OXIDATION OF STRUCTURAL FERROUS IRON IN VERMICULITES: I. OXIDATION BY Fe\(^{3+}\)

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ABSTRACT: Vermiculite prepared from biotite by interlayer cation exchange was reacted with solutions exhibiting redox potentials between 625 and 765 mV. The redox potential was controlled by the Fe\(^{2+}/Fe^{3+}\) activity ratio, measured with a Pt electrode, and kept constant by addition of hydrogen peroxide to balance electron transfer from structural Fe\(^{2+}\) to Fe\(^{3+}\) in solution. Oxidation of structural Fe\(^{2+}\) was followed by Eh-stat titration and the rate of oxidation was shown to depend on the amount of Fe\(^{3+}\) penetrating into interlayer positions. Consequently, it was affected not only by the redox potential, but also by the activity between Fe\(^{3+}\) and all other cations present in solution or in an exchangeable state. Oxidation and cation exchange are coupled reactions. In contrast to the redox potential in solution, the effective redox potential controlling the oxidation of structural Fe\(^{2+}\) was increased by preferential sorption of the Fe\(^{3+}\) ion.

Oxidation of octahedrally bound ferrous iron is part of the complex weathering process during biotite-vermiculite transformation in soils. Different aspects of the reaction have been discussed in the literature. Oxidation of structural Fe affects the exchange capacity of the minerals (Foster, 1963; Roth et al., 1969; Norrish, 1972) as well as the reactivity of interlayer cations (Barshad & Kishk, 1968; Robert & Pedro, 1968; Gilkes, 1973; Ross & Rich, 1974), contributes to acidification of soils by inducing release of either protons or structural ions which subsequently undergo hydrolysis (Vedder & Wilkins, 1969; Farmer et al., 1971; Gilkes et al., 1972; Veith & Jackson, 1974), and changes the structural parameters of the minerals (Farmer et al., 1971; Ross & Rich, 1973).

In order to produce oxidation of silicates in the laboratory, several methods have been applied including thermal treatment (Vedder & Wilkins, 1969; Ismail, 1970; Takeda & Morosin, 1975) and the use of oxidizing agents such as bromine water (Farmer et al., 1971; Gilkes et al., 1972) or hydrogen peroxide (Farmer et al., 1971; Ross & Rich, 1973; Veith & Jackson, 1974). Thermal treatment induces autoxidation at elevated temperatures (500–900°C) resulting in the release of hydrogen (Vedder & Wilkins, 1969). In aqueous systems, however, electrons are transferred to acceptors which are located mainly in the expanded interlayer space as deduced from the close correlation between oxidizability of structural Fe and degree of layer expansion (Robert, 1971).

The concentration of electron-accepting oxygen in the interlayers should depend on the partial pressure of oxygen in the system. Likewise, if ionic electron acceptors are used, oxidation should depend on the redox potential of the aqueous phase of the system. However, the effect of the redox potential in solution on the oxidation of vermiculites in aqueous...
suspensions has not been investigated. Therefore, a number of experiments have been performed to study the reaction mechanisms involved in the oxidation of structural Fe\(^{2+}\) in vermiculite by ionic oxidants, and to establish how these depend on the redox potential in solution.

Results are reported of experiments in which vermiculites, produced by exchanging interlayer K of biotites with hydrated cations, were oxidized at controlled redox potential and pH by using the ion couple Fe\(^{2+}\)/Fe\(^{3+}\) as the electron-accepting and potential-determining system.

**MATERIALS AND METHODS**

**Sample**

A biotite from Moss, Norway, supplied by F. Krantz Co., Bonn, was wet-ground and separated into different particle size fractions by sedimentation. Samples of the 5–20 \(\mu\)m fraction were repeatedly treated with 0.1 N BaCl\(_2\) solution at 80°C in a batch-type exchange procedure until more than 98% of the interlayer K was removed by Ba which was subsequently replaced by Mg, and the Mg-vermiculite was washed free of salt and air-dried.

