be said to be trapped. Various terms such as heated mica, Br₂ treated mica, etc., will be used as needed to identify mineral samples that have been subjected to alterations by specific treatments.

AREAS OF WORK

1. Indigenous interlayer K exchange

1.1 Extracting solution

- (a) Blocking effects and critical levels
- (b) Replacing cation
- (c) Salt concentration
- (d) pH and Al effects

1.2 Procedures

1.3 Reaction temperature

1.4 Mineral comparisons

- (a) Kinetic basis
- (b) Equilibrated systems

2. Exchange of K in soils

1.1 Curve linearity, slope index and maximum

1.2 Soil fractions

3. M degraded micas

1.1 Preparation

1.2 Expansion, hydration and structural properties

1.3 Exchange of hydrated cations

1.4 Exchange of fixed K and NH₄

4. Occurrence and exchange of indigenous interlayer Cs and Rb

5. Sorption and exchange of added Cs

5.1 Procedural requirements

- 5.2 Mineral effects
- 5.3 Complimentary cations
- 6. Role of structural Fe
 - 6.1 Determination and alteration of the redox status of Fe
 - 6.2 Relevance of deprotonation and dehydroxylation
 - 6.3 Effects of H_2O_2 and NaOCl treatments
 - 6.4 Br_2 treated minerals
- 7. Heated micaceous minerals
 - 7.1 Dioctahedral versus trioctahedral mineral behavior
 - 7.2 Relative effects of time and temperature of heating
 - 7.3 Correlation of exchange behavior with mineral alterations
- 8. Particle size effects
 - 8.1 Grinding versus size separations
 - 8.2 Impact on rate and mode of cation exchange
 - 8.3 Limitations imposed on maximum exchange
- 9. Macro mineral flakes
 - 9.1 Visual record of edge versus layer weathering
 - 9.2 Mineral alterations by Br_2 treatments
 - 9.3 Preparation of defined units for mineral property studies
- 10. Kinetics of exchange
- 11. Supporting and exploratory work
 - 11.1 Preparation of mineral samples
 - (a) Procurement of suitable materials
 - (b) Effects of wet and dry grinding
 - (c) Mechanical versus chemical dispersion of fractions
 - 11.2 Characterization of minerals
 - (a) Chemical analyses
 - (b) Layer charge, hydration and structural features

11.3 Supplies of K depleted minerals

- (a) Bulk versus individual samples
- (b) Time factor
- (c) Temperature and stability imposed errors

11.4 Specific chemical procedures

- (a) Cu termination of NaTPB treatments
- (b) Small volume techniques
- (c) Determination of Fe^{++} with adequate precision and accuracy

11.5 Miscellaneous trials of potential investigations

DISCUSSION

The exchange of interlayer cations in layer silicates involves not only the usual processes of ion exchange, but a transfer of ions in the interlamellar spaces and a variety of mineral alterations as well (the complexity and ramifications of interlayer cation exchange is described in great detail and referenced with 148 literature citations -- many of which are reviews of hundreds of papers on the subject -- in the background section of the 1973-74 project proposal). Thus, from its inception, the scope of the project had to be broad enough to cope with a maze of interacting facets of the overall process. Indeed, to achieve a comprehensive understanding of the process, the investigation had to include a determination of the susceptibility of interlayer cations in different micaceous minerals to exchange, a delineation of the principles governing both the sorption and release of cations and a kinetic study of all processes. In many instances, indigenous interlayer cations proved best suited to the pursuit of these objectives because the associated mineral properties and alterations were easier to define and control (indigenous interlayer Cs and Rb experiments are described in documents 13 and 18;

indigenous interlayer K is discussed in all annual reports and publications). As information on the role of mineral properties grew, however, more attention was given to the sorption of added cations and their subsequent release from interlayer positions (Cs -- documents 7, 8, 13, 18, 20 and 21; Rb and NH_4 -- documents 7 and 8; K -- documents 13, 18, 20; Sr -- document 7; other cations -- documents 5 and 8). Situations involving the exchange of Cs, Rb, and K were given particular consideration, but the behavior and role of other alkali and alkaline earth cations (documents 3 and 5) had to be taken into account as complimentary cations.

Throughout the life of this project the emphasis of the work was shifted back and forth among the various lines of investigation to ensure proper utilization of the information that was being attained. To some degree, this approach was dictated by the interactive nature of the factors and processes involved in layer cation exchange. Its use, however, led to a great deal of pressure for internal consistency among the conclusions drawn from the different lines of work and thereby to some delay in the publication of the results. The work on Cs sorption and release exemplifies this situation particularly well. Some of the very first experiments of this project were carried out with routinely prepared degraded mica samples that were mixed with fixable cations to characterize the sorption and subsequent release of interlayer fixed cations (documents 7 and 8). Subsequent experiments based on intervening observations, however, have shown our initial data for fixable cations were dictated by the particular procedural options we had adopted and that quite different results can be obtained by varying the mineral, mineral pretreatment, solution volumes, Cs or other fixable cation concentration and reaction temperature (document 21 and unreported results from 1975/76 project period). Several interim reports of the various developments in the work could

have been published but not without an expression of some inconsistencies or even erroneous interpretations.

