

IRON OXIDATION AND REDUCTION EFFECTS ON STRUCTURAL HYDROXYL AND LAYER CHARGE IN AQUEOUS SUSPENSIONS OF MICACEOUS VERMICULITES

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Abstract—Four Na₂S₂O₄-reduced Na-vermiculites, each with some trioctahedral mica interstratified, were oxidized with H₂O₂ at pH 6.5 and again reduced with Na₂S₂O₄ in suspensions at pH 7.5–8.0. The layer charge (CEC + K⁺), measured at pH 6.50, did not change significantly when octahedral Fe was oxidized (7–92 mmole 100 g⁻¹) or reduced (6–71 mmole 100 g⁻¹). Electroneutrality was maintained within the octahedral sheet when Fe was oxidized or reduced. When Fe(II) was oxidized, electroneutrality was maintained by deprotonation of octahedral OH⁻ groups,



and by ejection of (dissolution of structural) octahedral metallic cations,



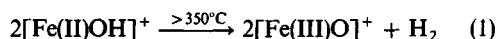
When Fe(III) was reduced, electroneutrality was maintained by reprotonation of the deprotonated sites (O*, equation a). Reaction (b) was not reversible. Thus, reversibility of the reaction, Fe(II) \rightleftharpoons Fe(III), within the octahedral sheet decreased with increasing amount of ejected metallic cations. The amount of Fe(III) and Mg²⁺ ejected per Fe(II) oxidized was related to the degree of vermiculitization, being greatest with Na-degraded biotite [0.03 Fe³⁺ and 0.11 Mg²⁺ per Fe(II) oxidized] and lowest (nearly zero) with South African vermiculite. The number of deprotonated (O*) and reversible sites increased from 0.69 per Fe(II) oxidized with the K-depleted biotite to approximately 1.0 with South African vermiculite. The weathering increment was small since, of the total amount of Fe + Mg, less than 1.3 per cent was ejected from any of the four vermiculitic materials. When biotite was K-depleted, about 20 m-equiv of layer charge per 100 g (300°C basis) was lost, while 51 mmole of Fe(II) per 100 g was oxidized in the presence of Na₂S₂O₄ and 82 mmoles in its absence in the aqueous suspensions. Since sequential reduction–oxidation–reduction treatments of K-depleted biotite and mica-containing vermiculites did not cause significant changes in layer charge ($r^2 = 0.04$), the layer charge changes were concluded to be entirely independent of the oxidation or reduction of Fe in these minerals.

INTRODUCTION

The objectives of this paper are to show quantitatively for biotite and micaceous vermiculites (a) that the layer charge changes are not equivalent to the Fe oxidized or reduced under near neutral aqueous conditions and (b) that electroneutrality is maintained by reversible de- and reprotonation of structural OH⁻ groups and (or) irreversible ejection of octahedral metallic cations. Micaceous vermiculites consist of vermiculites (14 Å basal spacing) interstratified with micas (10 Å basal spacing).

Thermal oxidation of Fe(II) in phyllosilicates has been studied extensively by Brindley and Youell (1953),

Tsvetkov and Val'Yashikhina (1956), Addison *et al.* (1962), Eugster and Wones (1962), Rimsaite (1956, 1967, 1970), Vedder and Wilkins (1969), Robert (1971). The results can be summarized as follows: when structural Fe(II) is oxidized thermally (above 350°C), the electron from the Fe(II) is accepted by a proton of a structural hydroxyl group. The hydrogen is either released as a gas,

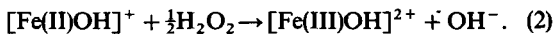


or, in the presence of atmospheric oxygen, as H₂O. This auto-oxidation has no effect on the layer charge, as shown in the equation (1).

In contrast to thermal oxidation, oxidation in aqueous suspension occurs only in the presence of an external oxidant which accepts the electron from the structural Fe(II) oxidized, creating one excess positive

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charge per Fe(II) oxidized in the structure,



The question of balancing this extra charge when structural iron changes its valency is still open for the aqueous oxidation case. One hypothesis (Gruner, 1934) suggests that a balancing loss of interlayer cations occurs when structural Fe(II) is oxidized. This hypothesis was supported by Ismail (1969, 1970) and by Barshad and Kishk (1970), who reported a significant change in layer charge when octahedral Fe changed its valency. On the other hand, data published by Newman and Brown (1966), Raman and Jackson (1966), Newman (1967), Roth *et al.* (1968, 1969), Leonard and Weed (1970), Farmer *et al.* (1971), Robert (1971) showed that the decrease in layer charge (in m-equiv) of K-depleted trioctahedral micas was always unequal to the amount of Fe(II) oxidized (in mmole). The layer charge of a degraded phlogopite, which contained no Fe, also decreases (Leonard and Weed, 1970).

The decrease in layer charge of depleted trioctahedral micas is believed to be independent of Fe oxidation and is caused by the incorporation of protons into the structure (Rosenqvist, 1963; Raman and Jackson, 1966; Newman and Brown, 1966; Newman, 1967; Leonard and Weed, 1970; Newman, 1970).