The biotite and the Mg-vermiculite were analysed after digestion with HF/HClO\(_4\) resulting in the following structural formulae:

- Biotite: \((\text{Si}_{3.35}\text{Al}_{2.65})(\text{Mg}_{1.25}\text{Fe}_{0.75}\text{Ti}_{0.32}\text{Al}_{0.03}\text{Si}_{0.45})\text{O}_{20}(\text{OH})_2\text{K}_{1.88}\text{Na}_{0.10}\)
- Mg-vermiculite: \((\text{Si}_{3.27}\text{Al}_{2.73})(\text{Mg}_{1.10}\text{Fe}_{0.86}\text{Ti}_{0.58}\text{Al}_{0.32}\text{Si}_{0.33}\text{O}_{20}(\text{OH})_4\text{Mg}_{0.90}\).

Thus, during vermiculitization, 1.35 out of 3.21 Fe\(^{2+}\) per unit-cell have been oxidized. The Mg-vermiculite, which still contained 54% of the Fe in ferrous form, was used for the oxidation experiments.

A sample (<2 \(\mu\)m) of beidellite from Unterrupsroth with a low content of total Fe (0.05%) was used to study the exchange behaviour of the ion species of Fe without interference from redox reactions with structural Fe. This sample was repeatedly treated with 5 N NaCl solutions for several days, separated from the supernatant solution after centrifugation, washed with water until salt-free, and freeze-dried.

The exchange capacity of beidellite as determined by analysing the Na content after HF/HClO\(_4\) digestion, was 143 mEq/100 g of air-dry material.

**Oxidation**

Oxidation was performed by adding the vermiculite to a solution, the redox potential of which was fixed by a certain Fe\(^{3+}\)/Fe\(^{2+}\) ratio. This ratio was kept constant during the reaction by addition of hydrogen peroxide, reestablishing the original Fe\(^{3+}\) concentration by balancing the consumption of Fe\(^{3+}\) that occurred through electron transfer from structural Fe\(^{2+}\) as well as through adsorption of Fe\(^{3+}\) by cation exchange. As a wide Mg\(^{2+}\)/Fe\(^{3+}\) ratio in the solution was used in most of the experiments, the contribution of cation exchange to the consumption of Fe\(^{3+}\) during the titration could be ignored. The Eh-stat titration then indicated the oxidation of structural Fe\(^{2+}\).

The reaction was carried out as follows: For the basic experiment (Fig. 1) 20 ml of 0.1 N MgSO\(_4\) solution containing small amounts of Fe\(^{2+}\) (2.5 \(\times\) 10\(^{-3}\) mole/l of reagent grade FeSO\(_4\)) were prepared at 30°C in a thermostat vessel connected to two automatic titrators (Metrohm Dosimat). The redox potential of the solution was set between 625 and 765 mV by
Oxidation of vermiculites by Fe$^{3+}$

Fig. 1. Rates of oxidation of Mg-saturated vermiculite in contact with solutions fixed at different redox potentials. Experimental conditions: 60 mg Mg-vermiculite, 20 ml solution (0.1 N MgSO$_4$; 0.0025 M FeSO$_4$); fixed: pH—2.8, T—30°C; varied: Eh.

addition of diluted H$_2$O$_2$ (0.05 M), pH was adjusted to 2.8 by addition of H$_2$SO$_4$, and both parameters were kept constant. After adding 60 mg Mg-saturated vermiculite as a suspension of small volume (0.2 ml) to the stirred solution, the consumption of H$_2$O$_2$ and H$_2$SO$_4$ was plotted vs. time. At different time intervals the reaction was stopped, minerals and solution were separated by filtration, and changes in the minerals and solutions occurring during the reaction were determined by chemical analysis.

In subsequent experiments, the added amounts of Fe as well as concentrations of MgSO$_4$ solutions were varied as indicated in the legends of Figs. 2 and 3. A bright Pt/calomel electrode and a glass electrode were used for controlling redox potential and pH, respectively. The redox potentials are calculated against the normal hydrogen electrode.

