CESIUM SORPTION REACTIONS AS INDICATOR OF CLAY MINERAL STRUCTURES

by

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ABSTRACT

At low cesium ion concentrations extremely high selectivities for cesium are exhibited by layer lattice silicates with unexpanded 10 Å c-spacing. The total amount of cesium which can be sorbed by these minerals depends on the edge area and the exchange capacity. At a concentration of 10^{-5} meq of cesium and 5 meq of sodium, a sample of biotite representing less than 0.025 meq of exchange capacity sorbed over 90 per cent of the cesium and a hydrobiotite with 50 percent vermiculite and representing 1.0 meq of exchange capacity sorbed 80 percent of the cesium.

After heating bentonites to 500–700° C more cesium is sorbed from solutions containing high sodium concentrations by the heated bentonite than the original material. The change in the amount of cesium sorbed as a result of heating may be a useful property for detecting the presence of montmorillonite in mixed or interlayered mineral systems. Lattice expansion of biotite results in improved cesium sorption; this behavior is due to generation of sufficient favorable exchange sites to offset the loss of edges with favorable 10 Å spacing.

INTRODUCTION

Removal of microconcentrations of cesium ions in the presence of macro-concentrations of competing sodium and aluminum ions was shown not to be directly related to exchange capacities of the clay minerals (Tamura and Jacobs, 1960; 1961). The removal mechanism under these conditions was strongly influenced by the 10 Å c-spacing of the 2:1 layer silicates. Observations substantiating this conclusion include: (1) the higher cesium removal by illite and fluorophlogopite as compared to the montmorillonites and kaolinites; (2) improved cesium removal by KCl-treated hydrobiotite; and (3) improved cesium removal by bentonites after they were heated to 500–700° C.

These tests, though originally intended to show the cause for the favorable cesium removal by the local shale formation, may be useful as a method of characterizing certain lattice features of minerals. They may be helpful in revealing the existence of montmorillonite whose presence is difficult to establish by other tests. The purpose of this paper is to present the results of

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389

further tests using both lattice collapse and lattice expansion to study cesium sorption reactions. The results are discussed in terms of changes induced in the c-spacings of the clay minerals.

MATERIALS AND METHODS

The clay minerals were obtained from Ward's Natural Science Est. and correspond to the reference clay samples of the American Petroleum Institute project 49. These include montmorillonite no. 23 from Chambers, Arizona; montmorillonite no. 26 from Clay Spur, Wyoming; kaolinite no. 2 from Macon, Georgia; and illite no. 35 from Fithian, Illinois. The biotite, muscovite and glauconite samples were also obtained from Ward's. The fluorophlogopites were synthesized and kindly supplied by the Bureau of Mines' Electrotechnical Laboratory at Norris, Tennessee. The hydrobiotite (referred to as *vermiculite* in this manuscript) was donated by the Zonolite Company from their mines in Traveler's Rest, South Carolina.

Cesium sorption was measured by mixing a known weight of material with solutions of known composition. The sodium/cesium ratio in the solutions was maintained at 8000 except when cesium concentration was a variable. The solution was tagged with Cs-137 and cesium sorption was calculated by counting the solution before and after it had been in contact with the mineral for a specified time. A 1-ml aliquot was counted in a well-type scintillation counter with a NaI(Tl) crystal. After counting, the aliquot was returned to the original solution.

After a desired heating period at a specified temperature in a muffle furnace, samples were removed and the remaining samples heated to a higher temperature for the same period. Samples prepared in this manner were cooled and stored in desiccators prior to use.

Lattice expansion was accomplished using the sodium tetraphenylboron technique described by De Mumbrum (1959); ion exchange capacities were determined by the calcium saturation, versene titration technique described by Jackson (1958).

