ILLITE: A MODEL BASED ON THE SORPTION BEHAVIOR OF CESIUM

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Abstract

Investigations of the cesium sorption capacities of a number of natural illite and illite-mixed-layer assemblages have shown that the cesium fixation is fundamentally one of surface and/or edge sorption. Monitoring of the clay mineral structures by x-ray diffraction and one-dimensional structural analyses have shown that no structural exchange has occurred which can be ascertained by these techniques, although approximately 90% of the Cs present in the contacting solution has been sorbed.

A model for illite based upon a "core-rind" concept gives an apparent best fit to the experimental data. This model proposes a structurally coherent silicate core for the clay platelet, surrounded by a more incoherent silicate rind area with a skeletal framework reminiscent of the more coherent portion. The physical and chemical characteristics of illite are compatible with this proposed model, as well as the general morphological character of the 10 Å materials.

The sorption behavior of Cs is considered then to be primarily due to the competition Cs with other ions in respect to potassium or potassium-depleted sites of the skeletal "incoherent" rind portion of the illite.

Introduction

A number of investigators have studied the sorption of various radionuclides by clay materials under varying physical and chemical conditions. The apparent selectivity in the sorption of cesium by illites has been shown, and a number of concepts have been advanced to account for this phenomenon. Jacobs and Tamura (1960), for example, have proposed the edge fixation of cesium by clay minerals with an approximate basal spacing of 10 Å. This 10 Å spacing, whether naturally occurring as in illite or artificially produced by the collapse of expanded materials such as vermiculite or montmorillonite by heating or potassium saturation, is deemed for steric reasons the essential factor in this selective edge fixation of cesium.

Other investigators (Schulz *et al.*, 1960) have explained the fixation of carrier-free cesium as a process of precipitation of the element on surfaces of micaceous minerals. They envision an alteration or extension of the existing clay mineral structure so that cesium is structurally incorporated by the clay minerals. In this manner, they account for the behavior of cesium under conditions of extraction by other cations.

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The investigations reported here are primarily concerned with the factors which apparently control the sorption of Cs by illite correlated to structural and chemical variations in the natural 10 Å clay minerals in the light of a proposed model for illite.

ANALYTICAL TECHNIQUES

Samples composed of the clay mineral illite and illite-mixed-layer material in the $<2\mu$ fraction have been utilized throughout the investigations. These samples, the Beavers Bend, Rock Island, Marblehead, and Fithian illites, and "Grundite," vary moderately in chemical composition, and the amount of mixed-layering present as diagnosed by x-ray diffraction techniques (Fig. 1). These materials have been described in some detail by Gaudette *et al.* (1966). Table 1 is a brief summary of the average values of four chemical analyses of these samples with the structural formulae derived from them. Total cation exchange capacities for each sample are also noted as determined by the versenate method.

The total cesium sorption capacity of each sample was obtained by batching 1.0 g (approximately 0.2 me) of sample with 100 ml of cesium nitrate solution ranging in concentration from 1 to 10^{-10}M. No competing cations were introduced in the solutions in order to better follow the clay-cesium reactions during the analyses. Polyethylene containers were used and the solutions were tagged with 0.45 microcuries of Cs-137 per ml. The clay suspension was agitated during the analytical runs, and at the end of prescribed time intervals, the suspension was centrifuged in its polyethylene container and 3 ml of the clear supernatant liquid removed for counting in a well-type scintillation counter. Comparison of the activity of the supernatant liquid was made to a 3 ml master sample of the original solution. After counting, the supernatant liquid was returned to the suspension, and the sample re-agitated until the next counting interval. The percentage of cesium fixed by the clay was determined from a comparison of the activity of the supernatant aliquot to the master sample.

