A KINETIC SURVEY OF THE CATION EXCHANGE AND OF THE OXIDATION OF A VERMICULITE

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Abstract—With the use of a $BaCl_2$ solution containing radioactive Ba^{2+} ions, kinetics of cation exchange have been done on a Kenya vermiculite, natural on one hand and previously oxidized either by 50°C water or oxygenated water on the other hand. Correlatively, the quantity of ferric iron in the layer has been determined by E.P.R. These two methods have shown that during an oxidation the proportion of iron which stays in the octahedral layer depends upon the nature of the oxidizing agent. During a weak oxidation, the iron stays entirely in an octahedral layer and the exchange capacity of the vermiculite decreases; on the other hand, during an oxidation by oxygenated water, part of the iron is extracted from the octahedral layer and the exchange capacity of the vermiculite is not changed, as established by the studies of Farmer (Farmer *et al.*, 1971). Kinetic data for Llano vermiculite also are reported and compared with those for the Kenya vermiculite.
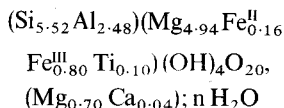
INTRODUCTION

Investigation of the exchange capacity and of the balancing cations has been done in many studies (Barshad, 1948, 1951; Le Dred, 1968). The exchange capacity is usually determined by replacing the exchangeable ions by means of a pH = 7 normal solution of ammonium acetate. This technique is unsuitable for a kinetic study of the exchange.
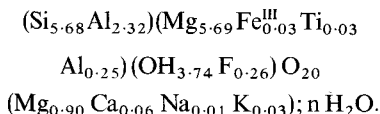
We chose a more suitable method involving the use of a saline solution containing a known proportion of radioactive cations. In this case the quantity of cations fixed in the silicate after a given time is directly proportional to the γ radioactivity of the treated sample. This method showed that the exchange capacity varies according to the experimental conditions and we linked this variation with the oxidation of the ferrous iron contained in the mineral.

1. EXPERIMENTAL CONDITIONS

The exchange kinetics have been done on a Kenya vermiculite whose structural formula is:

$$(Si_{5.52}Al_{2.48})(Mg_{4.94}Fe_{0.16}^{II})$$

$$Fe_{0.80}^{III}Ti_{0.10})(OH)_4O_{20},$$

$$(Mg_{0.70}Ca_{0.04}); n\,H_2O$$

and on a Llano vermiculite, containing practically no iron, whose structural formula is:

$$(Si_{5.68}Al_{2.32})(Mg_{5.69}Fe_{0.03}^{III}Ti_{0.03}$$

$$Al_{0.25})(OH_{3.74}F_{0.26})O_{20}$$

$$(Mg_{0.90}Ca_{0.06}Na_{0.01}K_{0.03}); n\,H_2O.$$

The cation exchange was done at 50°C during increasing periods of time in a normal solution of $BaCl_2$ containing a known proportion of $^{133}BaCl_2$. The

quantity of barium fixed in the vermiculite was determined by a multichannel analyser which gives the energy spectrum of the radioactive barium. To minimize experimental errors due to thermal drift of the electronic apparatus, the quantity of fixed barium was titrated solely from the area of the peak E_2 of the spectrum, (see Fig. 1). Under these conditions the whole of the experimental errors (titration, weighings, measuring) is then <3 per cent.
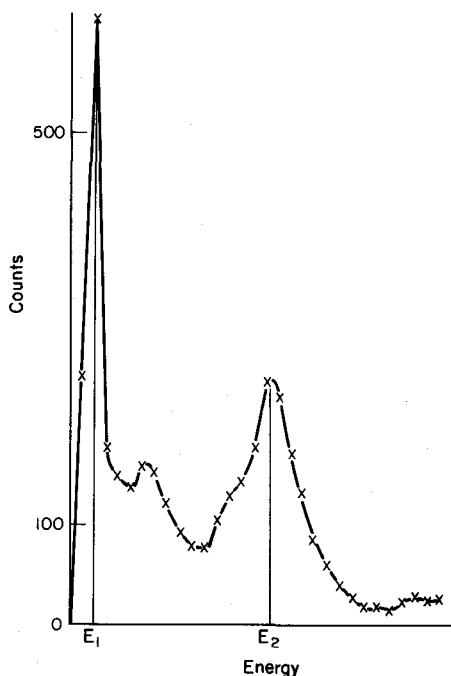