RESULTS AND DISCUSSION

Cesium Sorption by Arizona Bentonite

The cesium sorption curves of Arizona bentonite, after being heated to different temperatures for 1 hr and cooled, are shown in Fig. 1. The optimum temperature for maximum cesium sorption is 600° C. Below 600° C heating, the Arizona bentonite samples show a high initial removal of cesium followed by a decrease in removal as the solution–clay contact time increases. Above 600° C, initial sorption is reduced below the natural material, but with increasing contact time the amount of cesium sorbed increases. The existence of an optimum heating temperature is in agreement with the data presented earlier (Tamura and Jacobs, 1961). These data differ from Wyoming bentonite data by the long contact time apparently required by this Arizona bentonite

to reach equilibrium when heated to less than 600° C. The decreasing amount of cesium sorbed with increasing time of contact suggests that the heated clays are in a collapsed state initially and on contact with the sodium nitrate solution the lattice rehydrates and expands slowly. With rehydration and consequent expansion of the layers, the amount of sorbed cesium which can be in equilibrium with the solution is reduced. Higher heating temperatures, up to 600° C, appear to collapse more layers and the collapsed layers are slow to rehydrate.
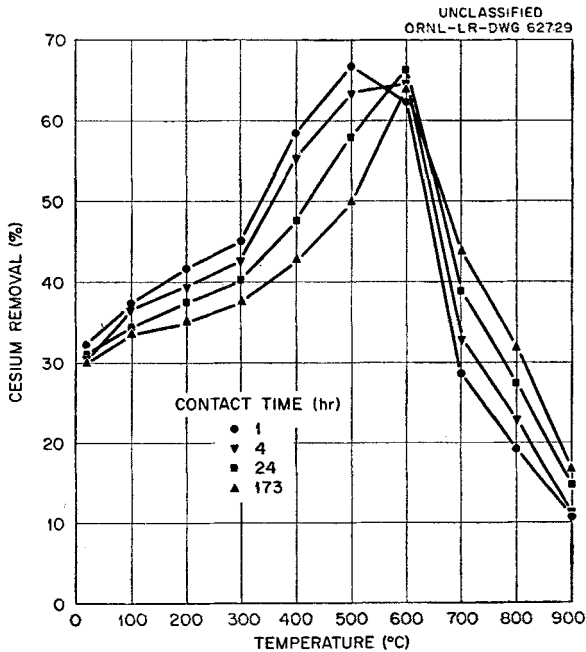

FIGURE 1.—Cesium removal by montmorillonite (Arizona bentonite): 20 ml 6 M NaNO₃ containing 100 mg Cs per liter contacted with 2.0 g based on the oven-dry weight of material. Heating = 1 hr at specified temperature.

Samples that are heated for 1 hr beyond the optimum temperature of 600° C may have been partially decomposed. Tamura and Jacobs (1961) showed earlier that once the optimum temperature was reached the longer heating periods resulted in samples which showed lower initial sorption of cesium but similar final sorption after sufficient contact time. The optimum temperature of 600° C is also characterized by a substantial decrease in exchange capacity in the bentonite samples (Table 1). The reduction in capacity by heating of clays has been related to the loss in rehydration of the montmorillonite lattice (Grim, 1953).

TABLE 1.—THE ION-EXCHANGE CAPACITY OF SEVERAL MINERALS AFTER BEING HEATED TO SPECIFIED TEMPERATURES

Heating temperature (°C)	Natural Arizona Bentonite	Calcium Wyoming Bentonite	Lithium Wyoming Bentonite	Natural Fithian Illite	Natural Glauconite	Natural Muscovite	Natural Grundite
			Exchange Capacity*				
25	112	—	89	29	26	6	23
100	112	83	91	28	26	5	20
200	113	—	88	—	—	—	—
300	102	84	28	—	—	—	—
400	104	—	19	—	—	—	—
500	102	84	—	30	28	3	22
600	81	50	18	31	23	5	27
700	19	16	15	—	—	—	—
800	18	8	10	—	—	—	—
900	14	—	—	—	—	—	—

* Ion-exchange capacity based on the weights of the materials heated to the specified temperatures is expressed as meq/100 g. All samples heated for 3 hr except the natural Arizona bentonite and lithium Wyoming bentonite which were heated for 1 hr.