Farmer *et al.* (1971) presented "... evidence for loss of protons and octahedral iron from chemically oxidized biotites and vermiculites". Their results were confirmed by Gilkes *et al.* (1972). The oxidation treatments in both papers were carried out in acid solutions, with either saturated bromine water and/or H₂O₂. The present study concerns oxidation in near neutral solutions. Under acid conditions, deprotonation of structural hydroxyl groups may be suppressed by diffusion of structural cations, which occurs easily. These cations are subsequently found not only in solution but also as interlayer complexes of Al and Fe (Jackson, 1963a, b; Rich, 1968; Coulter, 1969; Veith and Schwertmann, 1972).

MATERIALS AND METHODS

Samples. Three vermiculites (14 Å), each containing some trioctahedral mica (10 Å) interstratified, from Menominee County, Wisconsin (WI); Libby, Montana (MT); and Transvaal, South Africa (TSA); and one biotite (source unknown) were employed. The WI and MT vermiculites were separated from the saprolite by an exfoliation-floating method (Jackson, 1969).

Size. All samples were wet-ground in a Waring blender and the <20 μm size fraction obtained by sedimentation.

Depletion. Interlayer K was partially removed from the MT and TSA vermiculites by several treatments with 5 M NaCl and from biotite and WI vermiculite by two treatments with 0.1 M sodium tetraphenyl boron (NaTPB) + 0.2 M NaCl (Scott and Smith, 1966). One biotite was partially depleted with NaTPB in the presence of sodium dithionite (Na₂S₂O₄).

Red-ox treatments. The four K-depleted samples received the following treatments (30–60 min each): Reduction of Fe(III) and removal of free iron hydrous oxides with citrate-bicarbonate-dithionite, pH 7.5–8.0 (Mehra and Jackson, 1960; Jackson, 1969). One third of each sample was retained for further analysis and the remainder was treated for oxidation of structural Fe(II) with 30 per cent phosphorus-free H₂O₂ adjusted to pH 6.50 with NaOAc. One half of each sample was kept separately, the rest being reduced for a second time with Na₂S₂O₄ in 1 M NaHCO₃ adjusted to pH 7.5–8.0.

Na-saturation. The four differently treated samples of each micaceous vermiculite (control, red, red-ox, red-ox-red) were equilibrated three times with 1 M NaOAc (pH 6.50), washed twice with 0.01 M NaOAc (pH 6.50) and dried at 30°C. The amount of excess salt (<5 m-equiv 100 g⁻¹ in all cases) was calculated by weighing the samples before and after drying.

Elemental analysis. Na, K, Fe, Mg and Al were measured by atomic absorption after dissolution of 50- to 80-mg samples in 2 or 4 ml of concentrated HF (Jackson, 1969).

Layer charge (LC). Na + K, at pH 6.50.

Measurement of Fe(II). Fe(II) was determined by a method given by Wilson (1960) which was modified as follows: A 50-mg sample was suspended in 10 ml of H₂O. Then 10 ml of 0.01 M NH₄VO₃ + 5 ml of concentrated HF were added while the suspension was stirred. After dissolution, 5 ml of 10 M H₂SO₄ were added and the solution titrated with 0.02 M Fe(II)(NH₄)₂(SO₄)₂, with two drops of 0.2 per cent barium diphenylamine sulfate as an indicator. Fe(III) was calculated as follows: Fe(total)–Fe(II).

H₂O loss. H₂O loss from biotite, depleted biotite, and Na-vermiculites was measured by a Cahn balance thermogravimetric apparatus, between 30 and 900°C.

Ejection of octahedral metallic cations when structural Fe(II) is oxidized. When oxidation occurs at pH 6.4–7.0, practically all of the ejected Fe(III) is precipitated. This precipitate was dissolved in the presence of Na₂S₂O₄ in 2 M Na⁺ solution to prevent Fe²⁺ and Mg²⁺ adsorption. The amounts of ejected Fe(III) and Mg²⁺, i.e. structural cations dissolved, were measured by changes in the total analysis, in the case of Mg²⁺ directly after the oxidation treatment and in the case of Fe(III) after reduction following the oxidation.

Table 1. Chemical data and weight loss for biotite after varied treatments, weight basis at different temperatures

Treatment	Weight loss vs 30°C			(mmole 100 g ⁻¹)						Structural cations (300°C)			Al
	100°C	300°C	900°C	K present		LC*		ΔLC		Fe(II)	Fe(III)	ΔFe(III)	
	(%)	(%)	(%)	100°C	300°C	100°C	300°C	100°C	300°C				
None	0.5	2.7	8.0	169	172	196	200	0	0	222	36	0	207
NaTPB† + D‡ + D	2.5	9.7	16.5	21	22	169	181	-27	-19	172	87	51	205
NaTPB	1.3	9.4	16.0	22	24	166	180	-30	-20	149	118	82	207

* Layer charge.

