

# CATION EXCHANGE BEHAVIOR OF VERMICULITE-BIOTITE MIXTURES<sup>1</sup>

*by*

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## ABSTRACT

The cation exchange capacity of a series of commercially available vermiculite-biotite minerals (Traveler's Rest, South Carolina; Libby, Montana; and Polobora, South Africa) was measured by a column method using various cations. The selectivity of the clay mineral for various ion pairs was determined with particular attention given to the adsorption from a sodium chloride-cesium chloride mixed electrolyte solution. The mineral was found to be highly selective for cesium ion, a large part of the amount adsorbed probably replacing potassium ions in the biotite layers. This replacement in the biotite is a much slower process than normal ion exchange and greatly lengthened the time required to come to equilibrium in the column.

The cesium ion cannot be removed easily from cesium-saturated vermiculite. The fixation of cesium ion was close to 100 percent at room temperature in contact with a cesium chloride solution. An isotopic exchange, Cs 133 for Cs 134, removed only very small quantities of the fixed cesium. Boiling with sodium chloride was only slightly more effective. All the results are in general agreement with the theory explaining ion fixation on the basis of collapse of the vermiculite structure to that of biotite.

## INTRODUCTION

The mixed vermiculite-biotite structure, which forms an intermediate stage in the alteration of mica to vermiculite, is very common in nature. This material consists of mica and vermiculite interlayered in various proportions. The vermiculite structure is composed of biotite- or talc-like layers separated by layers of water molecules. Between these layers are located the exchangeable ions. According to Barshad (1948, 1949, 1950) the only difference between biotite and vermiculite stems from the nature of the exchangeable ions. In natural vermiculite the exchangeable ion is magnesium, or in some cases magnesium and calcium, and exchange occurs readily without the necessity of grinding the material. In biotite the interlayer ions are potassium, which are not easily exchangeable. The layers are collapsed and have no water molecules between them. Barshad (1948, 1949, 1950) has tested his theory of interconvertibility by treating biotite with magnesium chloride over a period of months. He reported that particles in the size range up to  $1\ \mu$  were shown by x-ray analysis to have been converted to vermiculite. Similarly,

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vermiculites treated with potassium chloride gave a product identical with biotite. Barshad reports a sample of Montana mineral to be 75 percent biotite and 25 percent vermiculite. The exchangeable ions in this material consisted of potassium, calcium, and magnesium in the proportions 75 : 15 : 10.

When studying the ion-exchange behavior, the different exchange characteristics of the two component minerals must be considered. Ions of different sizes behave differently with the two minerals: large ions, such as Mg, Ca, Li, and Na exchange readily with the vermiculite, and the normal *c*-axis spacing is maintained. These ions cannot easily enter and displace the potassium ions between the biotite sheets. K, NH<sub>4</sub>, Rb, and Cs on the other hand can enter and exchange in the biotite and can also cause the collapse of the vermiculite structure when they replace its normal exchangeable ions.

The ion-exchange properties of vermiculite-biotite mixtures have never been systematically investigated. The exchange capacities of vermiculite and biotite differ greatly. Capacities between 1.0 and 1.5 meq/g have been reported in vermiculites from pure deposits. Walker (1956) measured a capacity of 1.58 meq/g for a West Chester, Pa., vermiculite. Gaines (1957) found the exchange capacity of a mica to be 0.0015 meq/g for 40–60 mesh particles. Many of these determinations of the exchange capacity have been made by a batch equilibrium technique with separation of mineral and electrolyte solution by centrifugation after contact for a definite length of time. By measuring changes in solution concentration, data are obtained from which uptake can be calculated. At best the method gives a reproducibility of about 5 percent in the exchange capacity. The standard procedure given by Jackson (1958, p. 60) for soils containing vermiculite is to use a solution of calcium acetate in the capacity measurements. By using calcium the difficulty with the slow mica exchange is reduced. However, the amount of uptake is dependent on the time of contact of solution and mineral, and the method does not give the true exchange capacity. The method cannot be used with Cs, K, or NH<sub>4</sub> because these ions exchange into the biotite layers.