Cation exchange

Six 100 ml portions of solution were prepared, each containing 100 μmole of FeSO$_4$ and 80 μmole of H$_2$SO$_4$. Increasing portions of Fe$^{2+}$ were transformed to the ferric state by adding varying amounts of 0.02 N H$_2$O$_2$ solution before filling up to volume. The Fe$^{3+}$ content of these solutions varied between 0 and 20% of the total Fe (Table 1).

100 mg portions of Na-beidellite were weighed into centrifuge tubes, the solutions added and after bringing the system to equilibrium by shaking for 1 h, the suspensions were centrifuged and the supernatant solution decanted.

The amounts of solution retained in the sediment were determined gravimetrically before exchangeable ions were extracted by adding 100 ml of solutions containing 10 mmole of
FIG. 2. Rates of oxidation of Mg-saturated vermiculite in contact with solutions of different concentrations of Fe at equal redox potential. Experimental conditions: 60 mg Mg-vermiculite, 20 ml solution (0.1 N MgSO₄); fixed: pH—2-8, T—30°C, Eh—625 mV; varied: concentration of FeSO₄.

FIG. 3. Rates of oxidation of Mg-saturated vermiculite in contact with solutions of different MgSO₄ concentrations, at equal concentrations of Fe (50 µmole Fe/20 ml) and equal redox potentials (625 mV). Experimental conditions: 60 mg Mg-vermiculite, 20 ml solution (0.0025 M FeSO₄); fixed: pH—2-8, T—30°C, Eh—625 mV; varied: concentration of MgSO₄.
Oxidation of vermiculites by Fe\(^{3+}\)

TABLE 1. Cation exchange between Na-saturated beidellite and solutions containing varying proportions of Fe\(^{2+}\) and Fe\(^{3+}\).

<table>
<thead>
<tr>
<th>Starting solution µEq/100 ml</th>
<th>Equilibrium solution µEq/100 ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(^{3+})</td>
<td>Fe(^{2+})</td>
</tr>
<tr>
<td>1.80</td>
<td>200.4</td>
</tr>
<tr>
<td>11.94</td>
<td>198.4</td>
</tr>
<tr>
<td>24.99</td>
<td>189.0</td>
</tr>
<tr>
<td>37.20</td>
<td>182.8</td>
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<tr>
<td>50.40</td>
<td>175.2</td>
</tr>
<tr>
<td>62.70</td>
<td>165.8</td>
</tr>
</tbody>
</table>

Exchangeable cations µEq/100 mg

<table>
<thead>
<tr>
<th>Fe(^{3+})</th>
<th>Fe(^{2+})</th>
<th>H(^{+})(Al)</th>
<th>Na(^{+})</th>
<th>Sum</th>
<th>(K_{Fe^{2+}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>106.6</td>
<td>32.5</td>
<td>2.4</td>
<td>142.6</td>
<td>0.02</td>
</tr>
<tr>
<td>11.0</td>
<td>103.6</td>
<td>31.5</td>
<td>2.3</td>
<td>148.4</td>
<td>0.17</td>
</tr>
<tr>
<td>23.5</td>
<td>92.0</td>
<td>30.0</td>
<td>2.3</td>
<td>147.8</td>
<td>0.35</td>
</tr>
<tr>
<td>35.4</td>
<td>79.4</td>
<td>29.5</td>
<td>5.0</td>
<td>149.3</td>
<td>0.60</td>
</tr>
<tr>
<td>48.0</td>
<td>74.8</td>
<td>27.2</td>
<td>3.1</td>
<td>153.1</td>
<td>0.79</td>
</tr>
<tr>
<td>59.4</td>
<td>65.4</td>
<td>25.1</td>
<td>2.0</td>
<td>151.9</td>
<td>0.98</td>
</tr>
</tbody>
</table>

MgSO\(_4\) and 80 µmole of H\(_2\)SO\(_4\). The samples were shaken for 1 h and extracts separated by centrifugation.

