USE OF NEGATIVE SORPTION IN STUDIES OF ION FIXATION BY HYDROBIOTITE*

by

DONALD G. JACOBS

Oak Ridge National Laboratory, Oak Ridge, Tennessee

ABSTRACT

THE EXCLUSION of anions relative to tritiated water from the negatively charged inter-lamellar spacing of hydrobiotites that have a limited degree of lattice expansion permits measurement of the interlamellar volume. Measurement of the changes in the inter-lamellar volume and in the exchange capacity, when hydrobiotite lattices are collapsed by potassium treatment or expanded by treatment with sodium tetraphenyl boron, provides a means for estimating the distribution of the surface charge densities of these interstratified minerals.

In the hydrobiotite sample studied (Zonolite from Traveler's Rest, South Carolina), the biotite fraction was estimated to have a surface charge density of $2.0 \pm 0.14 \times 10^{-7}$ meq cm^{-2} and the vermiculite fraction, $1.5 \pm 0.51 \times 10^{-7}$ meq cm^{-2}. The charge density, and its relative distribution, was reflected in the tendency of these mineral fractions to collapse upon potassium treatment and to entrap trace concentrations of cesium in the interlayer spacing.

INTRODUCTION

CLAY minerals generally have a net negative charge that cannot be satisfied locally, since the counter-ions (ions having the sign of charge opposite to that of the surface) cannot penetrate the dense lattice. Thus the charge can be thought to reside effectively on the surface of the clay lattice, and an electric double layer is established with an accumulation of counter-ions and a deficit, or negative sorption, of co-ions (ions having the same sign of charge as the surface). The variation of the electric potential, ψ, with distance from the surface, X, is given by the standard Gouy-Chapman theory (Kruyt, 1952, p. 129):

$$\frac{d\psi}{dX} = (32\pi \, n_0 \, kT/\epsilon)^{\frac{1}{2}} \sinh \left(-ze\psi/2kT \right) \tag{1}$$

where

n_0 = the number of ions per cubic centimeter at a point far removed from the charged surface,

341

k = the Boltzman constant,

T = the absolute temperature,

ϵ = the dielectric constant of the medium,

z = the valency of the ions, and

e = the charge on an electron.

The local concentration of a given type of ion is given by the Boltzman expression:

$$C_i = C_{io} \exp\left(-ze\psi/2k\text{T}\right). \tag{2}$$

When these equations are combined and integrated over the electric double layer, the amount of co-ion exclusion from the double layer can be calculated. Schofield and Talibuddin (1948) have shown that the integrated expression can be given approximately as:

$$\Gamma^-/C = q/\sqrt{z\beta C} + 4/z\beta\Gamma \tag{3}$$

where

Γ^- = the surface deficit of anions;

q = a factor determined by the ratio of valency of the counter-ion and the co-ion (and is equal to two for symmetrical salts);

β = $8\pi F^2/1000\ \epsilon RT = 1.06 \times 10^{15}$ cm–meq^{-1} when water is used as the solvent at 25°C, and F = the Faraday, ϵ = the dielectric constant of the medium, R = the molar gas constant, and T = absolute temperature; and

Γ = the charge density of the surface in meq–cm^{-2}.

The value Γ^-/C obtained from equation (3) has units of length and is the effective distance from which co-ions are excluded from the charged surface. The internal exclusion volume can be calculated, if the surface area is known, or it can be determined experimentally from the intercept of the linear portion of the curve when the exclusion volume is plotted versus $q/\sqrt{z\beta C}$.

When two successive electric double layers overlap, a correction must be applied. If the surfaces are sufficiently close, however, the exclusion of anions in the region of overlap can be depicted adequately by Donnan membrane theory (Schofield and Talibuddin, 1948).

EXPERIMENTAL PROCEDURE

Sodium-saturated hydrobiotite* was used to fill ion exchange columns. Hydrobiotite exists as a mixed-layer mineral, having a rather random mixing of collapsed biotite-type layers with no interlamellar water, and vermiculite-type layers having two layers of interlamellar water. The spacing between the

* Zonolite from Traveler's Rest, South Carolina.

charged faces of the sodium-saturated vermiculite layers is 5.55 Å (Grim, 1953, p. 74); thus Donnan membrane theory can be used to describe the chloride exclusion from the interlamellar region.