The exchange data for lithium-saturated Wyoming bentonite are also shown in Table 1. Since lithium saturation causes irreversible collapse at approximately 200° C (Grim, 1953), sorption is expected to increase after heating Li-montmorillonite to a much lower temperature. The observed increase occurred at 300° and 700° C; samples heated above and below these temperatures showed lower removals. These tests further support the concept that the removal of very low cesium concentrations is directly related to the 10 Å spacing. The need of residual exchange capacity for cesium sorption by the mineral was illustrated by the poor sorption characteristic of talc—a 2:1 layer silicate without isomorphous substitution and with very low ion-exchange capacity.

The optimum temperature of 600° C for the natural Arizona bentonite should not be construed to mean that "no decomposition" or "no rehydration" took place. Until exact relationships are established one must, at best, conclude that this temperature suggests minimum decomposition and rehydration. The decrease in capacity *per se* is not favorable for cesium sorption; data presented in a later section will show that higher exchange capacity enables minerals to sorb more cesium.

Illitic Mineral Response After Heat Treatment

Similar response of several bentonites to heating, viz. metabentonite from Virginia, hectorite from California, montmorillonite from Wyoming, and this sample from Arizona, demonstrates that the enhanced sorption of cesium after heating is a property of bentonites in general. This conclusion suggested the possibility of using the change in sorption of cesium before and after heating to detect the presence of montmorillonite layers which are difficult to identify. Such a condition may exist in interstratified clay minerals; and particularly suspect of such heterogeneity is the mineral illite. According to Yoder and Eugster (1955) and Mehra and Jackson (1959), the Fithian illite which was used in these tests is a mixed-layered structure containing mica and montmorillonite; thus heating this mineral to an appropriate temperature should cause a reduction in the montmorillonite c-spacing and an increased affinity for cesium should result.

Figure 2 shows the results for Fithian illite compared with several other minerals. The materials were heated for 3 hr at the temperatures indicated on the curves. The increase in cesium sorption after heating at 600° C or higher is supporting evidence for the existence of expanded montmorillonite in the illite sample. The change in the optimum temperature from 600° to 500° C for the Arizona bentonite suggests the need for further study in establishing optimum heating temperature and optimum duration of heating. The absence of any increase noted for the phlogopite (Fig. 2) and a muscovite (Table 2) is evidence that the precollapsed lattices will not change in their affinity for cesium after heating. No change, of course, was expected for the 1:1 layer lattice kaolinite.

Data for a glauconite from New Jersey and a Grundite from Illinois (commercially available illite), also shown in Table 2, suggest that both of

these minerals contain montmorillonite. However, the ion-exchange capacities for the illite, grundite and glauconite do not change after the clays are heated; bentonite exchange was reduced after heating (Table 1). No obvious explanation for this difference in behavior is apparent at this time.
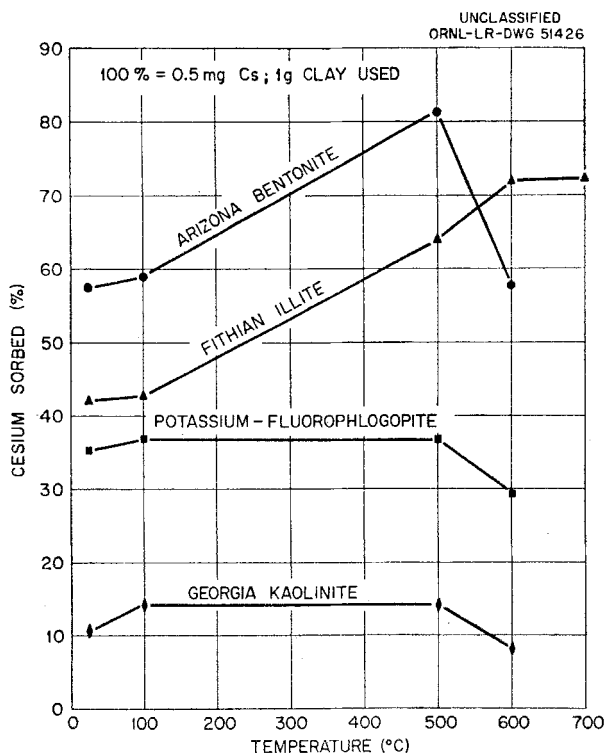

FIGURE 2.—Sorption of cesium from 1.5 M NaNO₃ solution by several clays previously heated.

