

## CALCIUM-MAGNESIUM EXCHANGE IN MONTMORILLONITE AND VERMICULITE\*

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**Abstract**—An experimentally determined Ca–Mg exchange isotherm of montmorillonite is reported. The selectivity coefficient of this exchange over a wide range of Mg saturation was calculated and found constant.

Standard free energies of exchange, thermodynamic equilibrium constants and activity coefficients of the exchangeable Ca and Mg ions in vermiculite and montmorillonite, were predicted from knowledge of the microstructure of these two clays, assuming that coulombic forces are the main ones playing a role in the interaction between the counterions and the charged clay surface. The standard free energies of exchange ( $\Delta G_{Ca}^{oMg} = 238$  cal/mole) predicted a preference for Ca in montmorillonite and a preference for Mg in vermiculite ( $\Delta G_{Ca}^{oMg} = -1665$  cal/mole). The predicted thermodynamic equilibrium constants were compatible with the experimentally determined selectivity coefficients  $K_{Ca}^{Mg} = 0.67$  as compared with  $K_{Ca}^{Mg} = 0.68$  in montmorillonite, which remains constant over all the range of Mg saturation, and  $K_{Ca}^{Mg} = 16.7$  as compared with  $K_{Ca}^{Mg} = 13.9$  in vermiculite at 95% Mg saturation. The activity coefficients of Ca and Mg counterions in montmorillonite were found to be  $f_{Ca} = 2.0 \times 10^{-3}$  and  $f_{Mg} = 2.2 \times 10^{-3}$ , respectively, and to remain constant. The activity coefficients of exchangeable Ca and Mg in vermiculite were found to be  $f_{Ca} = 7.1 \times 10^{-5}$  and  $f_{Mg} = 3.5 \times 10^{-5}$ , respectively, at an equivalent fraction of unity. The activity coefficient of exchangeable Mg increased as the saturation with Mg decreased, and was found to be  $1.7 \times 10^{-3}$  in the range of the low Mg saturation.

The microstructure, the isomorphic substitution and the surface charge density provided an understanding of the changes taking place in the activity coefficients of the counterions.

### INTRODUCTION

THE QUALITATIVE preference for a given counterion is expressed in the selectivity sequences of the cations (Helferich, 1962). According to the selectivity sequence, the Ca ion is preferred over the Mg ion, a fact which is explained by the larger equivalent volume of the hydrated ion. However, this selectivity is not the same for all clay minerals. For instance, in vermiculite at low Mg saturation, there is a preference for Ca, and as the saturation of the vermiculite with Mg increases, the preference for Mg increases (Peterson *et al.*, 1965). On the other hand, Dolcater *et al.* (1968) found that montmorillonite shows a preference for Ca. Data from ion exchange experiments, expressed in the selectivity coefficients, give the quantitative evaluation of this preference, but do not provide an insight into the forces acting between the counterions and the charged clay surface, and consequently do not provide any means of predicting the affinity of the clay for the specific ion.

If the forces acting between the counterions and the charged clay surface were known, the thermodynamic equilibrium constant of exchange could be predicted. The latter is related to the experimentally determined selectivity coefficient, where the interactions between the counterions and the clay surface are expressed in the activity coefficients of the exchangeable ions. In some cases the selectivity coefficient of exchange is a function of the composition of the clay mineral, as in vermiculite, an indication that the interactions between the counterions and the clay surface change, as the saturation with one of the counterions increases. This change in the interactions will be reflected in the activity coefficients of the exchangeable ions. When the selectivity coefficient remains constant at different saturation of the exchanger, it is an indication that the presence of two kinds of counterions does not change the interactions with the clay surface and that they remain the same as they were when only one kind of counterion saturates the oppositely charged surface.

The purpose of this research was to predict the thermodynamic equilibrium constants and the activity coefficients of exchangeable Ca and Mg in

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montmorillonite and vermiculite, using X-ray data, and compare them to the experimentally determined selectivity coefficients of exchange.

### THEORETICAL CONSIDERATIONS

For the exchange reaction,



where  $R$  stands for the negatively charged clay, the selectivity coefficient  $K_{sCa}^{Mg}$  is by definition

$$K_{sCa}^{Mg} = \frac{\overline{XMg} \cdot (Ca^{2+})}{\overline{XCa} \cdot (Mg^{2+})} \quad (2)$$

where  $\overline{XMg}$  and  $\overline{XCa}$  are the equivalent fractions of exchangeable Mg and Ca in the clay and  $Ca^{2+}$ ,  $Mg^{2+}$  are the activities of the Ca and Mg ions, respectively, in solution. All quantities were determined experimentally and the concentration of the soluble ions was corrected by their activity coefficients, respectively.

The selectivity coefficient is related to the thermodynamic equilibrium constant as follows:

$$K_{Ca}^{Mg} = K_{sCa}^{Mg} \cdot \frac{fMg}{fCa} \quad (3)$$

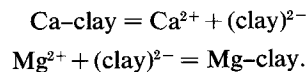
where  $K_{Ca}^{Mg}$  is the molar thermodynamic equilibrium constant and  $fMg$  and  $fCa$  are the molar activity coefficients of the exchangeable magnesium and calcium, respectively. Although in the calculation of the selectivity coefficient the equivalent fraction of the exchangeable ions was used, numerically the selectivity coefficient will not change if the concentration of the counterions is expressed on the molarity basis, because in this specific case the valency of both ions is the same.