The columns were pre-equilibrated with untagged NaCl solution of the desired concentration. Tritiated water solutions of NaCl of the same concentration and tagged with Cl^{36} were passed through the column at a constant flow rate. Each run consisted of a saturation and a leaching step, and the same column was used for all runs. Samples were counted simultaneously for H^3 and Cl^{36}, using a Packard Instruments Tri-Carb counter.

A computer program, written by George Atta, Mathematics Division, Oak Ridge National Laboratory, was used to correct the overlap of the two beta spectra and to fit the experimental data to a chromatographic breakthrough curve of the type (Glueckauf, 1955; Hashimoto, Deshpande and Thomas, 1964; Rifai, *et al.*, 1952):

$$C/C_0 = 1/2\{1\text{-erf }\sqrt{P} \ (V-\overline{V})/\sqrt{\overline{V}} - V\} \tag{4}$$

where

$C/C_0 =$ the fraction breakthrough of the tracer,

$P =$ the Peclet number for the column*,

$V =$ the throughput volume, and

$\overline{V} =$ the equivalent column volume.

CHLORIDE EXCLUSION

Experimental data showed that the apparent pore volume for tritium remains relatively constant with changes in NaCl concentration. For chloride there was a steady drop in the apparent pore volume with decreasing NaCl concentration. If the charged surfaces of the hydrobiotite had been sufficiently separated to permit full development of the electric double layers, a plot of the measured exclusion volume versus the right-hand side of equation (3) would have yielded a straight line with an intercept of zero and a slope corresponding to the surface area. The linear portion of the curve (Fig. 1) has a slope corresponding to 1.15 m² per g, but the intercept is 0.127 ml. per g, which is a measure of the interlamellar volume where the electric double layers overlap.

The measured exchange capacity of the sodium-treated hydrobiotite is 0.753 meq per g, and the total accessible internal and external surface area is calculated from the experimental data to be 459 m² per g; thus the mean surface charge density is 1.64×10^{-7} meq/cm². Using this value, the second term of equation (3) is evaluated as 2.3×10^{-8} cm, and the volume charge density of the internal pore volume is 5.93 N.

* $P = N/2 = \overline{v}l/4D$, where N is the number of theoretical plates in the notation of Glueckauf (1955); and where $\overline{v}$ is the linear pore velocity of the solution, l is the column length and D is the dispersion coefficient in the notation of Rifai *et al.* (1952).

23

To ensure that the above explanation of internal and external effects was correct, another series of experiments was conducted in which the hydro-biotite was subjected to potassium treatment for collapse of the vermiculite layers (Barshad, 1948) or to sodium tetraphenylboron treatment for expansion of the biotite layers (DeMumbrum, 1959). In this series 0.01 M NaCl solutions were used in the determination of the chloride exclusion volumes.
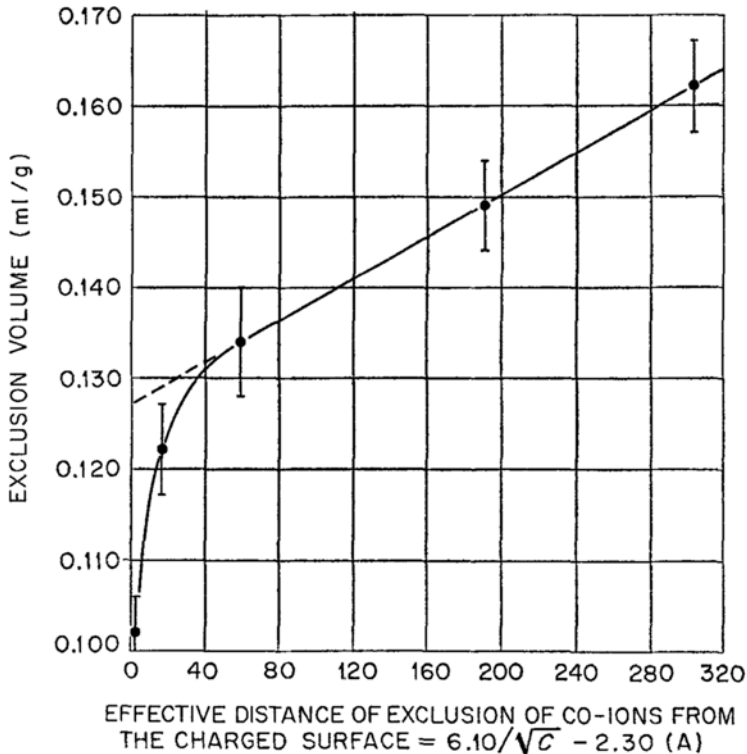

FIG. 1. Chloride exclusion by hydrobiotite.