Oriented aggregates of the clay samples, before and after cesium treatments, were obtained by centrifuging the clay suspensions on porous ceramic plates. X-ray diffraction analyses of these samples were made, and integrated intensities for each basal reflection obtained. One-dimensional structural analyses of each natural and cesium-treated sample
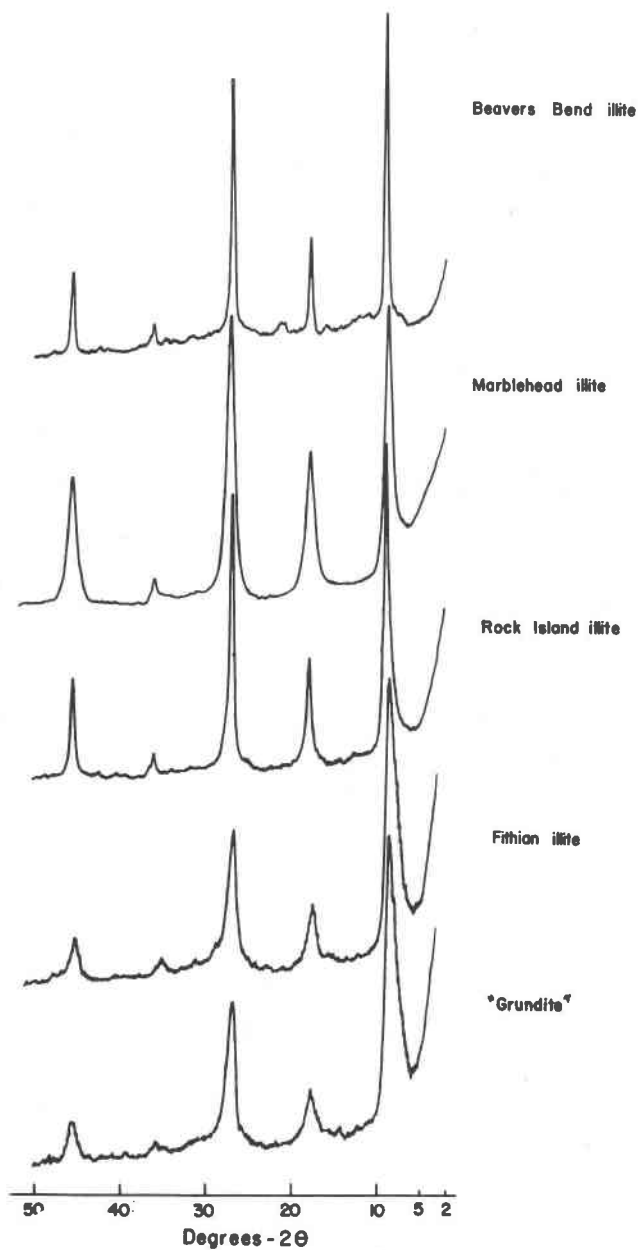
FIG. 1. Diffraction traces, untreated $<2\mu$ oriented aggregates.

Table 1. Chemical Analyses,[1] and Structural Formulae of the Illite Samples

	Beavers Bend	Marble-head	Rock Island	Fithian	"Grundite"
SiO_2	49.26	53.07	53.52	46.96	49.63
Al_2O_3	23.45	24.96	25.86	22.18	21.69
Fe_2O_3[2]	9.25	2.20	3.28	9.08	8.16
MgO	2.51	3.99	3.49	3.31	2.57
CaO	0.13	0.48	0.38	0.51	0.28
K_2O	6.52	8.08	6.68	5.78	5.81
Na_2O	0.23	0.27	0.27	0.32	0.32
TiO_2	0.57	0.93	0.65	0.67	0.58
Ignition Loss	6.28	6.13	6.18	11.91	7.73
Total	98.20	100.11	100.31	100.72	97.77
% Tetrahedral sub of Al	15.0	12.0	12.2	16.0	12.5
Total Ex Cap (me/100g)	18.48	21.18	18.95	20.52	24.20

Structural Formulae:

Beavers Bend: $(Al_{1.30}Fe_{.48}^{3+}Mg_{.26}Ti_{.03})(Si_{3.40}Al_{.60})$ $O_{10}(OH)_2(K_{.57}Na_{.03}Ca_{.01})$

Marblehead: $Al_{1.47}Fe_{.11}^{3+}Mg_{.39}Ti_{.04})(Si_{3.52}Al_{.48})$ $O_{10}(OH)_2(K_{.68}Na_{.04}Ca_{.03})$

Rock Island: $(Al_{1.51}Fe_{.16}^{3+}Mg_{.34}Ti_{.03})(Si_{3.51}Al_{.49})$ $O_{10}(OH)_2(K_{.56}Na_{.03}Ca_{.03})$