Thermodynamic equilibrium constant of exchange in clay minerals have been calculated by Gaines and Thomas (1953). The same approach has been used by Laudelout *et al.* (1968), Martin and Laudelout (1963), Van Bladel and Laudelout (1967), Hutcheon (1966) and Gast (1969). This approach, although correct, is very formal. It neither gives an insight into the forces acting between the exchangeable cations and the clay surface, nor takes into account the structure of the clay.

Because the coulombic forces are the main ones acting between the charged exchanger's surface and the counterions, Pauley (1954) predicted standard free energies of exchange, by determining the work necessary to remove each of the two types of cations involved, from the distance of closest approach to infinity, against the coulombic forces acting between the cation and the resin. The

distance of closest approach used by Pauley was the sum of the radii of the hydrated cation in solution and the resin anion. Shainberg (1970) applied Pauley's approach for the calculation of the standard free energy of exchange, but instead of using solution data for the radii of the cations, the structure of the clay mineral combined with X-ray data was used in the calculation of the distance of closest approach.

Following Pauley (1954) and Shainberg (1970), the total free energy of exchange of Ca and Mg in a clay was assumed to be the sum of the free energy required to remove the Ca ion from the clay surface to a point at infinite distance in the solution phase and the free energy required to bring Mg ions from the solution phase to the surface. Thus the exchange reaction of equation (1), may be divided into two processes



The free energy required for removing the Ca ion from the clay surface to a point at infinite distance in the solution phase is given by

$$\Delta G_{Ca}^{\circ} = + \int_{r_{Ca}}^{r_{\infty}} \frac{Z^2 e^2}{\epsilon r^2} dr = + \frac{Z^2 e^2}{\epsilon r_{Ca}}$$

where  $r_{Ca}^*$  is the distance between the plane midway between the clay platelets, where the Ca ions are located, and the plane of negative charge in the clay structure†.

Similarly, the free energy required for bringing the cations  $Mg^{2+}$  from the solution phase to the clay surface is given by equation

$$\Delta G_{Mg}^{\circ} = \int_{r_{\infty}}^{r_{Mg}} \frac{Z^2 e^2}{\epsilon r_{Mg}}$$

where  $r_{Mg}^*$  is the distance between the plane midway between the clay platelets and the plane of negative charges in Mg systems. The total molar free energy change is given by the sum of these equations.

$$\Delta G^{\circ} = \Delta G_{Ca}^{\circ} + \Delta G_{Mg}^{\circ} = \frac{Z^2 e^2 L}{\epsilon} \left( \frac{1}{r_{Ca}} - \frac{1}{r_{Mg}} \right) \text{ cal/mole} \quad (4)$$

and

$$\ln K_{Ca}^{Mg} = - \frac{\Delta G^{\circ}}{RT} \quad (5)$$

† The explanation of how these distances were chosen is given later.

where  $\Delta G^\circ$  = standard molar free energy of exchange

$e$  = charge of an electron ( $4.8 \times 10^{-10}$  e.s.u.)

$L$  = Avogadro's number =  $6.02 \times 10^{23}$ .  
Since the clay is negatively charged, the number of the divalent cations neutralizing a mole of negative charge is  $3.0 \times 10^{23}$  which is the number used in this calculation.

$\epsilon$  = dielectric constant, whose value consists of the values for the clay crystal and the water. The dielectric constant of the clay is 5 and that of the water between the platelets is also about 5, due to dielectric saturation. Thus, the value of the dielectric constant of the medium was taken as 5 Shainberg and Kemper (1966).

$r_{Ca}^*$ ,  $r_{Mg}^*$  = the effective radius of the distance of closest approach calculated from X-ray data and the structure of the clay.

$R$  = gas constant

$T$  = absolute temperature

$Z$  = valency of counterion.

#### *The activity coefficient of adsorbed ions*

The concept of an activity coefficient is well established in solution chemistry. In clay chemistry this concept has either been used formally (Gaines and Thomas, 1953) or discussed without reaching a definite conclusion as to its physical significance and importance (Bolt, 1960). The physical significance and importance of an activity coefficient lies in the fact that it corrects the concentration term for the interactions due to electric fields. The correction in an electrolyte solution is much smaller than that in a clay suspension, because the electric field in an electrolyte solution, due to the oppositely charged ions, is weaker than the electric field in a clay, due to the charged clay surface. In order to calculate the activity coefficient of an exchangeable ion, the microstructure of the clay should be well known, but the calculation will not differ principally from that of an activity coefficient of an ion in an electrolyte solution (keeping in mind all the limitations of a single ion activity).

According to the Debye-Hückel theory, the activity coefficient of an ion in solution is given by

$$\ln f_i = \frac{\Delta G(el)}{RT} \quad (6)$$

where  $f_i$  is the activity coefficient of an ion; and  $\Delta G(el)$  is the contribution of the electrical energy of ion  $i$  due to ionic interactions with the other ions

to the free energy of mixing (Robinson and Stokes, 1959).