The results, compiled in Table 1, give evidence that the model does provide an accurate description of the system. As the biotite expands, the exclusion volume increases, and as the vermiculite collapses, the exclusion volume decreases.

After the hydrobiotite had been subjected to five treatments with sodium tetraphenyl boron, the interlamellar exclusion volume was estimated to be 0.200 ml. per g. This is the value that would be expected if all of the inter-lamellar spacing is filled with water, except for the volume occupied by the sodium ions. Thus, it seems that this treatment caused complete expansion

Table 1.—Effect of Lattice Collapse on Anion Exclusion by Hydrobiotite

Hydrobiotite Treatment	Exchange capacity (meq/g)	Measured chloride exclusion volume (ml./g)
Sodium tetraphenyl boron (5 times)	1.31	0.207
Sodium tetraphenyl boron (4 times)	1.29	0.201
Sodium tetraphenyl boron (3 times)	1.12	0.190
Sodium tetraphenyl boron (2 times)	1.12	0.188
Sodium tetraphenyl boron (1 time)	1.09	0.176
Sodium chloride	0.740	0.129
0.075 meq KNO_3/g	0.661	0.095
0.188 meq KNO_3/g	0.556	0.089
0.375 meq KNO_3/g	0.399	0.082
0.75 meq KNO_3/g	0.183	0.056
1.5 meq KNO_3/g	0.084	0.022
Potassium saturated	0.064	0.016

of the biotite fraction. From this value it is further estimated that there is a total internal surface area of about 720 m² per g.

It was noted also that the breakthrough curves for chloride were steeper than those for tritium. This is reasonable, since the tritium must penetrate the restricted interlamellar spacing from which the chloride ion is excluded. It was assumed that differences in the experimental plate heights (obtained from the slopes of the H³ and Cl³⁶ breakthrough curves) would be due to a slow diffusion of tritium into the interlamellar spacing. Using Glueckauf's simplified model for the contribution of particle diffusion to the total plate height (Helfferich, 1962, p. 453), the particle diffusion coefficient for tritium in the interlamellar spacing was estimated to be $4.6 \pm 2.7 \times 10^{-7}$ cm² per sec. These values are of the same order of magnitude as those obtained by Keay and Wild (1962) for self-diffusion of barium ions in vermiculite. They also agree quite well with later estimates made using isotopic exchange data for sodium in similar columns of hydrobiotite, which yielded values of about 3×10^{-7} cm² per sec.

CESIUM FIXATION BY HYDROBIOTITE

The sorption of low concentrations of cesium by sodium chloride treated hydrobiotite is primarily due to the collapsed biotite layers (Jacobs and Tamura, 1960; Jacobs, 1963). When the concentration of cesium is raised beyond the point where all of the edge fixation sites have been satisfied, part of the additional cesium is sorbed at the basal surface of the vermiculite

layers. When sufficient cesium has been sorbed at the basal surface of a vermiculite layer, that layer collapses. Collapse of the vermiculite layers causes entrapment of the cesium sorbed at the basal exchange sites in a process of interlayer fixation.

Desorption Studies

Desorption of cesium entrapped by interlayer fixation is quite difficult (Table 2, column 1). The interlayer cesium is almost completely unexchanged by stable cesium salt, since the excess cesium tends to maintain the lattice in its collapsed state. Only slight amounts of the interlayer cesium are exchanged by acid, even when sufficient acid is used to cause apparent degradation of the hydrobiotite. The cesium held at the edges of the collapsed biotite layers (Table 2, column 2) is more easily exchanged by acid. A greater quantity is exchanged also by the first leach with $CsNO_3$, but the small additional quantities leached with successive leaches suggest that the $CsNO_3$ has been effective in collapsing the vermiculite lattices and entrapping the remaining cesium. When the hydrobiotite had been treated with sodium tetraphenyl boron to open the biotite layers, edge fixation of cesium was prevented and the sorbed cesium was readily exchanged by hydrochloric acid. Again desorption with $CsNO_3$ suggested that collapse of the lattices prevented desorption beyond the first leach cycle.