The equilibrated solutions, as well as the extracts, were analysed for Fe\(^{2+}\), Fe\(^{3+}\), Na\(^{+}\) and H\(^{+}\). Ion adsorption values were calculated from the changes in concentrations of ions in solutions as well as from the exchangeable amounts extracted by MgSO\(_4\) solutions, and close agreement was obtained between these values.

Chemical analysis

Fe\(^{2+}\) in solution was titrated with KMnO\(_4\) or—for low concentrations—determined photometrically by use of 2,2'-bipyridine. Structural Fe\(^{2+}\) was determined by dissolving the mineral in 3 M HCl at 70°C in the presence of H\(_2\)SO\(_4\), H\(_3\)PO\(_4\) and MnSO\(_4\) (Reinhardt-Zimmermann-solution, Jander et al., 1963) and by simultaneous titration with H\(_2\)O\(_2\). Total Fe was determined by AAS (Perkin Elmer 4000) after digesting 100 mg of sample with HF/HClO\(_4\) and dissolving the residue with HCl.

RESULTS AND DISCUSSION

Exchange equilibria of ion species of iron

Use of the ion-couple Fe\(^{3+}\)/Fe\(^{2+}\) for controlling the redox potential of a solution raises the question as to how cation exchange with minerals brought into contact with the solution...
Table 2. Oxidation and release of structural Fe$^{2+}$ in Mg-vermiculite at a redox potential of 645 mV after different time intervals (mmole/100 g of silicate)

<table>
<thead>
<tr>
<th>Reaction time (h)</th>
<th>Fe$^{2+}$ in mineral</th>
<th>Loss of Fe$^{2+}$ in mineral</th>
<th>H$_2$O$_2$ consumption</th>
<th>Gain of Fe$^{2+}$ in solution</th>
<th>Fe oxidized</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>214.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>163.8</td>
<td>50.7</td>
<td>47.5</td>
<td>n.d.</td>
<td>50.7</td>
</tr>
<tr>
<td>2</td>
<td>132.8</td>
<td>81.7</td>
<td>79.5</td>
<td>1.8</td>
<td>79.9</td>
</tr>
<tr>
<td>4</td>
<td>95.5</td>
<td>119.0</td>
<td>107.7</td>
<td>7.5</td>
<td>111.5</td>
</tr>
<tr>
<td>8</td>
<td>71.7</td>
<td>142.8</td>
<td>128.3</td>
<td>13.7</td>
<td>129.1</td>
</tr>
<tr>
<td>16</td>
<td>57.8</td>
<td>156.7</td>
<td>135.0</td>
<td>19.2</td>
<td>137.5</td>
</tr>
</tbody>
</table>

Affects the activity ratio of the ions. Preferential sorption of Fe$^{3+}$ would have the same effect as reduction in shifting the activity ratio in solution. To prevent redox reactions from interfering with cation exchange, the beidellite sample from Unterrupsroth, which is free of oxidizable components, was selected.

The cation distribution obtained after equilibrating the samples of beidellite with solutions containing varying proportions of Fe$^{3+}$ and Fe$^{2+}$ is shown in Table 1. Large amounts of Fe were adsorbed from solution, with Fe$^{3+}$ being the preferentially adsorbed species. Sodium was almost completely desorbed. Selectivity coefficients were calculated using the Gapon equation, and, in contrast to the usual finding, increased with increasing Fe$^{3+}$/Fe$^{2+}$ ratio. With selectivity coefficients averaging ~0.5, preferential sorption seemed to be caused by the valence effect and not by any specific affinity.

The sum of the exchangeable cations in Table 1 exceeds the exchange capacity of the beidellite (143 mEq/100 g). This can be explained by a partial conversion of Fe$^{3+}$ to FeOH$^{2+}$ at pH 2.8, which is in agreement with thermodynamic considerations. However, the precision of the experimental data presented in Table 1 is insufficient for a more detailed evaluation.

Two conclusions can be drawn from the exchange experiment. The cation distribution in the system must be determined in order to distinguish changes in the redox potential of solutions which are due to cation exchange with the solid phase, from those which are caused by electron transfer. Furthermore, preferential sorption of Fe$^{3+}$ has to be regarded as a possible part of the charge transfer process during the oxidation of structural Fe$^{2+}$.