In the experiments here reported the column technique of Frysinger and Thomas (1955) which gives much more detailed information on the course of the ion exchange, is used. In this procedure the clay mineral supported in a column is brought to chemical equilibrium with an electrolyte solution of known composition. The electrolyte solution used in equilibrating the column carries a radioisotopic tracer. Equilibrium is presumed to have been reached when the activity of the effluent becomes identical with that of the column input solution.

In measurement of the total exchange capacity a single electrolyte solution is used. For the experimental work given below this was a 0.01 N CsCl solution with a small amount of Cs 134 radioisotope. The difference between the milliequivalents of cation put into the top of the column and the milliequivalents in the effluent, corrected for the column free volume solution, is defined to be the exchange capacity of the total clay mineral in the column. The magnitude of the exchange capacity for several specific minerals has been

shown by Frysinger and Thomas (1955) to be independent of the cation or the anion employed.

When a mixed electrolyte solution of two cations and a common anion is used as the column input solution, the selectivity of the clay toward the two cations can be measured. The uptake of the radiotraced cation in the mixture is determined as above. Comparing this to the previously determined total exchange capacity, the amount of the other cation sorbed can be determined by difference. Alternately, the selectivity can be determined directly by radiotracing both cations. After chemical separation in the effluent the amount of each cation sorbed can be determined independently, and the sum will be the total exchange capacity.

## EXPERIMENTAL

The experiments reported are as yet fragmentary in nature, and a great deal more work will be necessary before the exchange properties of vermiculite can be said to be properly characterized.

Three different commercial vermiculites (Traveler's Rest, South Carolina; Libby, Montana; and Polobora, South Africa) were investigated. A sample supplied by the Zonolite Company from their Traveler's Rest, South Carolina, mine was used for all the exchange and selectivity measurements reported in this paper. The sample was ground to size range  $-40+80$  mesh and used directly in the chromatographic columns. If the vermiculite had not been washed, the first effluent contained a small amount of fines. There was no tendency for the column to clog or for the flow rate to decrease under gravity feed.

### 1. *Rate of Exchange*

The rate of exchange was observed in a batch experiment with three samples of 40–80 mesh vermiculite. To each was added 500 ml of 0.01 N Cs(Cs 134)Cl solution and the progress of the exchange was observed. Sample 1 was stirred at room temperature; sample 2 was stirred while kept near the boiling point on a steam bath; sample 3 was boiled in water under reduced pressure to remove as much occluded air as possible. Sample 3 was also heated on the steam bath and stirred after adding the Cs(Cs 134)Cl. The time required for total uptake is given in Table 1. Evidently absorbed gases on the mineral act as a barrier to the exchanging ions. The low rate of exchange found with these particles is to be compared with similar experiments on montmorillonites where complete uptake is reached in a matter of 3–5 min or less.

### 2. *Column Experiments*

In the column exchange experiments it was difficult to reach true saturation. An extent of exchange up to 85 percent was easily accomplished; the break-through curve is similar to those obtained with a montmorillonite.

For the last 15 percent the chromatogram trailed greatly. This effect may be due to slow diffusion toward the inner exchange sites of the vermiculite flakes or to a very low rate of exchange in the biotite layers. In any case the column was not running under equilibrium conditions; when the flow was stopped at the steepest portion of the curve, the concentration of cesium in the column solution fell greatly. Even at very low flow rates equilibrium could not be maintained.

TABLE 1.—PERCENT OF TOTAL UPTAKE  
ATTAINED

Time (hr)	Sample 1	Sample 2	Sample 3
0.5	45	60	80
1	60	80	100
2	75	90	—
3	90	100	—
4	100	—	—

Even when the concentration of cesium in the effluent was inappreciably different from that of the input, i.e. at apparent saturation, stopping the flow overnight led to a large decrease in the cesium content of the column solution. By repeating this process ten to fifteen times it was possible to bring the column to true saturation, this condition being defined as determined by no decrease in concentration on standing overnight. In a typical experiment, 5.44 g of vermiculite was contained in a  $6 \times 1$  cm column, through which was passed 0.01 N CsCl at a rate of about 180 ml/hr. Apparent saturation was reached after 750 ml. True saturation was reached after passing six additional 50–100 ml portions of solution through the column. Finally the cesium concentration remained unchanged after two days standing.