TABLE 2.—DESORPTION OF CESIUM FROM
HYDROBIOTITE

Amount of leaching solution (meq)	% Cesium leached		
	1*	2†	3‡
HCl			
1	0.15	1	6
5	0.5	4	34
10	1	7	51
50	2	27	71
100	4	42	82
500	12	76	96
$CsNO_3$			
1	0.1	2.6	7.2
5	0.2	3.1	8.7
10	0.3	3.6	9.4

* 2-g sample (NaCl-treated) containing 0.518 meq cesium.

† 2-g sample (NaCl-treated) containing 0.618×10^{-5} meq cesium.

‡ 0.66-g sample (Na-tetraphenyl boron–treated) containing 0.991×10^{-5} meq cesium.

Column Studies

Sodium chloride–treated hydrobiotite (10 g) was placed in 1/2-in.-diameter columns, and 7.5 l. of 0.5 M NaNO$_3$ containing 1.7 × 10^{-7} M CsNO$_3$ and various concentrations of potassium was run through the columns at a constant flow rate of 1.1 ml. min^{-1} cm^{-2}. Concentrations of potassium of less than 4 × 10^{-3} M in the influent solution had a slight depressing effect on the sorption of cesium (Fig. 2). At higher concentrations of potassium, however, the potassium caused lattice collapse, with a decrease in exchange capacity
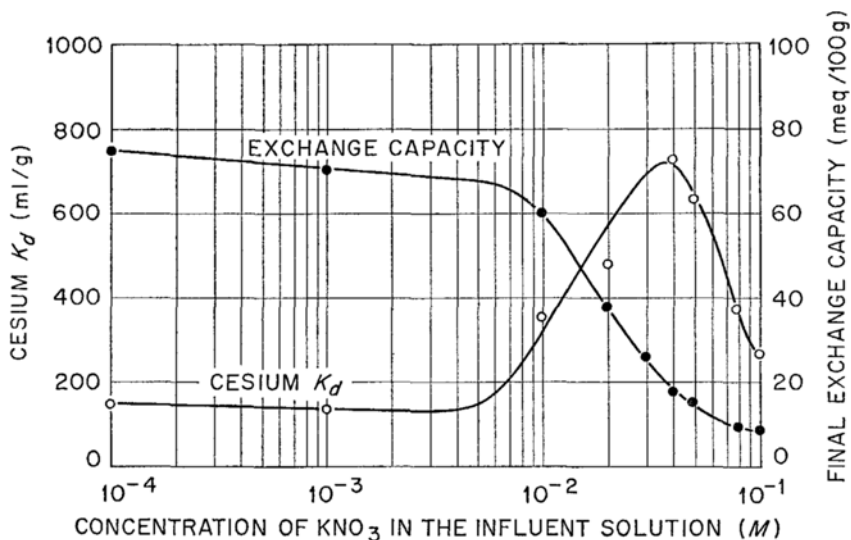

FIG. 2. The effect of potassium on the sorption of cesium from 0.5 M NaNO$_3$ by sodium chloride–treated hydrobiotite.

and interlayer fixation of the trace quantities of cesium. The peak cesium loading in this series occurred at about 0.04 M potassium; higher concentrations of potassium caused more lattice collapse but provided more competition for cesium sorption at the basal exchange sites.