† TPB = 0.1 M sodium tetraphenyl boron in 0.2 M NaCl.

‡ D = Na₂S₂O₄ in the presence of TPB, followed by a Na₂S₂O₄ treatment without TPB.

RESULTS

Changes on depletion of biotite

One of the NaTPB-treated samples was K depleted under reducing conditions by addition of Na₂S₂O₄, an additional Na₂S₂O₄ treatment being given immediately after depletion (Table 1). Even in the presence of a strong reductant in the suspension, considerable amount of the structural Fe(II) (51 mmole 100 g⁻¹) was oxidized, apparently reflecting the exclusion of the anion, S₂O₄²⁻, from the separated biotitic interlayers and the high lability of Fe(II) in the layers.

The chemical relationships are considerably different, when expressed on the 300°C basis (vs 100°C) as a result of the difference in H₂O content between the biotite and the hydrated Na-degraded biotite, a relationship noted also by Walker (1949). For example, the decrease in layer charge (ΔLC, Table 1) is about 20 mmole when calculated on the weight basis at 300°C compared to 30 mmole 100 g⁻¹ when calculated on the weight basis at 100°C. The additional interlayer water loss from depleted biotite when heated between 100 and 300°C is shown in Fig. 1.

The difference in layer charge of about 20 mmole 100 g⁻¹ between undepleted and depleted biotite is significant. While layer charge was decreased by 19 mmole, 51 mmole of Fe(II) was oxidized (Table 1). Furthermore, although the change in layer charge between the two depleted samples was only 1 mmole (20–19), 31 more mmole (82–51, Table 1) of Fe(II) was oxidized. The layer charge did not decrease as a function of Fe(II) oxidized in either of the samples (20 mmole layer charge decrease vs 51 and 82 mmole iron oxidized, Table 1).

Changes in oxidized and reduced micaceous vermiculites

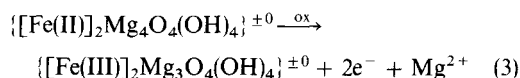
In order to determine whether changes in LC occur only during depletion of biotites and not during red-ox-treatments after depletion, 30 samples of four micaceous vermiculites were given various sequences of

reduction, reduction and oxidation, and reduction–oxidation–reduction treatments. The changes in LC and in Fe(II) and Fe(III) are plotted in Fig. 2. If the changes in layer charge (ΔLC) were a function of changes in iron valency (ΔFe(II, III)), then ΔLC would always be positive when Fe(III) is reduced (square symbols), and always negative when Fe(II) is oxidized (round symbols). The figure shows that the two symbols are found in both the positive and the negative fields. The mathematical result of $r^2 = 0.04$ indicates that there is no correlation between ΔLC and ΔFe(II, III). Thus the significant decrease in LC of 19 or 20 mmole 100 g⁻¹ after NaTPB-D + D treatment (Table 1) appears unlikely to have been caused by Fe(II) oxidation. The large changes in Fe(II) and Fe(III) content of micaceous vermiculites with little or no CEC change are in agreement with the results of Roth *et al.* (1969).

Maintenance of electroneutrality when Fe(II) ⇌ Fe(III)

Data for four depleted layer silicates before (control) and after various red-ox treatments show that layer charge remains constant ($r^2 = 0.04$) when partially K-depleted micaceous vermiculites are red-ox-treated (Table 2). Al, mainly in the tetrahedral position, remains unchanged (Table 2). The data are reported on a 30°C basis, since (a) differences in hydration are negligible for these depleted samples and (b) it is easier to reproduce values at 30 than at 100°C.

Ejection of octahedral cations. When Fe(II) was oxidized, the electroneutrality in the layers was maintained in small part by the ejection of (dissolution of structural) octahedral Mg²⁺ and/or Fe(III), except in the case of TSA vermiculite, from which no Mg or Fe was ejected (Tables 2 and 3),



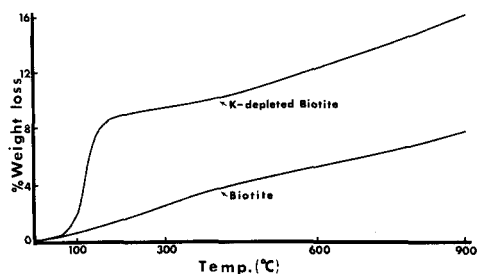
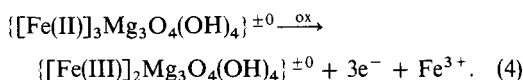
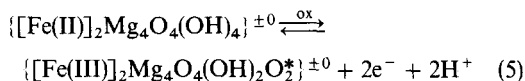


Fig. 1. Weight loss of biotite and Na-depleted biotite as a function of temperature ($10^{\circ}\text{C min}^{-1}$).



In all cases, equations (3 and 4) account for 31 per cent or less of the increase in net positive charges in the octahedra when structural Fe(II) was oxidized. The remainder of the charge increase (69 per cent or more) was apparently balanced by deprotonation of structural OH groups.