Fithian: $(Al_{1.22}Fe_{.49}^{3+}Mg_{.35}Ti_{.04})(Si_{3.36}Al_{.64})$ $O_{10}(OH)_2(K_{.53}Na_{.04}Ca_{.04})$

"Grundite" $(Al_{1.31}Fe_{.43}^{3+}Mg_{.27}Ti_{.03})(Si_{3.50}Al_{.50})$ $O_{10}(OH)_2(K_{.52}Na_{.04}Ca_{.02})$

[1] Average values of analyses by J. Witters, Ill. State Geol. Survey; J. T. Wilband, H. E. Gaudette, Dept. of Geol., Univ. of Ill.; and C. Koger, Southern Cement Co., Birmingham, Ala.

[2] Total iron expressed as Fe_2O_3.

were calculated, and electron density projections of these samples plotted in order to monitor any structural effects due to the cesium treatments, as well as to determine structural variations that might influence the apparent sorption capacity of the illite samples for cesium.

ANALYTICAL RESULTS

Results of the radiochemical tests of the sorption capability of the illites show that maximum percentages of cesium sorbed occurred within a relatively short period of time, usually within four hours.

Figure 2 shows the sorbtive behavior of cesium in the 10 Å clay-cesium system. In all of the radiochemical tests of the illite samples, the per cent sorbed by the clay ranged between 75 and 90 per cent in the lowest concentration range. The maximum sorption recorded in this range was for Fithian illite, followed closely by "Grundite," and Rock Island, Marblehead, and Beavers Bend illites. The amount of mixed-layering in these samples may be directly correlated to the cesium sorption capacity
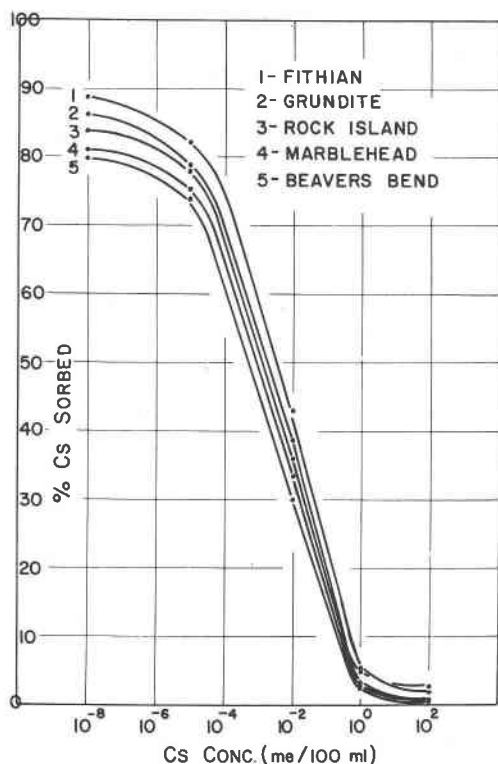
FIG. 2. Cs sorption of illite samples.

as Fithian illite and "Grundite" contain the greatest evidence, by x-ray diffraction of mixed-layering, and also have the highest sorption capacity. However, although the three remaining illite samples show little or no x-ray evidence of mixed-layering they exhibit only a slightly lesser affinity for cesium in the low concentration ranges.

One-dimensional structural analyses of the natural 10 Å materials of this study have been previously reported (Gaudette *et al.* 1966). Oriented aggregates of the natural and cesium-treated samples were made in order to provide a monitor for the stability of the clay during the sorption analyses. Diffraction analyses of these treated samples showed that the primary effects of cesium-sorption are a slight broadening and damping of the 00l intensities, with no appreciable changes in the basal spacings. Preparation techniques were such that any unsorbed cesium would have been removed before the diffraction analyses were made.

If cesium is able to locate itself within the structure of the illite as a substituent in any appreciable amounts for any atom which can be

structurally defined by x-ray diffraction procedures, the resultant structural analyses should differ significantly even on a semi-quantitative basis. The contrast of the scattering power of the cesium atom as opposed to that of the atoms which are generally considered to constitute the structural framework of illite, is sufficient to sharply delineate such substituting processes.

One-dimensional structural projections of the illite samples before and after appropriate treatments with cesium-bearing solutions indicate that at the levels of cesium concentration in the contacting solutions, no structural changes have taken place which can be defined by x-ray diffraction analysis. Thus an interpretation may be made that with cesium sorption at concentration levels which apparently exhibit evidences of a high sorption capacity of the 10 Å clay for cesium, no structural incorporation can be conclusively established.

