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

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J. A. Veith and M. L. Jackson

For Clays and Clay Minerals

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OF BIOTITIC VERMICULITES

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Abstract--Four Na₂S₂O₄-reduced biotitic Na vermiculites were oxidized with H₂O₂ (pH 6.5) and again reduced with Na₂S₂O₄ (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 to 92 mmoles/100g) or reduced (6 to 71 mmole/100g).

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, $[\text{Fe(II)Mg}_2(\text{OH})_2]^{4+} \rightleftharpoons [\text{Fe(III)Mg}_2\text{OH O}^*]^{4+} + \text{e}^- + \text{H}^+$ (a) and by ejection of octahedral metallic cations, $\{[\text{Fe(II)}]_5\text{Mg}(\text{OH})_4\}^{8+} \longrightarrow \{[\text{Fe(III)}]_4(\text{OH})_4\}^{8+} + 5\text{e}^- + \text{Fe}^{3+} + \text{Mg}^{2+}$ (b). 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

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metallic cations. The amount of Fe(III) and Mg^{2+} ejected per Fe(II) oxidized was related to the degree of vermiculitization, being greatest with Na-degraded biotite (0.03 Fe^{3+} and 0.11 Mg^{2+} 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. Of the total amount of Fe + Mg, less than 1.3% was ejected from 4 biotitic vermiculites. When biotite was K-depleted, about 20 meq of layer charge per 100g was lost, while 51 mmole of Fe(II) per 100g was oxidized in the presence of $\text{Na}_2\text{S}_2\text{O}_4$ and 82 mmoles in its absence. Since sequential reduction-oxidation-reduction treatments of K-depleted biotite and biotitic 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 biotitic vermiculites.

Kurzreferat--Es wurden vier $\text{Na}_2\text{S}_2\text{O}_4$ -reduzierte biotitische Vermiculite mit H_2O_2 (pH 6,5) oxydiert und wieder $\text{Na}_2\text{S}_2\text{O}_4$ -reduziert (pH 7,5-8,0). Die Schichtladung (Austauschkapazität + K^+), die bei pH 6,50 gemessen wurde, blieb unverändert, wenn oktaedrisches Fe oxydiert (zwischen 7 und 92 mmol/100g) oder reduziert (zw. 6 und 71 mmol/100g) wurde. Bei der Fe-Oxydation und Fe-Reduktion erfolgt der Ladungsausgleich innerhalb des Oktaeders: im Falle der Oxydation, durch Deprotonisierung von OH^- -Gruppen, $[\text{Fe(II)Mg}_2(\text{OH})_2]^{4+} \rightleftharpoons [\text{Fe(III)Mg}_2\text{OH O}^*]^{4+} + \text{e}^- + \text{H}^+$ (a), und durch Ausstoss oktaedrischer Metallkationen, $\{[\text{Fe(II)}]_5\text{Mg}(\text{OH})_4\}^{8+} \rightleftharpoons \{[\text{Fe(III)}]_4(\text{OH})_4\}^{8+} + 5\text{e}^- + \text{Fe}^{3+} + \text{Mg}^{2+}$ (b); im Falle der Fe-Reduktion erfolgt der Ladungsausgleich durch Reprotonisierung der O^* -Positionen in Gl. (a). Das Fe(III) in Gl. (b). ist dagegen nicht reduzierbar. Die Reduzierbarkeit von Fe(III) nimmt daher mit der Anzahl ausgestossener Metallkationen ab. Die Zahl ausgestossenem Fe(III) und Mg^{2+} je oxydiertem Fe(II) stand daher in umgekehrtem Verhältnis zum Vermikulitisierungsgrad und war somit am höchsten für Na-Biotit (0,03 Fe(III) und 0,11 Mg je oxidiertem Fe(II)) und am niedrigsten (ca. null) für Na-Vermikulit (Transvaal, S.A.). Die Anzahl reversibler Positionen (O^* , Gl. b) lag für Na-Biotit bei 0,69 je oxydiertem Fe(II) und bei etwa 1,0 für Na-Vermikulit (T.S.A.). Der Ausstoss an Fe + Mg war weniger als 1,3% für alle 4 biotitischen Vermiculite.

Bei der Überführung von Biotit in Na-Biotit (mit NaTPB) nahm die Schichtladung um etwa 20 mval/100g ab. Gleichzeitig, in Anwesenheit von $\text{Na}_2\text{S}_2\text{O}_4$, wurden 51 mmol Fe(II)/100g und, in Abwesenheit von $\text{Na}_2\text{S}_2\text{O}_4$, 82 mmole Fe(II) oxydiert. Wiederholte Red-Ox-Behandlungen von Na-Biotit und Na-Vermikulite verursachten keine signifikante Änderung der Schichtladung ($r^2 = 0,04$). Die Ladungsänderung während des K^+ -Austausches (Transformierung) war deshalb unabhängig von den Red-Ox-Vorgängen des Fe in biotitischen Vermikuliten.