Deprotonation of structural hydroxyl and reversibility of deprotonation. When structural Fe(II) was oxidized structural OH⁻ was deprotonated,



in which O* represents oxygen from deprotonated structural hydroxyl. This reaction was reversible.

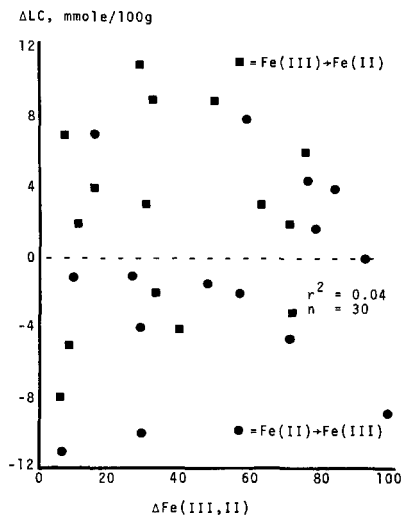


Fig. 2. Change in layer charge (ΔLC) as a function of change in iron valency, $\Delta\text{Fe(III,II)}$.

When H_2O_2 acts as an oxidant it accepts $2e^-$ from two structural Fe(II) and 2OH^- are formed:



A combination of equations (3–5) with the equation (6) gives the reactions which occurred when structural Fe(II) became oxidized by H_2O_2 in the pH range of 6.4–7.3,

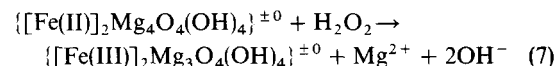


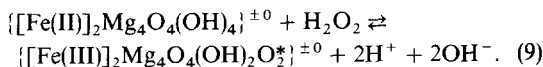
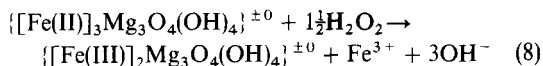
Table 2. Analyses of untreated and red-ox-treated K-depleted biotite and vermiculites (mmole 100 g⁻¹)

Sample	K	Treatm.	LC (Na + K)	Al _t *	Mg _t	ΔMg (loss)	Fe _t	ΔFe (loss)	Fe(II)	Structural ΔFe(II)	ΔFe(III)
Biotite (depleted)	20	Control	168	203	339		245		108	—	—
	18	red.†	167	200	342		237	8§	118	10	—
	20	ox	167	202	332		237		26	—	92
	19	red.	164	204	328	~4	234	~0	97	71	—
Verm (WI)	72	Control	142	230	38		432		3	—	—
	73	red.	145	234	41		370	62§	65	62	—
	72	ox	143	233	42		371		8	—	57
	71	red.	142	230	41	~0	359	13	50	42	—
Verm (MT)	19	Control	155	202	454		129		9	—	—
	19	red.	159	206	451		116	13§	36	27	—
	16	ox	155	202	453		113		8	—	28
	13	red.	153	200	448	~5	113	~0	40	32	—
Verm (TSA)	41	Control	163	186	620		63		13	—	—
	28	red.	165	186	625		60	~0	22	9	—
	13	ox	155	190	620		67		15	—	7
	9	red.	161	185	622	~0	62	~0	21	6	—

* The subscript, *t*, designates total of the element present.

† Red. = $\text{Na}_2\text{S}_2\text{O}_4$; ox = H_2O_2 .

§ Free $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$.



For each Fe(II) oxidized, $\frac{1}{2}\text{H}_2\text{O}_2$ is reduced and one OH^- is formed in solution and can react with one H^+ coming from a structural OH^- group (equation 9). When $\text{H}^+ = \text{OH}^-$, the pH of the suspension is the same before and after oxidation (equation 9). The number of deprotonated structural hydroxyls (O^* , equation 9) per Fe(II) oxidized is calculated from:

$$\text{O}^* = \text{Fe(II)}(\text{oxidized}). \quad (10)$$

If Fe(III) ejection occurs, 3OH^- are formed for each ejected Fe(III); however, at pH 6.4–7.3, practically all of it is precipitated as iron hydrous oxide by neutralization of the 3OH^- produced for each ion ejected (equation 8). The pH is thus unchanged by Fe(II) oxidation in equation (8). If reactions (8 and 9) occur together the number of deprotonated structural OH^- per Fe(II) oxidized is:

$$\text{O}^* = \text{Fe(II)}(\text{oxidized}) - 3\text{Fe(III)}(\text{ejected}). \quad (11)$$

In the case of Mg^{2+} ejection, however, the pH rises because the 2OH^- produced for each Mg^{2+} ejected (equation 7) do not react significantly with Mg^{2+} in the pH range of 6.4–7.3. If all three reactions (7, 8 and 9) occur together, the number of deprotonated structural OH^- per 100 mmole of Fe(II) oxidized is:

$$\text{O}^* = 100 - [3\text{Fe(III)} + 2\text{Mg}^{2+}]_{\text{ejected}}. \quad (12)$$