This project has produced a wealth of information about the processes and factors governing the exchange of interlayer cations (e.g. edge versus layer weathering -- documents 1, 3 and 5; particle size combinations -- documents 6 and 7; blocking effects of fixable cations -- document 8; small particle effects -- documents 1, 2, 3, 20 and 21; solution composition -- documents 19 and 21; reaction temperature -- documents 11 and 19; mineral properties -- documents 7, 9, 13, 15, 20, 21 and 22). Much of this success stems from the availability and development in this laboratory of methods of using sodium tetraphenylboron (NaTPB) to control the level of those cations in solution that can block exchange by a contraction of the layer silicates. Use of a variety of micas, mixed-layer minerals, illitic materials and soils with a prior or simultaneously developed background of information was also a major factor. In this regard, the preparation and use of expanded highly charged layer silicates was essential for the investigations on the sorption of contracting cations. Often the direction of the research undertaken in this project was determined by our success in devising suitable methods. For instance, most of the Cs exchange experiments depended upon the development of a Cu procedure for the termination of NaTPB treatments (document 13). On the other hand, progress with certain lines of work was restricted by our inability to overcome such difficulties as the instability of NaTPB in the systems with elevated temperatures or certain reagents like H_2O_2 (documents 10, 11 and 18).

Much of the progress that has been made in each of the areas of work listed earlier in this report has been presented before in an illustrative manner in annual and summary reports and need not be repeated here. There are, however, a few particular highlights that merit further emphasis. One of these is the observation that all interlayer cations in coarse particles of micaceous minerals, whether they

be indigenous or added, can be rapidly and completely exchanged by hydrated cations if the reaction conditions are appropriate (a comparison of indigenous interlayer K release by 10-20 μ samples of five micas is given in document 7; the release of sorbed Cs and K is described in document 13). The fact that interlayer cations can appear to be nonexchangeable is usually due to the blocking effects of fixable cations in the solution around the particles. Thus, the benefits of interlayer Cs sorption over the usual peripheral sorption of Cs for radionuclide waste management lies in the knowledge that the interlayer Cs can be kept there by a suitable regime of K or NH_4 in the solution while even K will replace Cs on external surfaces. In the absence of blocking effects, differences in the susceptibility of interlayer cations to exchange have also been shown to exist and to be due to characteristics of the mineral and cation involved. It is under these conditions that we have made great progress in the delineation and evaluation of the subtle effects of the many factors on interlayer cation exchange. The value of this information lies in our being able to decipher the in-between situations where both blocking and other factors are involved.

Since clay size particles are encountered in most of the situations where ion exchange has relevance (i.e. use of illites for radioactive Cs retention, soil fertility, stream transported sediments, etc.), recognition must be given to the attention this project has brought to the so called small particle effects. One of the first publications of this project (document 1) described the limited exchange of interlayer cations that can be achieved with small mineral particles even when the blocking effects of fixable cations are controlled. This observation has been verified by many other laboratories and with different extraction methods but no experimentally verified explanation has yet appeared. Subsequent work in this project has brought out many additional details about this small particle

effect (documents 2, 7, 10, 14, 19 and 20) and is leading to a distinction between ground mica and naturally fine grained materials in regard to the possible role of varying interlayer specificity (document 21 and unreported results from 1975/76 project period). Moreover, we have found the effects of particle size are mainly associated with indigenous interlayer cations and provide no great promise for radioactive cation management. Indeed, as a retainer of sorbed cations, small particles can have little value because they release cations much faster than coarser particles. In soils, however, the finer fractions are obviously of major importance to the chemistry and plant availability of K (documents 2 and 6).

A variety of heat and wet chemical treatments have been used very successfully to induce dramatic changes in the exchangeability of interlayer cations in micaceous minerals and thereby to assess the relative roles of mineral characteristics in the exchange (oral presentations A, B and C; documents 15, 17, 19, 20, 21 and 22). Both increases and decreases in the rate of exchange have been achieved with dioctahedral and trioctahedral minerals and in some cases the maximum level of exchange has been increased or reduced. In most cases, these changes in cation exchange have been identified with a dehydroxylation, deprotonation, Fe oxidation or reduction, change in basal spacing, etc., in the mineral. Uncertainties about the quantitative impact of each individual mineral characteristic still exist, however, because a great interdependence among the characteristics exists (e.g. some deprotonation occurs with Fe^{++} oxidation). On the other hand, significant progress has been made in downgrading the much publicized effects of wet Fe^{++} oxidation, focusing attention on the interlayer spacing, gaining a better perspective of the effects of H_2O_2 and Br_2 treatments, etc.

While our knowledge about many aspects of interlayer cation exchange has been greatly enhanced by this project it must be emphasized that much still remains to be learned. Quantitative assessments of the effects of individual factors are

particularly lacking and many interacting factors have to be further delineated. The results obtained so far have verified the complexity of the subject and have stressed the need for further study with a sorption approach.

Only a small part of the data accumulated in this project has been published or presented at professional meetings. As stated earlier, this situation is due in part to a need for consistency in the information given out from different lines of investigation. Equally important, however, has been the suppressive effect of having to prepare an extensive report and a "new" proposal for the project each year. Many papers are now underway to correct this situation and it is anticipated that these publications will sponsor further activity on the subject as they have in the past.

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