The same approach can be used to calculate the activity coefficients of exchangeable ions, but the electrical energy of interaction between the counterion and the charged surface should be calculated from detailed data on the microstructure of the clay mineral. These data are available from X-ray analysis and knowledge of the isomorphous substitution of the clay mineral. The equation used for the calculation of the activity coefficients of the exchangeable ions will be given after the discussion of the structure of vermiculite and montmorillonite.

#### *Microstructure of vermiculite and montmorillonite*

According to Grim (1953), MacEwan (1961) and van Olphen (1963), vermiculite and montmorillonite are members of the expanding three-layer clays. The difference between these two members is in the type and degree of the isomorphous substitution. The isomorphous substitution in vermiculite is mainly  $Al^{3+}$  for  $Si^{4+}$  in the tetrahedral layer, giving a surface charge density of  $6 \times 10^4$  e.s.u./cm<sup>2</sup> Barshad, 1950 and Walker, 1961), while the isomorphous substitution in montmorillonite is mainly  $Mg^{2+}$  for  $Al^{3+}$  in the octahedral layer, giving a surface charge density of  $3 \times 10^4$  e.s.u./cm<sup>2</sup> (Norrish, 1954). These clays expand when in contact with water vapor, water, or dilute salt solutions, the degree of swelling being a function of the surface charge density and the kind of counterion neutralizing the negative charge of the clay. The interlayer spacing during water uptake by montmorillonite as dependent on the counterion has been reported by Norrish (1954), while that of vermiculite by Walker (1961) and Barshad (1950). Based on the information of the  $c$ -spacing between the clay platelets, the thickness of a three-layer plate, the assumption that divalent cations are to be found in the water layers between two plates, and a speculation on the most reasonable place of the plane of the negative charge inside the clay plate, the Ca and Mg structure of montmorillonite and vermiculite are presented schematically in Fig. 1. From the figure it is evident that (a) the  $c$ -spacing of both Ca and Mg forms of the montmorillonite is larger than that of the vermiculite, giving rise to three molecular layers of water between the montmorillonite platelets compared with only two molecular layers of water between the vermiculite sheets; (b) the  $c$ -spacing of Mg montmorillonite is larger than that of Ca montmorillonite (19.2 Å and 18.9 Å, respectively) because of the larger hydrated radius of Mg as compared with that of Ca; and (c) in vermiculite, the  $c$ -spacing of Mg is smaller than that of Ca vermiculite (14.5 Å

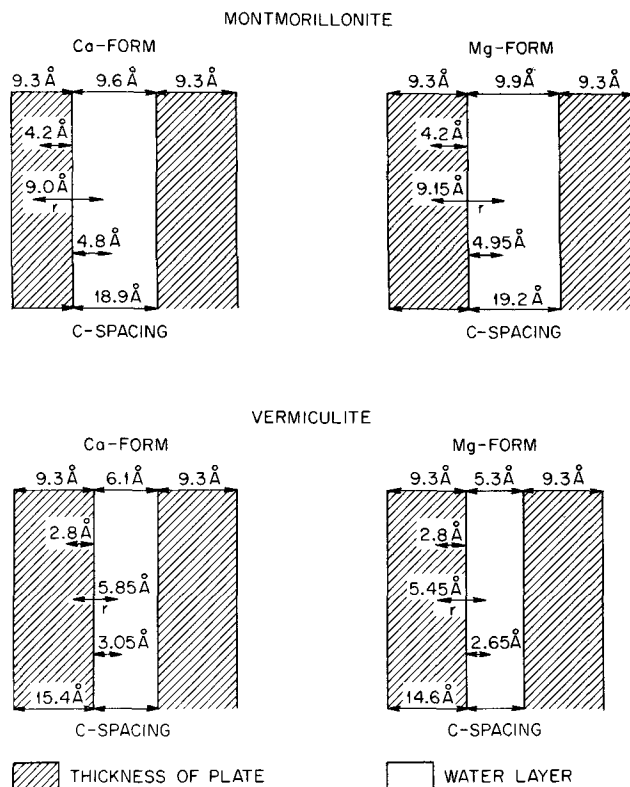


Fig. 1. Schematic representation of the different distances in montmorillonite and vermiculite (for explanation, see text).

and 15.3 Å, respectively) because the strong attraction forces between the vermiculite sheets prevent the full hydration of the interlayer ions, and the *c*-spacing is affected by the crystallographic radius of the ion.

The thickness of the clay plate is indicated in Fig. 1, being the same for both the Ca and Mg forms of the montmorillonite and the vermiculite. Walker (1961) found that the thickness of the dry vermiculite is 9.26 Å, while that of the dry montmorillonite plate was found 9.3 Å by Grim (1953) and 9.2 Å by van Olphen (1963). The mean value of these thicknesses gives 9.25 Å for montmorillonite, which is very close to that of vermiculite. Choosing the same thickness for both montmorillonite and vermiculite is also in agreement with the observation of Pezerat and Mering (1954) that the position of the layers in the *c*-direction is insensitive to isomorphic substitutions, constructing a rigid frame. The changes in the dry platelet are due to the counterions being only in the "a" and "b" directions. When the thickness of the dry plate is subtracted from the *c*-spacing of the fully hydrated clay, the thickness of the water layers is obtained. This thickness