The independent variables, Fe(III) and Mg in mmole per 100 mmole Fe(II) oxidized, were measured as follows: Fe(II) oxidized, by the difference between Fe(II) before and after oxidation; Fe(III) ejected, by the amount of Fe(III) dissolved by repeated treatments of

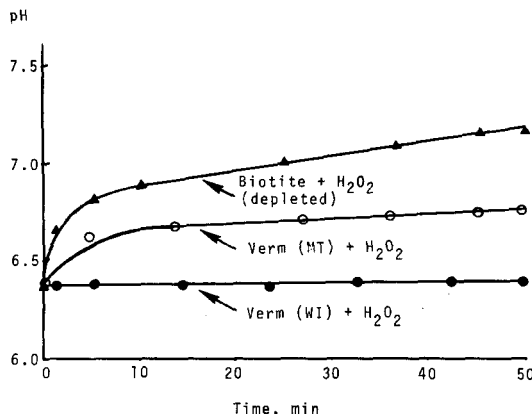


Fig. 3. Function between pH and time after addition of H_2O_2 to Fe(II)-containing samples.

the oxidized samples with $\text{Na}_2\text{S}_2\text{O}_4$ in the presence of 2 M Na^+ to keep Fe^{2+} desorbed; Mg^{2+} ejected was measured directly, after H_2O_2 treatment of the sample in a 2 M Na^+ solution (Table 2), and indirectly by titrating the suspension pH back to the initial pH to determine the amount of OH^- formed ($\text{Mg}^{2+} = 2\text{OH}^-$, equation 7).

The results (Fig. 3, Table 3) were obtained from the first $\text{Na}_2\text{S}_2\text{O}_4$ -treated samples (Table 2) of Na-biotite and Na-vermiculite (WI, MT) oxidized with H_2O_2 . The TSA vermiculite was not included in the titration experiment (Fig. 3), because only 7 mmole of Fe(II) 100 g^{-1} changed valence (Table 2). The pH of a 50-mg suspension of each reduced sample in 33 ml of H_2O was adjusted to 6.40. Then 2 ml of H_2O_2 (~30 per cent), which had been previously adjusted to pH 6.40 (with NaOH, when mixed with 33 ml of H_2O), were added. The pH rose in the suspensions of Na-biotite and MT vermiculite (equation 7) but not in those of WI vermiculite, showing that no ejection of Mg^{2+} had

Table 3. Ejected Mg^{2+} and Fe(III), deprotonation of structural hydroxyls during H_2O_2 treatment, and reversibility of the reactions

Sample	Fe(II) oxidized [(mmole/100 g)%]		[mmole/100 mmole Fe(II) oxidized]				Fe(II) \rightleftharpoons Fe(III) reversibility (mmole/100 g)	
	Dir.*	Indir.†	2Mg ²⁺ ejected Dir.*	3Fe(III) Dir.*	Deprotonated oxygen	(%)	(%)	
Biotite (depleted)	92	39	22	9	69	69	54	
Verm (WI)	57	16	0	63§	?	?	?	
Verm (MT)	28	22	20	18	80	80	23	
Verm (TSA)	7	11	0	n.d.	~100	~100	~7	

* Direct measurement of decrease in structural Mg or Fe.

† Indirect measurement as OH^- formed in solution (equation 7).

§ Sample contained free $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$.

occurred in the latter (Fig. 3). The amount of Mg^{2+} ejected, when measured directly, agrees with the result indirectly obtained from OH^- titration (Table 3). The value of 63/3 mmole of $Fe(III)$ 100 g^{-1} for WI vermiculite (Table 3) is too high because it includes an additional amount of free iron which was not totally removed during the first $Na_2S_2O_4$ treatments.

The values for deprotonated oxygen (Table 3) increase in going from Na biotite to TSA vermiculite, owing to a decreasing amount of ejection of octahedral metallic cations. This is consistent with the amount of oxidation of $Fe(II)$ in the four phyllosilicates used (Table 3): depleted biotite > WI vermiculite > MT vermiculite > TSA vermiculite. During the weathering transformation of trioctahedral mica layers to vermiculite, $Fe(II)$ becomes oxidized and octahedral metallic cations are ejected from this increment of mica weathered to vermiculite during the measurements. Hence, the greatest stability has been reached by the least ferrous sample, TSA vermiculite. As the same time the percentage reversibility of the oxidized $Fe(II)$ in the vermiculite layers increases in going from the freshly opened biotite layers to the low-iron TSA vermiculite (Table 3).