Oxidation of structural Fe$^{2+}$ at constant pH and Eh

In the first oxidation experiment the redox potential was fixed at 645 mV. Compositional changes of mineral and solutions were analysed after different time intervals and the results are shown in Table 2.

After 16 h, the content of Fe$^{2+}$ in the mineral was reduced to ~27% of its original value, but equilibrium had not yet been attained. The loss of Fe$^{2+}$ from the mineral exceeded H$_2$O$_2$ consumption, obviously caused by a transfer of structural Fe to solution. At the given pH of 2.8, considerable protolysis of the vermiculite could be expected. In addition, ejection of Fe from the structure could result from a charge-balancing reaction compensating positive charge gained during oxidation of structural Fe. On the other hand, Fe ions from solution are subject to cation exchange at interlayer exchange positions. Thus, the change of
Oxidation of vermiculites by Fe$^{3+}$

The concentration of Fe in solution was the net result of two opposing reactions, adsorption and release.

This was demonstrated in another experiment in which the contents of Fe and Mg in solution were analysed at short time intervals after the addition of the samples to solution (Fig. 4). During the first few minutes of the reaction, the content of Fe$^{2+}$ in solution decreased with a corresponding increase in Mg concentration as a result of cation exchange. However, the decrease in Fe was quickly overcompensated by a secondary reaction leading to a release of Fe and Mg to the solution.

The proportion of adsorption and release in relation to oxidation of structural Fe was studied at different redox potentials. In Fig. 1 the consumption of H$_2$O$_2$ was plotted against the reaction time for redox potentials fixed at different levels. As expected, raising the redox potentials accelerated oxidation, but the changing slope of the plots indicated a complex reaction mechanism.

The respective compositional changes in mineral and solution at the end of 2 h are summarized in Table 3. Again, there is good agreement between total oxidation of Fe$^{2+}$ and H$_2$O$_2$ consumption as well as between loss of structural Fe$^{2+}$ and net H$_2$O$_2$ consumption. Larger amounts of H$_2$O$_2$ had to be used for adjusting higher redox potentials in solution prior to the addition of the minerals.

The decrease in total Fe in solution with rising redox potentials indicated a strong adsorption of Fe$^{3+}$. Considering the gain in Fe in solution by either ejection or protolysis, the amount of adsorbed Fe must be considerably larger than indicated by the figures given in Table 3 for the losses of total Fe in solution. This raises the question about the specific role of adsorbed Fe in the oxidation mechanism. Oxidation of structural Fe could be considered as depending solely on electron transfer to exchangeably-bound ionic electron acceptors, as, e.g., Fe$^{3+}$ or Ag$^+$ in the interlayers of vermiculite, whereas the role of H$_2$O$_2$ could be restricted to maintaining the redox potential in solution. The latter is continuously disturbed by transport of electrons from the interlayer space to Fe$^{3+}$ in solution.

This hypothesis has been examined by varying the amount of Fe in solution at constant redox potential. As shown in Fig. 2, addition of Fe accelerated the rate of oxidation even though the redox potential was kept constant.
TABLE 3. Changes of Fe

<table>
<thead>
<tr>
<th>Redox potential (mV)</th>
<th>Loss of Fe(II) in mineral (mmole/100 g of silicate)</th>
<th>Change of Fe(II) in solution (mmole/100 g of silicate)</th>
<th>Fe oxidized (mmole/100 g of silicate)</th>
<th>Total H₂O₂ used (mmole/100 g of silicate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>625</td>
<td>42.7</td>
<td>6.3</td>
<td>36.3</td>
<td>36.5</td>
</tr>
<tr>
<td>645</td>
<td>81.6</td>
<td>1.8</td>
<td>79.8</td>
<td>79.8</td>
</tr>
<tr>
<td>685</td>
<td>121.8</td>
<td>-19.7</td>
<td>141.5</td>
<td>142.2</td>
</tr>
<tr>
<td>725</td>
<td>135.0</td>
<td>-58.3</td>
<td>193.3</td>
<td>196.7</td>
</tr>
<tr>
<td>765</td>
<td>136.0</td>
<td>-87.3</td>
<td>223.3</td>
<td>228.3</td>
</tr>
</tbody>
</table>