is also indicated in Fig. 1, being 9.6 Å and 9.9 Å for the Ca and Mg montmorillonite and 6.1 Å and 5.3 Å for the Ca and Mg vermiculite, respectively. The thickness of the water layers between the plates is of importance, because the calculation of the distance between the counterion and the surface of the plate is based on it. It is assumed, as suggested by Norrish (1954), that the counterions of the hydrated clay are found midway between two opposite plates, so that the distance between the exchangeable ion and the surface of the plate is calculated by dividing the thickness of the layers by two: for Ca and Mg montmorillonite being 4.80 Å and 4.95 Å and for Ca and Mg vermiculite 3.05 Å and 2.65 Å, respectively. Another parameter which is indicated in Fig. 1 is the distance between the plane of the negative charge inside the clay particle and the surface of the plate. The isomorphic substitution in montmorillonite is mainly in the octahedral layer. The plane of the negative charge may be supposed to be between the clay surface, which gives a distance of 4.65 Å (van Olphen, 1963) to the surface of the plate or, because polarization occurs, this distance was modified to be 4.2 Å

(Shainberg, 1970). In vermiculite the isomorphic substitution is mainly in the tetrahedral layer and the plane of the negative charge is supposed to be on the metallic cation of the tetrahedral layer, giving a distance of 2.8 Å. The sum of the distance of the negative charge to the surface of the plate and the distance of the counterion from the surface of the plate to midway between the water layers, is the effective radius used in the calculations of the standard free energy of exchange and the electric energy between the counterions and the clay surface.

These effective radii for Ca and Mg in the montmorillonite are (4.2 + 4.8 =) 9.0 Å and (4.2 + 4.95 =) 9.15 Å, respectively, and (2.8 + 3.05 =) 5.85 Å and (2.8 + 2.65 =) 5.45 Å for Ca and Mg vermiculite, respectively.

In order to calculate the activity coefficients of the exchangeable ions the electric energy between the ions and the clay surface should be evaluated. It was presumed, as suggested by Norrish (1954) that the main interaction is between the counterion and two negative charges on each clay plate. The interactions with the other negative charges of the plates and the counterions were assumed to be of secondary importance, because these forces and the resulting energies are of opposite signs and approximately cancel each other.

The electrical interaction of a counterion with the negative charges was calculated by use of the following equation:

$$\Delta E_i = \frac{Z_1 e (Z_2 e) / 2}{r_i \epsilon} \text{ e.s.u./ion} \quad (7)$$

where  $Z_1$  = valency of negative charge  
 $Z_2$  = valency of counterion  
 $e$  = electronic charge  
 $r_i$  = effective radius of counterion.

Equation (7) is based also on the integral form

of Coulomb's law, but because the positively charged counterion is found midway between two oppositely placed negative charges, the charge of the counterion has to be divided by two; otherwise, the interaction of the counterion with the negative charges is counted twice. The activity coefficient of a counterion, expressing the electrical interaction of the counterion with the clay surface, was calculated by use of equation (6).

$$\ln f_i = \frac{\Delta E_i}{RT} \quad (6a)$$

By use of equations (4, 5, 6a and 7), the effective radii of Ca and Mg, and by assigning to the dielectric constant,  $\epsilon$ , a value of 5, the standard free energy, the thermodynamic equilibrium constants and the activity coefficients of exchangeable calcium and magnesium were calculated; they are listed in Table 1.

It is evident from Table 1 that the standard molar free energy of calcium magnesium exchange predicts a preference for Ca in montmorillonite,  $\Delta G^\circ = 238$  cal/mole, and a preference for Mg in vermiculite,  $\Delta G^\circ = -1665$  cal/mole. The activity coefficients at an equivalent fraction of unity of Ca and Mg in montmorillonite are almost the same,  $f_{Ca} = 2.0 \times 10^{-3}$  and  $f_{Mg} = 2.2 \times 10^{-3}$ , while that of magnesium in vermiculite is twice as small as that of calcium,  $f_{Mg} = 3.5 \times 10^{-5}$ ,  $f_{Ca} = 7.1 \times 10^{-5}$ .

If the activity coefficients of the exchangeable ions do not change as their equivalent fraction changes, their ratio remain constant and the selectivity coefficient would also remain constant and could be predicted by use of equations (3), (5) and (7) and compared with the selectivity coefficient obtained from experimental data. If the activity coefficients change as their equivalent fraction changes, the selectivity coefficient will also be a function of the composition. The selectivity coefficient of Ca-Mg exchange in vermiculite has

Table 1. Standard free energy of exchange, thermodynamic equilibrium constant of exchange, energy of interaction, and activity coefficients of Ca and Mg at an equivalent fraction of unity

Clay	c-spacing, (Å)	Distance of plane of negative charge to surface of plate (Å)	Distance of counterion to surface of plate (Å)	Effective radius, (Å)	$\Delta G_{Ca}^{oMg}$ (cal/mole)	$K_{Ca}^{Mg}$	$\Delta E$ (cal/mole)	$\bar{f}$
Montmorillonite-Ca	18.9	4.2	4.8	9.0			3671	$2.0 \times 10^{-3}$
Montmorillonite-Mg	19.2	4.2	4.95	9.15	237.9	0.68	3610	$2.2 \times 10^{-3}$
Vermiculite-Ca	15.4	2.8	3.05	5.85			5648	$7.1 \times 10^{-5}$
Vermiculite-Mg	14.6	2.8	3.65	5.45	-1665	16.7	6062	$3.5 \times 10^{-5}$

been calculated from experimental data by Peterson *et al.* (1965), and it is evident that the activity coefficient ratio is not constant, because the selectivity coefficient changes drastically as the saturation of vermiculite with Mg increases. Before making an attempt to understand the reasons for this change in the selectivity coefficient, the results of Ca-Mg exchange in montmorillonite will be reported. It was found necessary to perform this exchange isotherm because no data on the Ca-Mg exchange in montmorillonite over the full range of saturation with one of the cations were available in the literature†.