DISCUSSION

The gain in positive charges in the iron-containing octahedra through iron oxidation appears to be balanced within the octahedra themselves by different proportions of equations (7–9), through loss of protons from the OH^- groups and ejection of Mg^{2+} and $Fe(III)$ to form dioctahedral areas. During the vermiculitization, structural $Fe(II)$ becomes oxidized and some octahedral Mg^{2+} and $Fe(III)$ are ejected (Walker, 1949; Newman and Brown, 1966; Wilson, 1970). In the above experiments, the amount of $Fe(III)$ and Mg^{2+} ejected, during an increment of weathering, depended inversely on the degree of previous vermiculitization, i.e. on the amount of trioctahedral mica remaining. Thus, the loss of $Mg^{2+} + Fe(III)$ was greatest for H_2O_2 -treated freshly opened Na saturated biotite and least for H_2O_2 -treated TSA vermiculite (Table 3). The total amount of ejected $Mg^{2+} + Fe(III)$, in the experimental increment of weathering, was less than 1.3 per cent of the total structural $Fe + Mg$ in all samples, yet the charge balance and mechanism were quantified in these experiments. A greater loss of octahedral metallic cations under natural conditions is, of course, a result of longer time of weathering and may have been affected by the presence of inorganic and organic acids (Veith and Schwertmann, 1972) in leaching waters.

The oxidation of $Fe(II)$ is accompanied by deprotonation of octahedral OH^- groups, under the neutral conditions (Table 3) used in the present experiments; earlier work showed corresponding dehydroxylation under more acid conditions (Farmer *et al.*, 1971; Gilkes *et al.*, 1972). A deficit in structural $OH^- + F^-$ (<4 per unit cell) and therefore an excess of oxygen (>20 per unit cell) occurs in many trioctahedral micas (Eugster and Wones, 1962; Foster, 1964; Rimsaite, 1967, 1970). This excess oxygen is equivalent to that resulting from deprotonation of hydroxyl (O^* , in the above), formed during oxidation of $Fe(II)$ in biotitic materials by H_2O_2 treatment in suspension. The results obtained on naturally weathered samples would indicate that deprotonated biotite samples are relatively stable. The deprotonation process to compensate a positive charge increase in the octahedra was not considered by a number of authors (reviewed by Foster, 1963).

When structural $Fe(III)$ is reduced, only the deprotonated octahedral positions (equations 5 and 9) can be reprotonated. The calculated reversibility (Table 3) is 69 per cent for depleted biotite, 80 per cent for Na-vermiculite (MT) and about 100 per cent for Na-vermiculite (TSA), if reversibility is restricted to the reprotonation of deprotonated structural hydroxyls. From the data in Tables 2 and 3, it appears that $Fe(III)$ is easily reduced as long as deprotonated sites (O^*) exist. As the amount of deprotonated sites (mmole O^* 100 g^{-1}) decreases from biotite to Na-vermiculite (TSA), the amount of $Fe(III)$ reduced (Table 3) decreases (Tables 2 and 3) to about 15 per cent of the total $Fe(III)$ present (Table 2).

Contrary to the above findings, a change in LC when structural Fe changes its valency, in accord with the Gruner (1934) hypothesis, was inferred by Ismail (1969, 1970) and Barshad and Kishk (1970). Ismail (1969) states that after $Fe(II)$ oxidation, "The change in surface charge was measured by the amount of Na and K that diffused to the oxidizing solution". To achieve different pH values, either $CaCO_3$ and/or $Ca(OH)_2$ or 0.25 M $Al(OH)_{1.5}Cl_{1.5}$ were added. These added electrolytes would cause the exchange of Na^+ and K^+ into solution independently of his intended measurements of layer charge decrease. That greater amounts of Na^+ and K^+ were exchanged when Al was added is shown by his data. In the oxidation of octahedral $Fe(II)$, "... a supply of hydrogen ions from dissociated water would be available to receive the electrons resulting from the oxidation process ..." according to Ismail (1970). This would involve evolution of H_2 ; however, H_2 is well known to be a stronger reductant than $Fe(II)$ and, therefore, the proposed oxidation reaction with H_2 evolution from water is physicochemically unlikely.

A reversible increase in CEC after reduction of structural Fe(III) was inferred from data for 11 vermiculite-clays (Barshad and Kishk, 1970). Although no measurements of iron valency were given, the assumptions were made that all of the structural Fe(III) had been reduced after $\text{Na}_2\text{S}_2\text{O}_4$ treatment and that all of the structural Fe(II) had been oxidized after NaOCl treatment, contrary to the measurements made in the present study and those of Roth *et al.* (1968, 1969). Even after 24 hr of $\text{Na}_2\text{S}_2\text{O}_4$ treatment of some of our samples, only about 30 per cent or less of the structural Fe(III) in MT and TSA vermiculites was reduced. In order to compare NaEC values of different samples, the NaCl-treated materials should be washed, not with H_2O , but with dilute NaCl (at least 10^{-2} M) to prevent hydrolysis of exchangeable Na (Mokma *et al.*, 1970; Bar-on and Shainberg, 1970) and resuspension and loss of some of the clay particles.