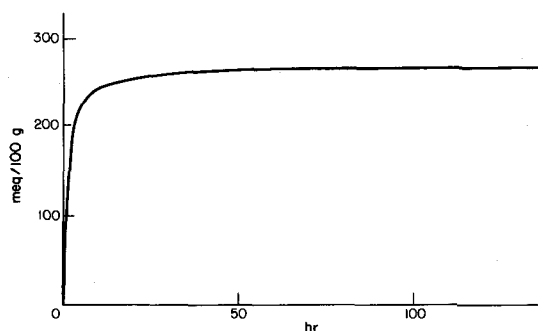Fig. 1. ^{133}Ba Spectrum.

✠ Deceased.

Fig. 2. Kinetics of the cation exchange in a Llano vermiculite.

The exchange kinetics were studied on samples made of microcrystals less than $10\,\mu m$ long obtained by cutting bigger crystals in water (we preferred this technique to grinding in order to avoid the structural degradation which eventually happens during grinding). In the case of the Kenya vermiculite, this work has been completed by the study of a sample consisting of single crystals, a few millimeters long.

The vermiculite crystals of these two fractions were left in contact with $BaCl_2$ solution during periods of time increasing from a few minutes to some hundreds of hours. They were then washed to eliminate the salt fixed on the edges and were dried at 90°C. It has been verified by weighing after calcination at 1000°C that in these conditions the vermiculite is still hydrated with six water molecules between the layers. Lastly, in order to check quantitatively the kinetics of the exchange capacity we chose a reference quantity slightly different from that habitually used. Most authors measure exchanged cations in m-equiv./100 g *calcined product* (at 1000°C). The weight of the interlayer cations interferes then in the global weight of calcined product. Thus, according to the nature of the cations, the exchange capacity will have a different numerical value for the same silicate. To avoid this difficulty, especially for a kinetic exchange study, we reduced the quantity of exchanged cations to a 100 g of the *calcined product* (at 1000°C) *without any interlayer cations* which allows us to keep a constant reference weight independent of the nature of the fixed cation.

2. THE KINETICS OF EXCHANGE

When the quantity of barium fixed in the vermiculite is plotted against the exchange time, we get curves which differ according to the vermiculite origin and the particle size of the sample.

2.1 Llano vermiculite in microcrystals

The curve displays the classical shape of a saturation graph (Fig. 2) and shows in 100 hr an exchange corresponding to 265 ± 9 m-equiv./100 g of product calcined at 1000°C "without any interlayer cations". If one considers that K cations are difficult to exchange, the theoretical exchange capacity deduced

from the structural formula, lies between 271 m-equiv./100 g (K completely exchanged) and 262 m-equiv./100 g (no K exchanged). Thus, the value of 265 ± 9 m-equiv./100 g found after a 100 hr exchange corresponds to the entire expected exchange capacity.

2.2 Kenya vermiculite in microcrystals

The quantity of fixed barium reaches a maximum after one hr of exchange (195 ± 6 m-equiv./100 g). After longer periods of time (about 150 hr), the quantity of fixed barium decreases to a limiting value (170 ± 5 m-equiv./100 g). If one calculates from the structural formula the quantity of barium which can be fixed in 100 g of calcined vermiculite "without interlayer cations" one sees that this quantity (197 m-equiv./100 g) corresponds within 1 per cent to the maximum of graph *b* in Fig. 3.

2.3 Kenya vermiculite in single crystals

We find again, for the exchange kinetics, (Fig. 4) a curve whose shape is that of a saturation graph, but with the maximum quantity of fixed barium no more than 170 m-equiv./100 g. This maximum corresponds to the limiting value obtained for the microcrystallized sample after 150 hr, and is about 14 per cent less than the value expected from the structural formula. We assumed that, for the Kenya vermiculite, this loss in exchanged capacity could be explained by the oxidation of Fe^{2+} to Fe^{3+}.

3. OXIDATION OF Fe[II] IN THE VERMICULITE

The phenomenon of the exchange capacity loss has been pointed our by Farmer et al. (1971) in the transformation of biotites into vermiculites by successive extractions of the potassium by a NaCl solution (the 31 A biotite goes from 222 to 183 m-equiv./100 g; Luindi biotite from 219 to 182 m-equiv./100 g).