INTRODUCTION

Thermal oxidation of Fe(II) in silicates has been studied extensively by Brindley and Youell (1953), Tsvetkov et al. (1956), Addison et al. (1962), Eugster and Wones (1962), Rimsaite (1956, 1967, 1970), Vedder and Wilkins (1969), and 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 change, 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 charge per Fe(II) oxidized in the structure:

The question of balancing this extra charge when structural iron changes its valency is still open. 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), and Robert (1971) showed that the decrease in layer charge (in meq) of K-depleted trioctahedral micas was always smaller than the amount of Fe(II) oxidized (in mmole). The layer charge of a degraded phlogopite, which contained no Fe, also decreased (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; and 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 with either saturated bromine water and/or H_2O_2 in acid 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 inter-layer complexes of Al and Fe (Jackson 1963a,b; Rich, 1968, Coulter, 1969; Veith and Schwertmann, 1972).

The objectives of this paper are to determine quantitatively for biotite and biotitic vermiculites the extent to which (a) layer charge changes equal Fe oxidized or reduced, and (b) electroneutrality is maintained by de- and reprotonation of structural OH^- groups and (or) ejection of octahedral metallic cations.

MATERIALS AND METHODS

Samples Three biotitic vermiculites, 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 obtained by an exfoliation-floating method (Jackson, 1956).

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

Depletion K was 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 depleted with NaTPB in the presence of sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$).

Red-ox treatments The four K-depleted samples received the following treatments (30 to 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). One third of each sample was retained for further analysis and the remainder was treated for oxidation of structural Fe(II) with 30% phosphorus-free H_2O_2 adjusted to pH 6.50 with NaOAc. One half of each sample was kept separately, the rest being reduced for a second time with $\text{Na}_2\text{S}_2\text{O}_4$ in 1 M NaHCO_3 adjusted to pH 7.5-8.0.

Na saturation The four differently treated samples of each biotitic 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 meq/100g 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 conc. HF.

Layer charge (EC) 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 conc. HF were added while the suspension was being 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% 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 is dissolved when Na₂S₂O₄ is added in the presence

of 2 M Na^+ to prevent Fe^{2+} and Mg^{2+} adsorption. The amounts of ejected Fe(III) and Mg^{2+} were measured by changes in the total analysis, in the case of Mg^{2+} directly after the oxidation treatment and in the case of Fe(III) after reduction following the oxidation.

RESULTS

Changes on depletion of biotite

Insert
Table 1 One of the NaTPB-treated samples was K depleted under reducing conditions by addition of $\text{Na}_2\text{S}_2\text{O}_4$, an additional $\text{Na}_2\text{S}_2\text{O}_4$ treatment being given immediately after depletion (Table 1). Even in the presence of a strong reductant, considerable amount of the structural Fe(II) (51 mmole/100g) was oxidized, apparently reflecting the exclusion of the anion, $\text{S}_2\text{O}_4^{2-}$, from the biotite interlayers and the high lability of Fe(II) in the opened biotite.

The chemical relationships are considerably different, when expressed on the 300°C basis (vs. 100°C) as a result of the difference in H_2O 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/100g 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 Figure 1.

Insert
Fig. 1

The difference in layer charge of about 20 mmole/100g between undepleted and depleted biotite is significant. When layer charge was decreased by 19 meq, 51 mmole of Fe(II) was oxidized. Furthermore, although the change in layer charge between the two depleted samples was only 1 meq (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 biotitic vermiculites

Insert
Fig. 2

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 4 biotitic 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 Figure 2. If the changes in layer charge (ΔLC) were a function of changes in iron valency ($\Delta Fe(II, III)$), 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 $\Delta Fe(II, III)$. Thus the significant decrease in LC of 19 or 20 mmole/100g 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 biotitic vermiculites with little or no CEC change are in agreement with the results of (Roth et al., 1969).

Maintenance of electroneutrality when Fe(II) $\rightarrow$ Fe(III)

Insert
Table 2 Data for 4 depleted layer silicates before (control) and after various red-ox treatments show that layer charge remains constant ($r^2 = 0.04$) when depleted biotitic vermiculites are red-ox-treated (Table 2). Al, mainly in the tetrahedral position, remains unchanged (Table 2). The data are measured at 30°C since (a) differences in hydration are negligible for these depleted samples and (b) it is easier to reproduce values at 30°C 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 octahedral Mg^{2+} and/or Fe(III), except in the case of TSA vermiculite, from which no Mg or Fe was ejected (Tables 2 and 3),

In all cases, equations (3) and (4) account for 31% 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% or more) was apparently balanced by deprotonation of structural OH groups.