Many papers report the loss in layer charge when biotite is weathered either naturally or artificially (Newman and Brown, 1966; Raman and Jackson, 1966; Scott and Smith, 1966; Marques and Scott, 1968; Leonard and Weed, 1970). Some of the changes in CEC had been based on the weight at about 100°C . As the depleted biotite is much more hydrated than the biotite (Walker, 1949; Newman, 1967; Davis *et al.*, 1970), ΔCEC and therefore ΔLC values are too high when based on drying at 100°C (Table 1, Fig. 1). If this effect of interlayer water is excluded, the change in LC before and after depletion is less and the discrepancy between ΔLC and Fe(II) oxidized is even greater.

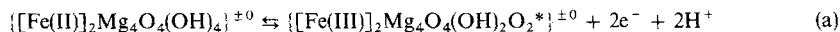
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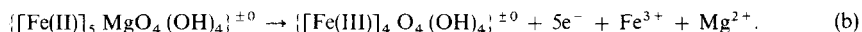
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Résumé—Quatre vermiculites Na réduites par $\text{Na}_2\text{S}_2\text{O}_4$, contenant chacune un mica trioctaédrique interstratifié, ont été oxydées par H_2O_2 à pH 6,5 et de nouveau réduites par $\text{Na}_2\text{S}_2\text{O}_4$ en suspension à pH 7,5–8,0. La charge du feuillet (CEC + K^+) mesurée à pH 6,50 ne change pas significativement quand Fe octaédrique est oxydé ($7\text{--}92 \text{ mmol } 100 \text{ g}^{-1}$) et réduit ($6\text{--}71 \text{ mmol } 100 \text{ g}^{-1}$). L'électroneutralité est maintenue à l'intérieur de la couche octaédrique quand Fe est oxydé ou réduit. Quand Fe(II) est oxydé, l'électroneutralité est maintenue par déprotonation de groupes OH^- octaédriques,



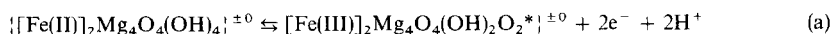
et par éjection (dissolution) de cations métalliques octaédriques du réseau,



Quand Fe(III) est réduit, l'électroneutralité est maintenue par reprotonation des sites déprotonés [0* équation (a)] La réaction (b) n'est pas réversible.

Ainsi, la réversibilité de la réaction $\text{Fe(II)} \rightleftharpoons \text{Fe(III)}$ à l'intérieur de la couche octaédrique diminue quand augmente la quantité de cations métalliques éjectés. La quantité de Fe(III) et Mg^{2+} éjectés, par Fe(II) oxydé, est reliée au degré de vermiculitisation; elle est la plus grande avec la biotite dégradée Na ($0,03 \text{ Fe}^{3+}$ et $0,11 \text{ Mg}^{2+}$ par Fe(II) oxydé) et la plus petite (environ zéro) avec la vermiculite d'Afrique du Sud. Le nombre de sites déprotonés (0*) et réversibles augmente de 0,69 par Fe(II) oxydé avec la biotite appauvrie en K, à environ 1,0 avec la vermiculite d'Afrique du Sud. L'incrément d'altération est petit, puisque, sur la quantité totale de Fe + Mg, moins de 1,3 pour cent a été éjecté de chacun des 4 matériaux vermiculitiques. Quand la biotite est appauvrie en K, environ 20 m-equiv de charge du feuillet par 100 g (référence 300°C) disparaissent, tandis que sont oxydées 51 mmoles de Fe(II) par 100 g en présence de $\text{Na}_2\text{S}_2\text{O}_4$ et 82 mmoles en l'absence de ce réactif, en suspension aqueuse. Puisque les traitements répétés réduction–oxydation–réduction de la biotite appauvrie en K et des vermiculites contenant du mica, n'entraînent pas de changements significatifs dans la charge du feuillet ($r^2 = 0,04$) on en a conclu que les modifications de charge du feuillet sont entièrement indépendantes de l'oxydation et de la réduction de Fe dans les minéraux.

Kurzreferat—Vier $\text{Na}_2\text{S}_2\text{O}_4$ -reduzierte Na–Vermiculite, alle in Wechsellagerung mit etwas trioktaedrischem Glimmer, wurden bei pH 6,5 mit H_2O_2 oxidiert und in Suspension bei pH 7,5–8,0 mit $\text{Na}_2\text{S}_2\text{O}_4$ wieder reduziert. Die Schichtladung (AK + K), gemessen bei pH 6,50, zeigte keine deutliche Veränderung, wenn das oktaedrische Fe oxidiert ($7\text{--}92 \text{ mmol } 100 \text{ g}^{-1}$) oder reduziert ($6\text{--}71 \text{ mmol } 100 \text{ g}^{-1}$) wurde. Bei Oxidation und Reduktion des Eisens in der Oktaederschicht wurde die Elektroneutralität aufrecht erhalten. Bei der Oxidation von Fe(II) wurde die Elektroneutralität durch Deprotonierung der oktaedrischen OH^- -Gruppen,



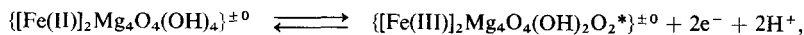
und durch Abgabe (Lösung) von metallischen Gitterkationen aus Oktaederposition,



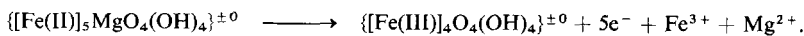
gewahrt.