### EXPERIMENTAL

The montmorillonite was prepared from Wyoming bentonite (A.P.I. No. 26). The clay was suspended in distilled water by rigorous stirring. The concentrated suspension was diluted with distilled water obtaining a suspension of 1%. The diluted suspension was allowed to settle by sedimentation leaving the particles with an apparent diameter of less than  $2\mu$  in suspension. This suspension was siphoned off, the sediment redispersed in distilled water, and the procedure repeated several times until the supernatant did not contain any appreciable amount of clay. Part of the  $2\mu$  suspension was converted to Ca montmorillonite and part of it to Mg montmorillonite by use of 1N chloride solutions of these cations, shaking with the appropriate salt, and centrifuging.

The procedure was repeated three times and the excess of salt was washed with distilled water until no  $\text{Cl}^-$  was detected in the supernatant by test with  $\text{AgNO}_3$ . This method of preparation of monoionic clays followed the one recommended by van Olphen (1963). A batch of the montmorillonite was dried at  $60^\circ\text{C}$  and a second batch was freeze-dried. The C.E.C. of the montmorillonite was found to be 100 me/100 g clay, with an error of 4%.

The montmorillonite was equilibrated with two sets of solutions, one set having a total salt concentration of 60 me/l and another of 10 me/l of  $\text{CaCl}_2$  and  $\text{MgCl}_2$ . The equivalent fraction of  $\text{MgCl}_2$  in the two sets varied from 1 to 0.

The equilibration with the mixed solutions was performed with the Ca and Mg forms of the montmorillonite in a batch procedure. The time of contact between the montmorillonite and the solution was about 72 hr, and the samples were shaken for half of the time. That equilibrium was reached was indicated by the fact that the same isotherm

was obtained whether the exchange was started with the Ca-montmorillonite or the Mg-montmorillonite. After reaching equilibrium the samples were centrifuged, the solution decanted and the concentration of Ca and Mg in the solution determined by titration with EDTA. The soluble salts were washed out in some samples with alcohol, in others determined from the amount of the remaining solution after centrifugation. The exchangeable cations were extracted by repeated leaching with 1N solution of  $\text{CH}_3\text{COONH}_4$ . Mg was determined in the acetate extract by an atomic absorption spectrophotometer (Unicam 90) at a wavelength of  $2864\text{\AA}$ . Exchangeable Ca was calculated from the C.E.C. of the montmorillonite minus the determined exchangeable magnesium.

All the determinations were performed in duplicates, the error in the soluble components was about 2%, and in the exchangeable about 4%.

### RESULTS AND DISCUSSION

Figure 2 represents the Ca-Mg exchange isotherm of the montmorillonite. Different symbols are given for the results obtained by the two methods of drying, for the two methods of eliminating the soluble salts and the two sets of solutions. When montmorillonite is dried at  $60^\circ\text{C}$ , larger particles are obtained as compared with those from the freeze drier. It could be expected, as was verified experimentally, that the size of the particles did not affect the exchange results because those are equilibrium ones. There was no significant difference in the results due to the methods used for the washing of the soluble salts, which can be explained by the fact that the valency of the ions used was divalent, and the volume of exclusion of salt from the exchanger was small and negligible for the divalent ion.

From the experimentally determined equivalent fractions, the selectivity coefficient of Ca-Mg exchange in the montmorillonite was calculated. Two approaches in this calculation were used. In the first one, for each experimentally determined point, the  $K_{s\text{Ca}}^{\text{Mg}}$  was calculated. In the second one, the  $K_{s\text{Ca}}^{\text{Mg}}$  was calculated using the mean values of the equivalent fraction of soluble magnesium,  $\bar{X}\text{Mg}^{2+}$  and the mean value of the exchangeable magnesium,  $\bar{X}\text{Mg}$ . Selectivity coefficient of Ca-Mg exchange as a function of Mg saturation calculated by the two different approaches is given in Table 2.

The expected error in  $K_{s\text{Ca}}^{\text{Mg}}$  is about 15%, so that although the selectivity coefficient of Ca-Mg exchange of montmorillonite seems to change with the Mg saturation of the montmorillonite, this change is within the error of the calculation. A mean value of 0.68 was calculated from all the values of  $K_{s\text{Ca}}^{\text{Mg}}$ .

†Recently, Hunsaker, V. E. and Pratt, P. H. published the exchange isotherm of Ca-Mg exchange of montmorillonite. *Soil Sci. Soc. Am. Proc.* 35, 151-152 (1971).