When the columns were filled with hydrobiotite treated with sodium tetraphenyl boron, two distinct peaks occurred in the interlayer cesium fixation curve as the concentration of potassium in the influent solution is increased (Fig. 3), rather than the single fixation peak found for the sodium chloride–treated hydrobiotite. Each peak is accompanied by a distinct inflection in the exchange capacity curve. The sharp peak occurring between 10^{-3} and 10^{-2} M KNO$_3$ reflects the recollapse of the opened biotite layers, while the broader peak occurring between 10^{-2} and 10^{-1} M KNO$_3$ is due to the collapse of the vermiculite layers.
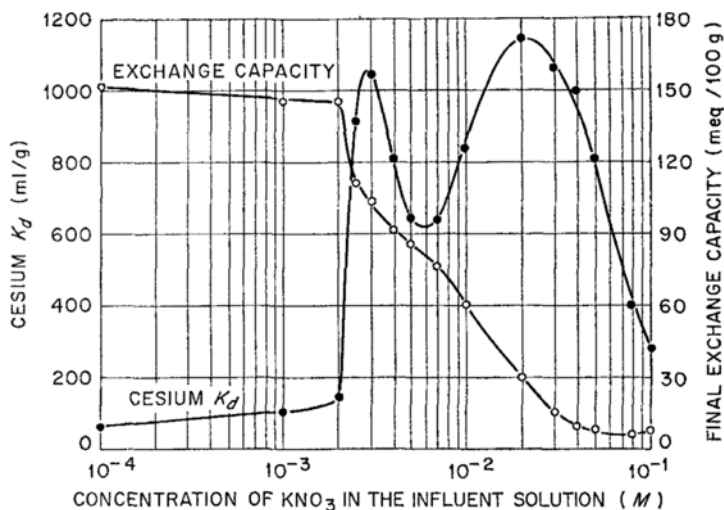
FIG. 3. The effect of potassium on the sorption of cesium from 0.5 M NaNO$_3$ by sodium tetraphenyl boron–treated hydrobiotite.
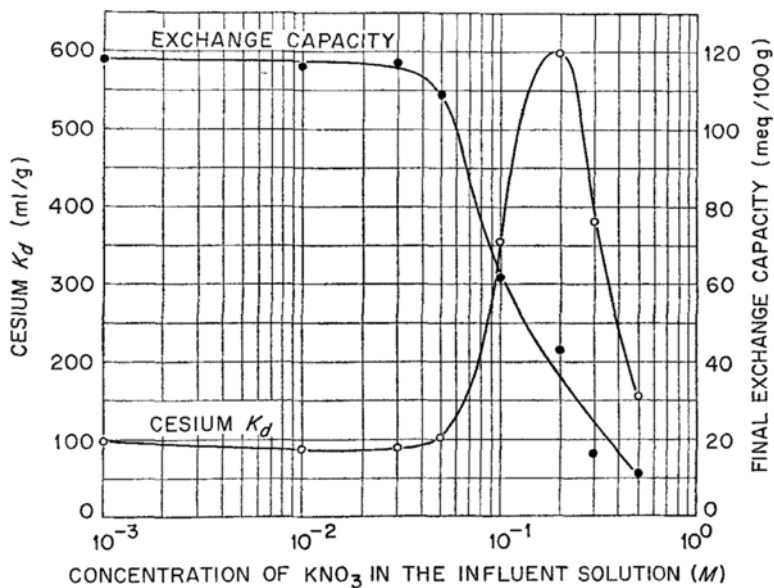

FIG. 4. The effect of potassium on the sorption of cesium from 0.5 M NaNO$_3$ by South African vermiculite.

From the data presented in Table 1, the average interlayer charge density can be estimated as $2.00 \pm 0.14 \times 10^{-7}$ meq/cm² for the biotite layers and $1.50 \pm 0.51 \times 10^{-7}$ meq per cm² for the vermiculite layers. It seems that the position and width of the cesium fixation curves reflect the charge density distribution of the collapsible lattices. As noted by Barshad (1948, 1949, 1950) and Weaver (1958), the higher the charge density the more susceptible is the lattice to collapse; hence a smaller $K^+ : Na^+$ ratio is required to induce collapse. The distinct peaks arising from the biotite and vermiculite-type layers indicate that this hydrobiotite does not consist of an even gradation from low-charge density vermiculite to high-charge density biotite, but that there are two distinct mineral species in the sample.

Differences in the behavior of the biotite and vermiculite layers of the Zonolite were observed also in time studies of potassium release, in which it was noted that the collapsed vermiculite lattices had a much greater tendency for re-expansion than the biotite lattices (Jacobs, 1963).