Correlatively, these authors have noticed a slight oxidation of Fe^{2+} by the water of the saline solution. But when Farmer et al. used more energetic oxidizers such as H_2O_2 or bromine, they noted that the oxidation does not modify the exchange capacity but
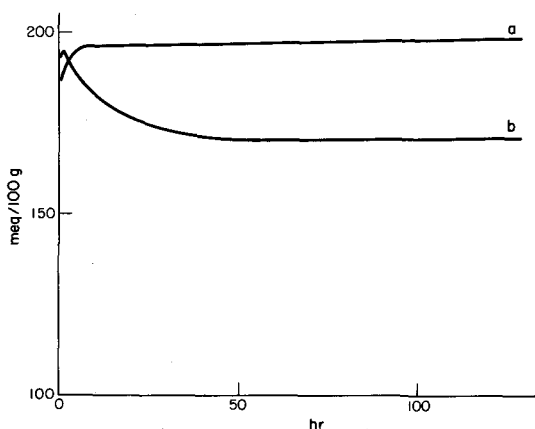

Fig. 3. Kinetics of the cation exchange in a Kenya vermiculite of particle size $<10\,\mu m$: (a) Treated H_2O_2 (b) Not treated.
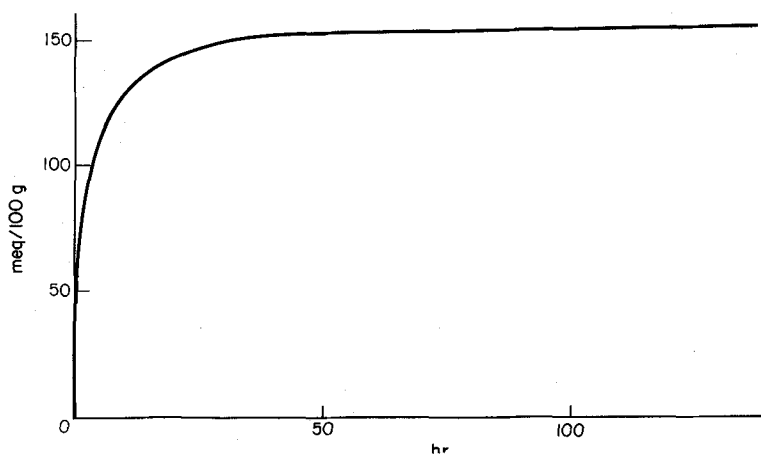
Fig. 4. Kinetics of cation exchange in a Kenya vermiculite in single crystals 3–5 mm wide.

instead iron is removed from the octahedral layer.

In the continuation of this study we tried on one hand to confirm our hypothesis about the exchange kinetics and on the other to link our results to those of Farmer *et al.*, specifying the part played by the oxidizing agent.

4. TITRATION OF FERRIC IRON BY E.P.R.

Trivalent iron can be detected by electron paramagnetic resonance (E.P.R.). Thus, it is possible to verify by this technique the change of Fe^{3+} concentration during the cation exchange of the vermiculite.

It is known that the lines of the E.P.R. spectrum are characterized by the value of the resonance field for a given irradiation frequency. The ratio between this frequency and the resonance field (which is the Lande factor, g) depends on the coupling of the paramagnetic spin with its orbit and its surroundings. This ratio is sensitive to the symmetry of the local crystalline structure. Moreover, the amplitude of the resonance is proportional to the number of detected ions, but the proportionality ratio is difficult to know for it depends on the electrical properties of the hyperfrequency cavity, on the detection processes and on the irradiation power ... In any case, relative measurements can be made and the ion concentration of several samples can be compared by using a reference sample in a double cavity assembly.

Using such an assembly we have compared the spectra given by the Kenya vermiculite, treated as follows; (a) in its natural state, (b) after 120 hr in distilled water at 50°C (slight oxidation by the oxygen normally dissolved in water), (c) after 120 hr in a $BaCl_2$ solution at 50°C (slight oxidation) and (d) after 48 hr in oxygenated water at 100 vol (more energetic oxidation). The spectra corresponding to the four experiments described above show a very wide line ($\Delta H \sim 1360\,G$) centered at $g_1 = 2.07$ as well as a thinner and less intense one ($\Delta H \sim 240\,G$), centered at $g_2 = 4.02$ (Fig. 5).