The experiment indicated an exchange capacity for cesium of 0.695 meq/g. An exactly similar experiment with sodium gave the value 0.243 meq/g. It is probable that the higher value for cesium is due to the fact that the cesium enters the biotite layers whereas the sodium does not. This conclusion is substantiated by the fact that in a sodium experiment, when the column was stopped overnight, no drop in concentration was observed.

The relative selectivity of the vermiculite for cesium over sodium was determined with a solution containing both electrolytes. A solution 0.1 N in NaCl and 0.01 N in Cs(Cs 134)Cl was passed through a column containing 3.5 g of the mineral until true saturation was reached. This required about 7.5 l. of solution. The uptake of cesium was determined to be 0.669 meq/g. If the cesium capacity is used to calculate the amount of sorbed sodium, i.e. sodium is determined by difference, then 96.2 percent of the sorbed ion is cesium and only 3.8 percent is sodium. The mineral thus shows a high selectivity for cesium.

3. *Leaching*

Unlike other clay minerals, vermiculite will not easily release cesium once it is adsorbed. In an experiment in which CsCl solution (with no tracer) was passed through a column previously brought to true saturation with Cs(Cs 134)Cl, the amount of tracer in the effluent measures the extent of isotopic exchange, Cs 133 for Cs 134, on the mineral. After one column volume, containing the equilibrium amount of the traced solution, only a very small amount of activity was eluted. This additional amount corresponded to only 0.3 percent of the exchange capacity. The activity quickly dropped to less than twice background. At this very low rate of exchange it was estimated that 7,750 l. of solution would have been required to complete the elution of the radioisotope. Various vermiculite samples and different concentrations of cesium eluant gave similar results.

One vermiculite sample was eluted with 0.02 N CsCl until (6 column volumes) the effluent activity dropped to background. The column was then eluted with 0.01 N HNO<sub>3</sub>. After a small initial surge, the eluant activity remained steady at about three times background. Thus moderately strong acid does not easily remove the sorbed cesium ion. The small amounts released can be accounted for by acid attack on the silicate structure of the mineral.

As a more rigorous test cesium-saturated vermiculite was boiled with 0.01 N NaCl and also with 0.01 N CsCl. Samples of the solution were taken at intervals and counted; the results are given in Table 2. These results on the

TABLE 2.—LEACHING OF CS-VERMICULITE-BIOTITE  
A, WITH CsCl; B, WITH NaCl

Time of Boiling	Leachate Activity (counts/min g mineral)			
	Dried at Room Temperature		Heated at 110°C	
	A	B	A	B
10 min	512	397	438	209
1 hr	1230	1276	978	1287
1 day	1645	—	2423	3831
2 days	1982	—	2812	3940
5 days	2402	3214	3197	4056
10 days	3127	4355	7187	4596

difficulty in removal of cesium from vermiculite are consistent with Barshad's (1948, 1949, 1950) ideas on the fixation of potassium in vermiculite. When cesium enters a vermiculite layer, a collapse occurs in which water is, so to speak, extruded and the mineral is in effect converted to the biotite structure.

In this mica structure the cesium is effectively held out of contact with the solution and its removal must depend on the extremely slow diffusion from site to site between essentially anhydrous mica layers. The results of the leaching tests in which sodium appeared to be somewhat more effective in displacing the cesium are consistent with this idea: the hydrated sodium ion is possibly more effective in "prying apart" the collapsed silicate sheets. Even in this case, however, the leaching is extremely slow. In the ten-day boiling test above described only 1.6 percent of the cesium was removed.

To test the possibility that moderate heating of a cesium vermiculite would cause a more effective extrusion of water from the mineral and consequently a firmer fixation, several samples of Cs-saturated vermiculite were heated for 12 days at 110°C and were then subjected to the boiling leach above described. The results in Table 2 quite conclusively demonstrate that no advantage is thereby gained. If indeed the fixation is due to layer collapse with exclusion of water, it occurs quite effectively when the mineral is immersed in an aqueous solution.

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