Due to its higher charge, Fe³⁺ was preferentially adsorbed. With increasing additions of Fe to the solution phase, an increasing amount of Fe³⁺ diffused into the interlayer space, where it accepted electrons from structural Fe²⁺, thereby affecting the rate of oxidation. The shape of the reaction curves at low additions suggests an autocatalytic effect which is probably also related to the release of structural Fe and its subsequent exchange into interlayer positions.

Finally, the close interaction between cation exchange and oxidation was confirmed by the results of an experiment in which the concentration of MgSO₄ was varied between 0.02 and 2 N at constant Fe concentration and redox potential (Fig. 3). Because Fe and Mg ions were competing for interlayer exchange positions, oxidation rates were negatively correlated with the concentration of Mg²⁺ in solution.

CONCLUSIONS

From the observations described, it seems that the oxidation of Fe²⁺ in the octahedral sites of vermiculite by solutions containing oxidizing ions is a coupled reaction in which the redox process is interrelated with cation exchange.

For Fe²⁺ in octahedral sites of vermiculite, the probability of being oxidized depends on the number of Fe³⁺ ions acting as electron acceptors in interlayer exchange positions. In turn the number of exchangeable Fe³⁺ ions is influenced by the exchange equilibrium with other ions in solution. If the equilibrium is shifted in favour of exchangeable Fe³⁺, either by increasing the redox potential in solution or by increasing the amount of ionic Fe in the
system, the rate of oxidation is accelerated. In this connection, the effect of preferential sorption of Fe\(^{3+}\) on the exchange equilibrium has to be considered as it results in a comparatively high proportion of Fe\(^{3+}\) in the adsorbed state. Hence, the "effective redox potential" of adsorbed ions is probably considerably higher than that for ions in solution. As the adsorbed ions are the transmitters of electrons between structural Fe and Fe in solution, the effects of the oxidation potential of the solution on the oxidation of structural ions is amplified by cation exchange.

As long as other cation species e.g. Mg, are involved in exchange equilibration, the equivalent portion of Fe\(^{3+}\) in exchange positions does not depend solely on the redox potential in the solution phase. At a given redox potential in solution, different rates of oxidation can be observed, depending on the equivalent ratio of Fe\(^{3+}\) to other cations after equilibration.

During the oxidation of structural Fe, the exchange equilibrium is continuously disturbed as a result of electron transfer to Fe\(^{3+}\) in interlayer positions. If the redox potential in solution is kept constant, the exchange equilibrium of Fe\(^{2+}\) and Fe\(^{3+}\) between interlayer space and solution is reestablished by the transfer of negative charge to solution. This transfer may be accomplished either by counter-diffusion of Fe\(^{2+}\) and Fe\(^{3+}\) between solution and interlayer positions, or by electron-hopping to Fe\(^{3+}\) in solution, and finally to react with hydrogen peroxide.

Preliminary findings point to the reversibility of electron transfer between interlayer and structural cations. Pre-oxidized structural Fe\(^{3+}\) was observed to be at least partially reduced by adsorbed Fe\(^{2+}\). However, the results are inconclusive as to whether a redox equilibrium exists between adsorbed and structural ions of Fe. Firstly, as will be elaborated in a later paper, the overall mechanism of oxidation includes side reactions which interfere with electron transfer. The second and more important reason lies in the instability of the system at low pH. The pH had to be kept at 2.8 to maintain Fe\(^{3+}\) in solution but this is well below the stability range of vermiculite, as indicated by consumption of H\(_2\)SO\(_4\) for balancing pH during the reaction. Consequently, the oxidation could only be followed for a comparatively short period of time, insufficient for reaching redox equilibrium.

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REFERENCES


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