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

in which O* represents oxygen from deprotonated structural hydroxyl. This reaction is reversible. When H₂O₂ is used as an oxidant it accepts 2e⁻ from two structural Fe(II) and 2 OH⁻ are formed:

A combination of equations (3-5) with the equation (6) gives the reactions which occur when structural Fe(II) becomes

oxidized by H₂O₂ in the pH range of 6.4 to 7.3:

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 H⁺ coming from structural OH groups (equation 7). When H⁺ = OH⁻, the pH of the suspension is the same before and after oxidation (equation 7).

The number of deprotonated structural

hydroxyls (O^* , eq. 7) per Fe(II) oxidized is calculated from:

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

If Fe(III) ejection occurs, 3 OH^- are formed for each ejected Fe(III); however, at pH 6.4 to 7.3, practically all of it is precipitated as iron hydrous oxide by neutralization of the 3 OH^- produced for each ion ejected (equation 8). The pH is thus unchanged by Fe(II) oxidation in equation (8). If reactions (7) and (8) occur together the number of deprotonated structural OH^- per Fe(II) oxidized is:

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

In the case of Mg^{2+} ejection, however, the pH rises because the 2 OH^- produced for each Mg^{2+} ejected (equation 9) do not react significantly with Mg^{2+} in the pH range of 6.4 to 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:

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

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 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 9).

Insert

Fig. 3

Insert

Table 3

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 as only 7 mmole $\text{Fe(II)}/100\text{g}$ was present.

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%), 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 9) but not in those of WI vermiculite, showing that no ejection of Mg^{2+} had 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 $\text{Fe(III)}/100\text{g}$ 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 $\text{Na}_2\text{S}_2\text{O}_4$ treatments. The values for deprotonated hydroxyls (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 content of biotite in the 4 phyllosilicates used: depleted biotite > WI vermiculite > MT vermiculite > TSA vermiculite. During the weathering transformation of biotite to vermiculite, Fe(II)

becomes oxidized and octahedral metallic cations are ejected. Hence the greatest stability has been reached by the least ferruginous sample, TSA vermiculite. At the same time the reversibility of the oxidized Fe(II) increases in going from the biotite to TSA vermiculite.

DISCUSSION

The gain in positive charges in the biotitic octahedra through iron oxidation appears to be balanced within the octahedra themselves by different proportions of equations (7), (8), and (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 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 depended inversely on the degree of vermiculitization, i.e. on the amount of biotite remaining. Thus, the loss of $\text{Mg}^{2+} + \text{Fe(III)}$ was greatest for H_2O_2 -treated Na biotite and least for H_2O_2 -treated TSA vermiculite (Table 3). The total amount of ejected $\text{Mg}^{2+} + \text{Fe(III)}$ was less than 1.3% of the total structural $\text{Fe} + \text{Mg}$ in all samples, a much lower value than that commonly reported for other biotites and for weathered soil biotites. The greater loss of octahedral metallic cations under natural conditions could be caused 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 neutral conditions (Table 3) as well as under more acid conditions (Farmer *et al.*, 1971; Gilkes *et al.*, 1972). A deficit in structural $\text{OH}^- + \text{F}^-$ (< 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. These 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 (review by Foster, 1963).

When structural Fe(III) is reduced, only the deprotonated octahedral positions (equations 3 and 7) can be reprotonated. The calculated reversibility (Table 3) is 69% for depleted biotite, 80% for Na-vermiculite (MT) and about 100% 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 $O^*/100g$) decreases from biotite to Na vermiculite (TSA), the amount of Fe(III) reduced decreases (Tables 2 and 3).

Contrary to the above findings, a change in LC when structural Fe changes its valency, in accord with the Gruner (1936) 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 $\text{Al(OH)}_{1.5}\text{Cl}_{1.5}$ 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 NaClO treatment, contrary to the measurements made in the present study and those of Roth et al. (1968, 1969). Even after 24 hours of $\text{Na}_2\text{S}_2\text{O}_4$ treatment of some of our samples, only about 30% 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 H₂O, 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 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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Fig. 1. Weight loss of biotite and Na depleted biotite as a function of temperature ($10^{\circ}\text{C}/\text{min}$).

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

Fig. 3. Function between pH and time after addition of H₂O₂ to Fe(II)-containing samples.

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

Treatment	Weight loss vs. 30°C			K present		LC*		ΔLC		Structural cations			
	100°C	300°C	900°C	100°C	300°C	100°C	300°C	100°C	300°C	Fe(II)	Fe(III)	ΔFe(III)	Al
	----- % -----							mmole/100g		----- 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.

Table 2. Analyses of untreated and red-ox-treated biotitic vermiculites

Sample	K	Treatm.	LC (Na+K)	Al _t [*]	Mg _t	ΔMg (loss)	Fe _t	ΔFe (loss)	Fe(II) -----	ΔFe(II) structural	ΔFe(III) -----
							mmole/100g				
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. = Na₂S₂O₄; ox. = H₂O₂.

[§]Free Fe₂O₃·xH₂O.

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

*Direct measurement of decrease in structural Mg or Fe.

†Indirect measurement as OH^- formed in solution (equation 9).

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