Cesium Sorption by Biotite and Vermiculite

Whereas it has been possible to increase the selectivity for cesium by treating vermiculite with KCl and thus collapse the lattice, heat treatment of vermiculite has been unsuccessful in increasing the selectivity. Unlike the bentonites, which show little or no loss in exchange capacity until a critical temperature is reached, the vermiculite sample showed a gradual decrease with the same heating treatment; part of the decrease was associated with the oxidation of iron since heating in a nitrogen atmosphere reduced the loss.

One of the difficulties with the vermiculite used in these tests is the biotite impurity that is interstratified with the vermiculitic portion. Since the high selectivity for cesium is associated with the collapsed structure of micas, it is

TABLE 2.—EFFECT OF HEATING AND SOLUTION-SORBENT CONTACT TIME ON THE PERCENTAGE REMOVAL OF CESIUM BY SEVERAL NATURAL MINERALS. ONE GRAM ON AN OVEN-DRY WEIGHT BASIS IN CONTACT WITH 10 ML OF 3 M NaNO₃ SOLUTION CONTAINING 50 MG CESIUM PER LITER; 3 HR HEATING EXCEPT SAMPLES KEPT AT ROOM TEMPERATURE

Contact time (hr)	Glauconite Temperature (°C)				Grundite Temperature (°C)				Muscovite Temperature (°C)			
	25	100	500	600	25	100	500	600	25	100	500	600
						Percent Removal						
0.5	28.0	34.7	43.6	39.4	32.1	29.9	37.5	50.0	—	—	—	—
1	27.4	35.5	48.0	43.7	34.1	34.5	41.8	53.8	21.5	20.6	23.8	19.2
5	—	—	—	—	—	—	—	—	30.5	30.4	33.6	27.6
28	29.6	37.3	54.4	52.0	36.2	37.6	44.8	60.5	32.0	33.7	38.4	32.3
120	28.3	36.2	56.5	53.4	36.6	39.9	45.3	61.8	—	—	—	—
292	—	—	—	—	—	—	—	—	37.6	37.4	42.2	42.2
364	28.7	37.0	54.2	54.7	36.3	38.7	41.0	62.0	—	—	—	—

likely that the biotite impurity is responsible for the removal in the very dilute cesium concentration range. A comparison of cesium removal by a pure biotite and the vermiculite of similar particle size is shown in Fig. 3. A 1 meq portion was taken for the vermiculite (1.38 g) but since 1 meq of biotite would require a prohibitive amount (50–75 g) for these tests, 1.38 g was used. Below 5×10^{-4} meq of cesium, the biotite sample removed more

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Δ Na-VERMICULITE
● BIOTITE
▲ NaBϕ$_4$–TREATED VERMICULITE
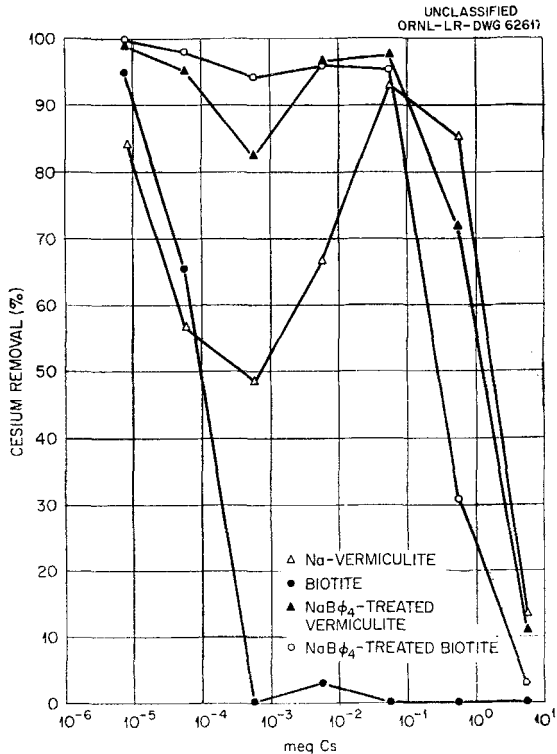○ NaBϕ$_4$–TREATED BIOTITE