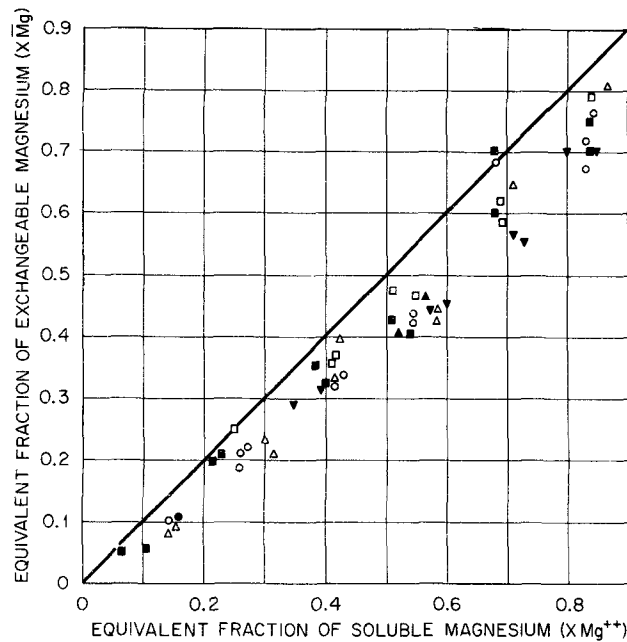


Fig. 2. Calcium-magnesium exchange isotherm of the montmorillonite. 0.06 N,  $\Delta$  Ca mont.,  $\circ$  Mg mont., 0.01 N  $\blacktriangle$  Ca mont.,  $\blacktriangledown$  Mg mont.; soluble salts determined from the amount of solution after centrifugation. 0.06 N,  $\bullet$  Ca mont.,  $\square$  Mg mont.; soluble salts washed with alcohol.  $\blacksquare$  Mg mont. freeze dried.

Table 2. Selectivity coefficient of Ca-Mg exchange,  $K_{sCa}^{Mg}$ , montmorillonite calculated by two different approaches†, as a function of Mg saturation

$\bar{X} Mg$	First approach	$M_{sCa}^{Mg}$ Second approach	Mean value
0.09	0.56	0.61	0.58
0.22	0.79	0.83	0.81
0.34	0.72	0.81	0.77
0.64	0.63	0.64	0.64
0.69	0.63	0.69	0.66
0.74	0.71	0.52	0.61

†See text.

In Fig. 3 the selectivity coefficients of Ca-Mg exchange in vermiculite† and montmorillonite as functions of Mg saturation are plotted.

As is evident from Fig. 3, the selectivity coefficient of Ca-Mg exchange in montmorillonite remains constant through the entire range of the Mg saturation of the montmorillonite, in marked contrast to the  $K_{sCa}^{Mg}$  of vermiculite. This is an indication that the ratio of the activity coefficients of

the exchangeable Mg and Ca remains constant in montmorillonite, while in vermiculite it changes.

The calculated activity coefficients of exchangeable Ca and Mg in montmorillonite (Table 1) are almost the same, and hence their ratio is unity. The selectivity coefficient, calculated from the experimental data, is in very good agreement with the calculated thermodynamic equilibrium constant, which is an indication that the assumptions used in the calculation of the thermodynamic equilibrium constant were correct. If the solution hydrated radii of Ca and Mg ions were used to predict the thermodynamic equilibrium constant, the preference

†Results reported by Peterson *et al.* (1965) performed with vermiculite from Libby, Montana.

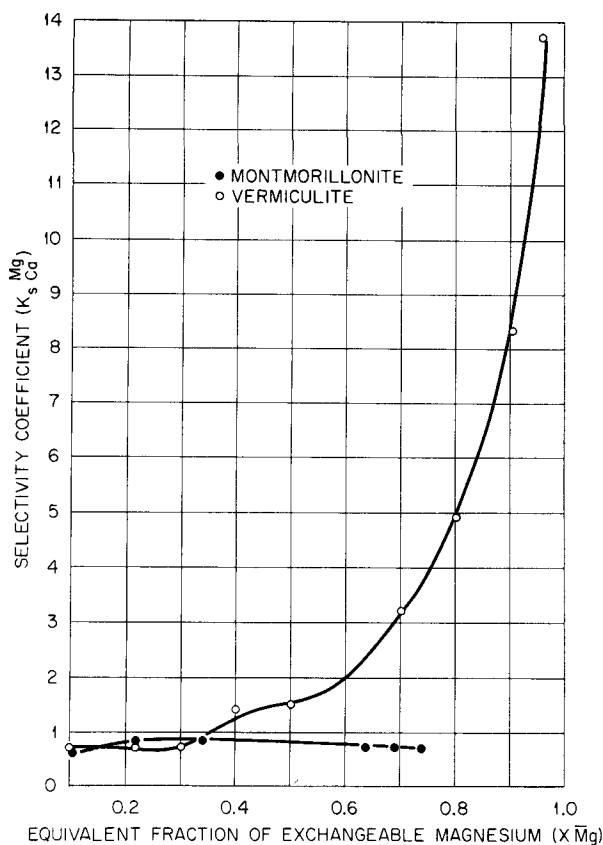


Fig. 3. Selectivity coefficients of Ca-Mg exchange of montmorillonite and vermiculite (data from Peterson *et al.* (1965) as functions of Mg saturation.

predicted should have been higher than the experimentally determined one. The electrical forces of attraction between the montmorillonite plates in the tactoid are comparable with the hydration forces of the ions; thus the adsorbed ions are not so hydrated as in true solution, but still the ion with the smaller crystalline radius (Mg) is more hydrated than the Ca ion.