Discussion

In view of the sorption capacity of the illite samples as shown by the radiochemical data, and the information furnished by the structural analyses of the natural and cesium-treated clays, it seems warranted to postulate some mechanism other than ideal structural substitution to account for the sorption behavior of illite for cesium, particularly in the low concentration ranges.

One explanation of the sorption curves shown in Fig. 2 may be a dependence of the cesium sorption upon the amount of sample with which it associates. Since the weight of the sample (1 g), and therefore the exchange capacity of the clay (approximately 0.2 me) was kept constant throughout the analyses, the interaction of the cesium in solution with the clay may be completely dependent upon the number of exchange sites available. At high cesium concentrations, these exchange sites would be completely filled by only a small number of the cesium atoms readily available, and a low sorption percentage would result. At lower cesium concentrations, however, the number of exchange sites may be equal to, or greater than the number of cesium atoms in solution, and higher sorption percentages may be expected. If this is a valid hypothesis, an S-shaped relationship similar to the ones shown in Fig. 2 should exist between cesium concentration and the percentage of cesium sorbed. However, this relationship should extend to greater percentages in the low concentration ranges than are exhibited by the analytical data. Hence, it may be deduced that some additional factor is prominent in controlling the sorption behavior of illite for cesium at low concentrations.

Jacobs and Tamura (1960) in a study of the behavior of cesium with

various clay materials considered kaolinite and montmorillonite to follow mass-action considerations closely over the entire range of cesium concentrations which they investigated. They considered that, with these clays, the entire exchange complex is available to all exchangeable ions, and that the clay surface is uniform, or nearly so. Their sorption data for illite, which are very similar to those of this study, necessitated further considerations. Their assumption of a small number of exchange sites highly selective for cesium allowed the observed data to be explained. For steric reasons, these highly selective sites were assumed to be edge fixation sites, and thus the 10 Å basal spacing for illite became a primary consideration in the sorption process.

In the light of the analytical data accumulated during this investigation, and analyses from similar studies, a proposed model for the clay mineral illite is presented similar to the model discussed by Jackson (1963). The potash contents and degree of hydration of the illites are sufficient to distinguish them from well-crystallized dioctahedral muscovite, however, the basic structural representation of illite is apparently the same with some modifications.

Based upon this modified structural representation, it would appear that illite may be considered to be made up of a structurally coherent silicate core which may be somewhat deficient in potassium content in the interlayer positions but which produces the characteristic 10 Å diffraction data. Surrounding this coherent core, it is envisioned that illite is further made up of a more "incoherent" rind similar to the "frayed edge" of Jackson (1963) which serves as a locus for sorption and cation exchange, and which is primarily the area from which the physical properties and characteristics for a particular 10 Å material are derived. The contact between such core and rind areas is considered to be gradational. The rind differs from the core in containing even less potassium (by replacement with other ions or perhaps H_2O) and a slightly larger and somewhat irregular "c" dimension, but with a skeletal framework reminiscent of the more coherent portion of the clay platelet. A well-crystallized 10 Å material would then have a larger coherent core area with the incoherent portion restricted to the very edges of the clay platelets. In this case, diffraction data would be excellent, polymorphic type easily identifiable and cation exchange capacity and sorption capacity relatively lower. In contrast, in a poorly crystallized 10 Å material one could postulate that the diffracting core would be relatively small as compared to a surrounding incoherent rind. Thus the larger rind area would produce a relatively greater cation exchange and sorption capacity, as well as induce a greater response to chemical treatments. Considerations of other physical and chemical properties of illite are compatible to this

proposed model, and correlation may be made between these properties and the amount of core-rind areas postulated from x-ray diffraction and other analytical techniques. The general morphological characteristics of the 10 Å materials as disclosed by electron microscopy are also consistent with this model for illite which has been presented.

Any selectivity of illite for Cs may then be considered as primarily due to the behavior of Cs in contrast to other ions in respect to potassium or potassium-depleted sites of the skeletal "incoherent" rind portion of the illite. An inverse correlation between the amount of K^+ per unit cell from chemical analysis and the Cs sorption capacity of the illites can then be made.

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