Wenn Fe(III) reduziert wurde, wurde die Elektroneutralität durch Reprotonierung der deprotonierten Gitterplätze [O* in Gleichung (a)] bewirkt. Reaktion (b) war nicht reversibel. Die Reversibilität der Reaktion $\text{Fe(II)} \rightleftharpoons \text{Fe(III)}$ innerhalb der Oktaederschicht nahm somit mit steigender Menge abgegebener metallischer Kationen ab. Die je oxidiertes Fe(II) abgegebene Menge an Fe(III) und Mg^{2+} stand zum Grad der Vermiculitisierung in Beziehung und war bei durch Na umgewandeltem Biotit am größten (0,03 Fe^{3+} und 0,11 Mg^{2+} je oxidiertes Fe(II)) und bei Vermiculit Süd-Afrika am geringsten (nahezu 0). Die Zahl der deprotonierten (O*) und reversiblen Gitterplätze stieg von 0,69 je oxidiertes Fe(II) bei Biotit nach K-Freisetzung auf ungefähr 1,0 bei Vermiculit Süd-Afrika an. Die Zunahme der Verwitterung war gering, da von der Gesamtmenge an Fe + Mg weniger als 1,3 Prozent von jeder der vier Vermiculitsubstanzen abgegeben wurde. Bei der K-Freisetzung aus Biotit gingen etwa 20 mval der Schichtladung je 100 g (bezogen auf bei 300°C behandeltes Material) verloren, während in den wässrigen Suspensionen 51 mmol Fe(II) 100 g^{-1} in Gegenwart und 82 mmol in Abwesenheit von $\text{Na}_2\text{S}_2\text{O}_4$ oxidiert wurden. Da aufeinanderfolgende Reduktions-Oxidations-Reduktions-Behandlungen der K-freien Biotite und glimmerhaltigen Vermiculite keine signifikante Veränderung in der Schichtladung hervorriefen, ($r^2 = 0,04$) wurde geschlossen, daß die Veränderungen der Schichtladung in diesen Mineralen von der Oxidation oder Reduktion des Fe vollständig unabhängig sind.

Резюме — Четыре Na-вермикулита с восстановленными $\text{Na}_2\text{S}_2\text{O}_4$, каждый с пропластками триоктаэдральной слюды подвергали окислению в присутствии H_2O_2 при pH 6,5, а затем вновь восстанавливали $\text{Na}_2\text{S}_2\text{O}_4$ в суспензии при pH 7,5–8,0. Заряд слоев (CEC + K⁺), измеренный при pH 6,5, почти что не изменился ни при окислении октаэдрального Fe (7–92 ммоль/100 г) ни при его восстановлении (6–71 ммоль/100 г). В октаэдральном листе при окислении или восстановлении Fe поддерживается электронейтральность. При окислении Fe(II), электронейтральность сохраняется путем потери протонов октаэдральных групп OH⁻, (a),



и путем выбрасывания (растворение структурных) октаэдральных металлических катионов, (b),



При восстановлении Fe(III), электронейтральность поддерживается репротонацией потерянных протонов (O*, уравнение a). Реакция (b) необратима. Таким образом, обратимость реакции, $\text{Fe(II)} \rightleftharpoons \text{Fe(III)}$, в октаэдральном листе понижается с увеличением количества выброшенных металлических катионов. Количество Fe(III) и Mg^{2+} , выбрасываемых окисленным Fe(II), зависит от степени вермикулитизации, происходящей больше всего в Na-деградированном биотите [0,03 Fe^{3+} и 0,11 Mg^{2+} /окисленный Fe(II)] и меньше всего (почти что нуль) в южно-африканском вермикулите. Количество потерянных протонов (O*) и количество обратимых заложенных повышается от 0,69 в Fe(II) окисленном биотитом с истощенным K до примерно 1,0 в южно-африканском вермикулите. Выветривание почти что было незаметно, так как из общего количества Fe + Mg менее, чем 1,3 процента было выброшено из каждого из четырех вермикулитов. При истощении K из биотита, примерно 20 м-экв заряда слоя на 100 г (базис 300°C) было потеряно, в то время как 51 ммоль Fe(II) на 100 г окислялось в присутствии $\text{Na}_2\text{S}_2\text{O}_4$ в водной суспензии и 82 ммоль при его отсутствии. Так как, последовательная обработка «восстановление-окисление-восстановление» биотита с истощенным K и вермикулитов содержащих слюды не повела к заметным переменам в заряде слоя ($r^2 = 0,04$), заключили, что изменения зарядов слоев совершенно не зависят от окисления или восстановления Fe в этих материалах.