CESIUM REMOVAL (%)

meq Cs

FIGURE 3.—Cesium sorption by vermiculite and biotite from 0.1 M NaCl solution.

cesium than the vermiculite—strong evidence that the number of edges in the collapsed state is the determining factor for the high selectivity under these conditions. Above 5×10^{-4} meq, vermiculite shows a sharp increase in cesium removal; this phenomenon was shown to be due to the cesium ions inducing collapse of the expanded vermiculite lattice (Jacobs and Tamura, 1960). On the other hand the minimal exchange capacity of the biotite sample cannot remove cesium at these levels of cesium concentration.

The importance of the exchange reaction in contrast to the edge fixation reaction for vermiculite and biotite is also shown in Fig. 3. These minerals

were treated with sodium tetraphenylboron in order to remove the potassium ions from the lattice exchange positions; after treatment X-ray diffraction showed that the c-spacings of the materials had been expanded. The resultant products after two treatments showed exchange capacities of 135 and 72 meq/100 g for vermiculite and biotite respectively. Based on the potassium analysis of the original and treated materials, the calculated exchange capacities which should have been generated are 64 and 73 meq/10 g for vermiculite and biotite respectively. Since the original vermiculite measured 72 meq/100 g, the observed and calculated capacities appear to be in good agreement.

The data in Fig. 3 reveal that the treated materials remove cesium more effectively in the low cesium concentration ranges than the untreated materials. This is particularly noticeable for vermiculite since 0.75 g of the treated vermiculite is compared to 1.38 g of the untreated. One can also conclude from the data that the capacity and the selectivity of the newly generated sites offset the loss of the highly selective sites of the collapsed edges.

When the cesium concentration is increased to 0.5 meq, the response by the treated and untreated vermiculite is reversed from that observed at the low cesium concentrations, and more cesium is sorbed by the untreated vermiculite. The biotite sample, whose exchange capacity was nearly all generated by the sodium tetraphenylboron treatment, also shows a relatively low removal. Similar behavior by these materials was noted when the system contained only cesium or potassium ions. This observation should make one hesitate in assuming that the treatment caused simple removal of potassium with no change of the material except lattice expansion and sodium saturation. Indeed, when the material and the NaCl solutions came in contact, the solution turned brown; preliminary tests indicate iron is dissolved, and this component must have originated from the vermiculite or biotite lattice.

These experiments on cesium sorption by expanding and collapsing lattices of vermiculite, biotite, and montmorillonites suggested that optimum removals at low cesium concentrations may be achieved by a vermiculite system whose c-spacing is reduced but not necessarily to 10 Å and whose exchange capacity is not reduced in spite of a decrease in the c-spacing. Promising results have been obtained thus far with barium-saturated vermiculite; the material showed a c-spacing of 11.1 Å in comparison to 12.5 Å for the unteated vermiculite and identical exchange capacity (65 meq/100 g) with the untreated material. The removal by barium-vermiculite was 3.5 times more than by the natural material under identical test conditions.

CONCLUSIONS

These studies, though preliminary in nature, show that cesium sorption tests can be a useful indicator of the structural conditions of the 2:1 layer lattice silicates. In general, the response of materials which had been heated, altered by chemical treatment, or variously saturated with different cations is in good agreement with existing concepts of clay mineral structure. In

addition, the sorption tests show differences within the montmorillonite series such as between Arizona and Wyoming bentonites. Sorption tests of vermiculites altered by sodium tetraphenylboron show that fixation by lattice collapse is reduced in comparison to untreated vermiculite but that the removal of cesium in very dilute concentrations is enhanced. Promising results have been obtained thus far on the use of cesium sorption reactions as a method for detecting the presence of montmorillonites.

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