The electrical attraction between the vermiculite platelets differs from that of montmorillonite. The higher surface charge density and the fact that the main isomorphous substitution is in the tetrahedron sheet increases the attraction forces between the plates and as a result restricts the swelling of the vermiculite. The forces of hydration of the water molecules in the first sheet around the naked ions are stronger than the electrical attraction between the platelets and thus an octahedral sheet of water molecules is formed. The energy gained by the absorption of a second sheet of water molecules around the adsorbed ions is less than the energy

required to increase the distance between the platelets, thus limiting the swelling in vermiculite. The difference in the *c*-spacing between the Ca and Mg vermiculite results from the difference in the crystalline radius of Ca and Mg forming the octahedron of water molecules between the vermiculite plates. The change in the selectivity coefficient with Mg saturation is an indication of the change of the interactions of the counterions as their amount changes. This change in the interactions will be reflected in the activity coefficients of the exchangeable ions and they also will change with Mg saturation. By use of equation (3) the values of the predicted thermodynamic equilibrium constant and the experimentally determined selectivity coefficient (Peterson *et al.*, 1965), the ratio of the activity coefficients of exchangeable Mg and Ca as functions of Mg saturation in the vermiculite was calculated. These results are listed in column 3 of Table 3.

The activity coefficient ratio of the exchangeable cations varies from unity at almost 100% Mg saturation, to more than 20 times unity, as the Mg saturation decreases. This phenomenon can easily be explained by the fact that at the high Mg saturation the *c*-spacing contracts, so that the larger Ca ion cannot easily penetrate, but as the Mg saturation decreases the *c*-spacing increases and the smaller Mg ion will be more loosely held.

It may be assumed that either the activity coefficient of exchangeable Ca remains constant through the entire range of Mg saturation, or that both activity coefficients change as their concentration varies. The first assumption gives the possibility to calculate the activity coefficient of exchangeable Mg as a function of the composition of the vermiculite. The calculated activity coefficient of exchangeable Mg is listed in column four of Table

Table 3. The change in the activity coefficients of exchangeable as a function of Mg saturation in vermiculite†

% Mg saturation	$K_{sCa}^{Mg}$	$\frac{fMg}{fCa}$	$fMg \times 10^{-5}$
Up to 30	0.7	23.8	168.0
40	1.4	11.9	84.5
50	1.5	11.1	78.8
70	3.2	5.2	37.0
80	4.9	3.4	24.2
90	8.3	2.0	14.2
95	13.9	1.2	8.5

† Calculated by use of equation (2) the predicted thermodynamic equilibrium constant,  $K_{Ca}^{Mg} = 16.7$ , and the activity coefficient of exchangeable Ca,  $fCa = 7.1 \times 10^{-5}$ .



3. From the table it is evident that there is a 50-fold increase in the activity coefficient of exchangeable Mg as its saturation decreases.

No X-ray data are available indicating the *c*-spacing of vermiculite as a function of its composition. If the *c*-spacing of Mg-vermiculite increases gradually as the saturation with Mg decreases, the activity coefficient of the exchangeable Mg will change continuously reflecting the decrease in the electrical attraction between the Mg ion and the charged surfaces.

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**Résumé**—On décrit dans ce travail un isotherme d'échange Ca-Mg déterminé expérimentalement avec une montmorillonite. Le coefficient de sélectivité de cet échange pour une gamme étendue de saturation en Mg a été calculé; il a été trouvé constant.

Les énergies libres standard d'échange, les constantes d'équilibre thermodynamiques et les coefficients d'activité des ions Ca et Mg échangeables dans la vermiculite et la montmorillonite, ont été prédits d'après la connaissance de la microstructure de ces deux argiles, en supposant que les forces coulombiennes sont les principales à jouer un rôle dans l'interaction entre les cations compensateurs et la surface chargée de l'argile. Les énergies libres standard d'échange ( $\Delta G_{Ca}^{Mg} = 238$  cal/mole) permettent de prévoir une préférence pour Ca dans le cas de la montmorillonite et une préférence pour Mg dans celui de la vermiculite ( $\Delta G_{Ca}^{Mg} = -1665$  cal/mole).

Les constantes d'équilibre thermodynamiques que l'on peut prévoir sont compatibles avec les coefficients de sélectivité déterminés expérimentalement,  $K_{Ca}^{Mg} = 0,67$  étant à comparer à  $K_{S_{Ca}}^{Mg} = 0,68$  pour la montmorillonite, ce coefficient restant constant sur toute la gamme de saturation en Mg, et  $K_{Ca}^{Mg} = 16,7$  étant à comparer à  $K_{S_{Ca}}^{Mg} = 13,9$  pour la vermiculite à une saturation en Mg de 95%. Les coefficients d'activité des ions compensateurs Ca et Mg sont pour la montmorillonite respectivement  $f_{Ca} = 2,0 \times 10^{-3}$  et  $f_{Mg} = 2,2 \times 10^{-3}$ ; ils restent constants. Les coefficients d'activités des ions Ca et Mg échangeables dans la vermiculite sont respectivement  $f_{Ca} = 7,1 \times 10^{-5}$  et  $f_{Mg} = 3,5 \times 10^{-5}$ , pour une fraction équivalente unitaire. Le coefficient d'activité du Mg échangeable augmente quand la saturation en Mg diminue, et il prend la valeur de  $1,7 \times 10^{-3}$  dans le domaine des basses saturations en Mg.