These spectra have been normalized to a constant sample weight and to a constant amplitude relative

to the signal of the reference. One notes that these spectra, which are the derivatives of the absorption curves, are closely similar to one another. It is possible in this case to compare the absorption intensities of the four samples in calculating the maximum ratios of the curves. The measurement precision in this case is ± 5 per cent.

This study shows that the quantity of ferric iron increases when one goes from the natural sample to that oxidized by the oxygenated water and then to those which have stayed in distilled water or in $BaCl_2$ (for the two latter the spectra merge).

This increase in ferric iron can be evaluated by taking as a reference the composition of the octahedral layer corresponding to the structural formula ($0.16\,Fe^{II} + 0.8\,Fe^{III}$ for 6 octahedral cavities).

(a) For the sample oxidized by the oxygenated water the quantity of ferric iron determined in graph a, Fig. 3, is 1.10 times that of the natural sample. This result leads us to put $0.88\,Fe^{III}$ in an octahedral position.

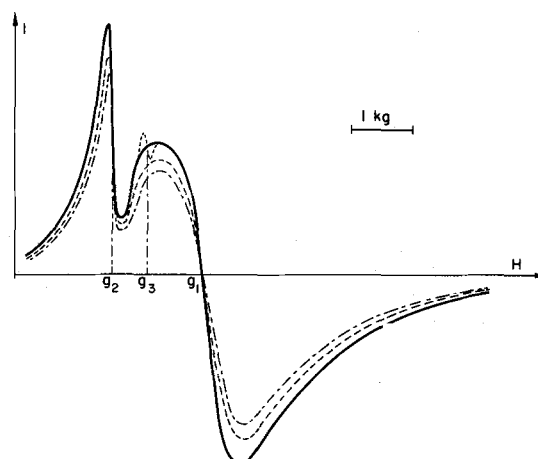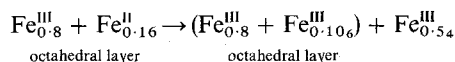Moreover, if we take the oxidation process with

Fig. 5. E.P.R. curves of 4 vermiculite samples: Mixed line, Mg–vermiculite natural (sample a). Straight line, Mg–vermiculite treated by distilled water (sample b). Dotted line and straight line, Ba–vermiculite (sample c). Dashed line, Mg–vermiculite treated by H_2O_2 (sample d).

the octahedral iron loss quoted by Farmer *et al.* (1971), for which the layer charge remains constant, we can write:

$$Fe_{0.8}^{III} + Fe_{0.16}^{II} \rightarrow (Fe_{0.8}^{III} + Fe_{0.106}^{III}) + Fe_{0.54}^{III}$$
$$\text{octahedral layer} \qquad \text{octahedral layer}$$

which gives, after oxidation, a quantity of iron per cell equal to $0.90_6 Fe^{III}$. This value is in very good agreement with the quantity we experimentally determined by E.P.R.; $0.88 Fe^{III}$.

(b) For the samples which stayed in pure water or in a $BaCl_2$ solution the quantity of ferric iron indicated by E.P.R. reaches 1.25 times the quantity which is present in the natural vermiculite. This level places $1.0 Fe^{III}$ ion in the octahedral layer. Moreover, if all of the ferrous iron of the octahedrally coordinated iron is transformed into the ferric form we must find: $0.8 + 0.16 = 0.96 Fe^{III}$ per cell. This value is in good agreement with the experimentally evaluated quantity, which shows, in this case, that all the iron stays in the octahedral layer.

Furthermore, it must be pointed out that the spectra of samples *b* and *c* differ from one another according to the degree of dehydration. As a matter of fact, while Mg–vermiculite treated in pure water always gives the same spectrum (straight line) whether 'air dried' or dried at 100°C for 6 hr, the Ba–vermiculite dried at 100°C under the same conditions shows an extra thin line ($\Delta H \sim 100 G$) centered at $g_3 = 2.88$ (dotted line, Fig. 5). This line disappears when sample *c* is again exposed to ambient humidity. Lastly, this line does not exist in the case of the natural sample. These observations show that the symmetry of the crystalline field around Fe^{3+} ions is modified in the Ba–vermiculite dried at 100°C.