South African vermiculite, supplied by the Phosphate Development Corporation (Pty) Limited, Phalaborwa, Transvaal, South Africa, was also studied for cesium fixation. In this case, a potassium concentration of 0.2 M was required to obtain optimum interlayer fixation of cesium from 0.5 M $NaNO_3$ (Fig. 4). The results of negative sorption of chloride indicate that the surface-charge density of this material is slightly less than that of the sodium chloride–treated Zonolite. The measured exchange capacity of the African vermiculite was 1.08 meq per g. From negative sorption data, the external surface area was estimated to be 1.16 m² per g with an interlamellar volume of 0.196 ml. per g. Thus the total accessible surface area is calculated to be 706 m² per g and the surface charge density is 1.49×10^{-7} meq per cm² compared to 1.64×10^{-7} meq per cm² obtained for sodium chloride–treated Zonolite. The volume charge density of the interlamellar volume is calculated to be 5.50 N compared to 5.93 N for the sodium chloride–treated Zonolite.

SUMMARY

The response of hydrobiotite from South Carolina to cesium fixation indicates that two distinct minerals are present in the sample. The tendency for the two species to collapse and entrap trace quantities of cesium is related to their interlayer surface charge densities. These interlayer charge density distributions can be determined by combining the results of anion exclusion with cation exchange data as various fractions of the mixed-layer minerals are opened or collapsed by chemical treatment.

ACKNOWLEDGMENT

D. Colvett for their painstaking efforts in obtaining the data. In addition, he would like to thank his supervisors, F. L. Parker and E. G. Struxness, for their support of these studies.

REFERENCES

BARSHAD, I. (1948) Vermiculite and its relationship to biotite as revealed by base exchange reactions, X-ray analyses, differential thermal curves and water content, *Am. Mineralogist* **33,** 655–78.

BARSHAD, I. (1949) The nature of lattice expansion and its relation to hydration in montmorillonite and vermiculite, *Am. Mineralogist* **34,** 675–84.

BARSHAD, I. (1950) The effect of the interlayer cations on the expansion of the mica type of crystal lattice, *Am. Mineralogist* **35,** 225–38.

DEMUMBRUM, L. E. (1959) Exchangeable potassium levels in vermiculite and K-depleted micas and implications relative to potassium levels in soils, *Soil Sci. Soc. Am. Proc.* **23,** 192–4.

GLUECKAUF, E. (1955) Theory of chromatography. Part 9. The " Theoretical Plate " concept in column separations, *Trans. Faraday Soc.* **51,** 34–44.

GRIM, R. E. (1953) *Clay Mineralogy*, McGraw-Hill, New York.

HASHIMOTO, I., DESHPANDE, K. B., and THOMAS, H. C. (1964) Peclet numbers and retardation factors for ion exchange columns, *Ind. and Eng. Chem. Fundamentals* **3,** 213–8.

HELFFERICH, F. (1962) *Ion Exchange*, McGraw-Hill, New York.

JACOBS, D. G. (1963) The effect of collapse-inducing cations on the cesium sorption properties of hydrobiotite, *International Clay Conference, Sweden* (Edited by Th. Rosenqvist and P. Graff-Peterson), pp. 239–48, Pergamon Press, New York.

JACOBS, D. G., and TAMURA, T. (1960) The mechanism of ion fixation using radio-isotope techniques, *Trans. 7th Intern. Cong. Soil Sci.* **2,** 206–14.

KEAY, J., and WILD, A. (1962) The kinetics of cation exchange in vermiculite, *Soil Sci.* **92,** 54–60.

KRUYT, H. R. (1952) *Colloid Science*, vol. 1, Elsevier, Amsterdam.

RIFAI, M. N. E., KAUFMAN, W. J., and TODD, D. K. (1952) *Dispersion Phenomena in Laminar Flow Through Porous Media*, California Univ. Div. Civil Eng., Sanitary Eng. Res. Lab., IER ser. 93, no. 2.

SCHOFIELD, R. K., and TALIBUDDIN, O. (1948) Measurement of internal surface by negative adsorption, *Discussions Faraday Soc.* **3,** 51–6.

WEAVER, C. E. (1958) The effects and geologic significance of potassium " fixation " by expandable clay minerals derived from muscovite, biotite, chlorite, and volcanic material, *Am. Mineralogist* **43,** 839–61.