La microstructure, les substitutions isomorphiques et la densité de charge superficielle permettent de comprendre les modifications qui apparaissent dans la valeur des coefficients d'activité des ions compensateurs.

**Kurzreferat**—Es wird über eine experimentell bestimmte Ca-Mg Austauschisotherme von Mont-

morillonit berichtet. Der Selektivitätskoeffizient dieses Austausches über einen weiten Bereich der Magnesium-Sättigung wurde berechnet und als konstant festgestellt.

Standard freie Austauschenergien, thermodynamische Gleichgewichtskonstanten und Aktivitätskoeffizienten der austauschbaren Ca und Mg Ionen in Vermiculit und Montmorillonit wurden aus der Kenntnis des Mikrogefüges dieser beiden Tone vorausgesagt, unter der Annahme, dass die Coulomb'schen Kräfte die wesentliche Rolle bei der Wechselwirkung zwischen Gegenionen und der geladenen Tonoberfläche spielen. Die Standard freien Energien des Austausches ( $\Delta G_{Ca}^{oMg} = 238$  cal/mol) sagten eine Bevorzugung für Ca in Montmorillonit und eine Bevorzugung für Mg in Vermiculit ( $\Delta G_{Ca}^{oMg} = -1665$  cal/mol) voraus. Die vorausgesagten thermodynamischen Gleichgewichtskonstanten waren vereinbar mit dem, experimentell bestimmten Selektivitätskoeffizienten  $K_{Ca}^{Mg} = 0,67$ , verglichen mit  $K_{Ca}^{Mg} = 0,68$  bei Montmorillonit, gleichbleibend über den gesamten Bereich der Mg-Sättigung, und  $K_{Ca}^{Mg} = 16,7$  verglichen mit  $K_{Ca}^{Mg} = 13,9$  in Vermiculit bei 95% Mg Sättigung. Für die Aktivitätskoeffizienten von Ca und Mg Gegenionen in Montmorillonit wurden Werte von  $\bar{f}Ca = 2,0 \times 10^{-3}$  und  $\bar{f}Mg = 2,2 \times 10^{-3}$  festgestellt, die konstant blieben. Die Aktivitätskoeffizienten von austauschbarem Ca und Mg in Vermiculit ergaben sich als  $\bar{f}Ca = 7,1 \times 10^{-5}$  und  $\bar{f}Mg = 3,5 \times 10^{-5}$  bei einer äquivalenten Einheitsfraktion. Der Aktivitätskoeffizient von austauschbarem Mg nahm mit abnehmender Sättigung an Mg zu, und ergab sich im Bereich der niedrigen Mg Sättigung als  $1,7 \times 10^{-3}$ .

Das Mikrogefüge, der isomorphe Ersatz und die Oberflächenladungsdichte gaben Einsicht in die Veränderungen, die in den Aktivitätskoeffizienten von Gegenionen stattfinden.

**Резюме** — Проведено экспериментальное определение изотермы обмена Ca-Mg в монтмориллоните. Вычислен коэффициент селективности этого обмена для широкой области насыщения Mg, который оказался постоянным. Значения стандартной свободной энергии замещения, константы термодинамического равновесия и коэффициенты активности обменных ионов Ca и Mg в вермикулите и монтмориллоните были предсказаны по данным о микроструктуре этих двух глин при предположении, что кулоновские силы играют основную роль во взаимодействии между пограничными ионами и заряженной поверхностью глины. Значения стандартной свободной энергии замещения ( $\Delta G_{Ca}^o = 238$  кал/моль) указывали на предпочтительную связь Ca в монтмориллоните и Mg в вермикулите ( $\Delta G_{Ca}^o = -1665$  кал/моль). Предсказанные константы термодинамического равновесия согласовались с экспериментально определенными коэффициентами селективности  $K_{Ca}^{Mg} = 0,67$  по сравнению с  $K_{Ca}^{Mg} = 0,68$  для монтмориллонита (коэффициент оставался постоянным для всей области насыщения Mg) и  $K_{Ca}^{Mg} = 16,7$  по сравнению с  $K_{Ca}^{Mg} = 13,9$  для вермикулита (при 95% насыщения Mg). Найдены коэффициенты активности пограничных ионов Ca и Mg в монтмориллоните ( $\bar{f}Ca = 2,0 \times 10^{-3}$  и  $\bar{f}Mg = 2,2 \times 10^{-3}$  соответственно), которые остаются постоянными. Получены коэффициенты активности обменных ионов Ca и Mg в вермикулите ( $\bar{f}Ca = 7,1 \times 10^{-5}$  и  $\bar{f}Mg = 3,5 \times 10^{-5}$  соответственно, в эквивалентных долях единицы. Коэффициент активности обменного Mg увеличивается при уменьшении насыщения Mg; в области низкого насыщения Mg он равен  $1,7 \times 10^{-3}$ .

Микроструктура, изофонные замещения и поверхностная плотность заряда позволяют понять изменения коэффициентов активности пограничных ионов.