E.P.R. curves seem to show that in Ba–vermiculite dehydrated at 100°C, the location of the exchangeable Ba^{2+} cations can be different from that of Mg^{2+} cations, a difference which could be attributed to the different sizes of Ba^{2+} and Mg^{2+} ions (Alcover and Gatineau, 1971).

5. RELATIONSHIP BETWEEN THE OXIDATION CONDITIONS AND THE EXCHANGE KINETICS

A confirmation of the oxidation process can be obtained by examining the exchange kinetics:

(a) *Sample previously oxidized by oxygenated water.* The maximum reached after 30 hr exchange of the Kenya microcrystals corresponds to the complete exchange capacity expected from the structural formula (197 m-equiv./100 g). Thus, there was no decrease of the exchange capacity, and the oxidation process proposed by Farmer *et al.* is confirmed in the case of a powerful oxidizing agent.

(b) *Sample treated in* $BaCl_2$ *solutions or in pure water.* For the Kenya vermiculite microcrystals the decrease of the exchange capacity observed between one and 150 hr represents 24 m-equiv./100 g, curve *b*, Fig. 3. If one considers the hypothesis suggested by the E.P.R. determination and admits an *in situ* oxi-

dation of ferrous iron, the exchange capacity would decrease by 21.3 m-equiv./100 g, a value in good agreement with the observed experimental decrease.

Indirect confirmation of this hypothesis is given by the exchange kinetics of the Llano vermiculite (iron-free) which does not show the characteristic decrease in exchange capacity (Fig. 2). Direct confirmation is obtained from the study of Kenya vermiculite microcrystals, which were placed in the $BaCl_2 + {}^{133}BaCl_2$ solution only after treatment in pure water at 50°C for 120 hr. After one hr in the tagged $BaCl_2$ solution, the quantity of fixed barium determined by measuring γ radioactivity leads to an exchange capacity of 168 ± 5 m-equiv./100 g which doesn't change with further treatment time. This value corresponds to the limiting value reached after 150 hr for a vermiculite which had never been previously in water.

Thus we see that, under the action of a weak oxidizing agent, an oxidation process occurs with no iron loss but with a decrease in the exchange capacity. Such a process has been proposed by certain authors (Bradley and Serratosa, 1960; Le Dred, 1968) according to the scheme:

$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$
$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$$
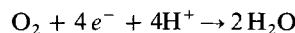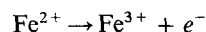
This process of complete oxidation of ferrous iron with no iron departure may be possible only in a mineral where the ferrous iron is not the major element of the octahedral layer, as in the Kenya vermiculite.

Finally, it must be pointed out that the exchange kinetics of the Kenya vermiculite single crystal sample can be explained by the existence of a competition between two phenomena: (a) the cation exchange process itself, (b) the phenomenon of Fe^{2+} iron oxidation.

When a vermiculite in microcrystals of less than 10 μm size is treated with a $BaCl_2$ solution, the evolution of the iron oxidation can be seen on the curve which gives the kinetics of the cation exchange. In the case of single crystals a few millimeters long, this exchange is slower than the oxidation of Fe^{2+} and the kinetic curve is similar to that of previously oxidized vermiculite.

6. CONCLUSIONS

The use of ${}^{133}Ba$ γ radiation to evaluate the exchange capacity of a phyllosilicate makes it possible to study very precisely the exchange kinetics without introducing systematic errors due to the usual indirect titration methods. By this technique, different behavior of the vermiculite has been shown when oxidized by more or less energetic agents. After checking the quantity of ferric iron by E.P.R. we have verified that:

(a) In the presence of weak oxidizers (oxygen normally dissolved in water) all the ferrous iron of a vermiculite can be oxidized *in situ*; the charge compensation is then shown by a decrease of the number of balancing cations.

(b) With stronger oxidizers (oxygenated water) the oxidation of the ferrous iron is done at constant octahedral layer charge, there is no decrease of the number of balancing cations, but rather expulsion of part of the oxidized ferrous iron as shown by Farmer *et al.* (1971).

The weak oxidation of the ferrous iron as observed in the vermiculite is probably a general phenomenon which should be taken into account especially during cation exchange on phyllosilicates.

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