

## DEFERRATION EFFECT ON STRUCTURAL FERROUS–FERRIC IRON RATIO AND CEC OF VERMICULITES AND SOILS

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**Abstract**—Deferration by reduction of free  $\text{Fe}_2\text{O}_3$  with  $\text{Na}_2\text{S}_2\text{O}_4$  in the presence of Na citrate and  $\text{NaHCO}_3$  caused a change in valence state of 10 to 35 per cent of the total structural iron in micaceous vermiculites, soils, nontronite, and muscovite. An increase in  $\text{Fe}^{2+}$  on deferration was accompanied by an equivalent decrease in  $\text{Fe}^{3+}$ . Subsequent treatment with  $\text{H}_2\text{O}_2$  reoxidized the structural  $\text{Fe}^{2+}$  previously formed.

Sesquioxide coatings on micaceous vermiculites were examined electron microscopically. These coatings were composed predominantly of  $\text{Fe}_2\text{O}_3$  with approximately 10 per cent by weight of  $\text{Al}_2\text{O}_3$  and small amounts of  $\text{SiO}_2$ , as determined by chemical analysis of the deferration extracts.

The cation exchange capacity (CEC) increased 10–60 per cent as a result of deferration of micaceous vermiculites and soils. Treatment of the deferrated sample with  $\text{H}_2\text{O}_2$  restored the  $\text{Fe}^{3+}$  content to approximately the original value but the CEC was not affected. Consequently, the increase in CEC on deferration was attributed to the removal of the positively charged sesquioxide coating. The reversible change in valence of structural iron without an equivalent change in CEC was attributed to deprotonation-protonation of the structure ( $\text{OH}^- \rightleftharpoons \text{O}^{2-}$ ) simultaneous with the oxidation-reduction of iron ( $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$ ) in the phyllosilicate layer.

### INTRODUCTION

SESQUIOXIDES commonly occur as products of the chemical weathering of various minerals in soils and may take the form of discrete particles (Deshpande *et al.*, 1968; Greenland *et al.*, 1968) as well as coatings on silicate particles (Davidtz and Sumner, 1965; Follett, 1965; de Villiers and Jackson, 1967; Roth *et al.*, 1967, 1968). The location (Lutz, 1936; Sumner, 1963; Rich, 1968) and composition (Clark *et al.*, 1963; Tweneboah *et al.*, 1967; Roth *et al.*, 1968) of the sesquioxides have been shown to influence the physicochemical properties significantly. Aggregation and cation exchange capacity (CEC) of soils and their constituent minerals are affected, for example. The increase in CEC of approximately 30 per cent in a micaceous vermiculite from Colorado was attributed to the removal of a positively charged sesquioxide coating by  $\text{Na}_2\text{S}_2\text{O}_4$  treatment (Roth *et al.*, 1968). The increase was not attributable to the increase in structural  $\text{Fe}^{2+}$  content, since the latter was reversible with  $\text{H}_2\text{O}_2$ .

The purpose of this paper is to report for a repre-

sentative range of micaceous vermiculites and soils (a) the changes in surface micromorphology resulting from deferration with  $\text{Na}_2\text{S}_2\text{O}_4$  and treatment with  $\text{H}_2\text{O}_2$ , (b) the changes in structural ferrous and ferric iron as a function of reduction with  $\text{Na}_2\text{S}_2\text{O}_4$  and oxidation with  $\text{H}_2\text{O}_2$ , and (c) the changes in CEC together with constituents dissolved as a result of these deferration and oxidation treatments.

### MATERIALS

Micaceous vermiculites were obtained from Transvaal, South Africa; Grouse Creek, UT; and Libby, MT (Wards Scientific Establishment, Rochester, NY). Micaceous vermiculites were also collected from a weathered granite (Wausau, WI), and a micaceous vermiculitic saprolite from the somewhat poorly drained Brill soil (Menominee County, WI). Micaceous vermiculitic soils included were: Sharkey clay soil from the University of Missouri, Delta Research Experiment Station Farm (Portageville, MO); and White Mountain soil collected by W. E. Wildman from a flat crest of a ridge one mile southeast of White Mountain Peak (Mono County, CA). Nontronite (Wards, Clay Mineral Standard H-33a, Garfield, WA) and muscovite (source unknown) served as controls.

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## METHODS

### *Sample preparation*

The vermiculites from Transvaal, Utah, Montana, and Wisconsin were purified by an exfoliation-flotation procedure (Jackson, 1956) in which 200 g of the vermiculite was placed in a beaker, 400 ml of 15% phosphorus-free  $\text{H}_2\text{O}_2$  added and the suspension heated to about  $80^\circ\text{C}$  on a steamplate. The exfoliated vermiculite that floated to the surface was decanted and placed in 400 ml of 15%  $\text{H}_2\text{O}_2$  and heated to  $80^\circ\text{C}$  a second time. The exfoliated vermiculite that floated to the surface in this second  $\text{H}_2\text{O}_2$  treatment was decanted into 100-ml glass centrifuge tubes, treated with 0.5 N NaCl solution and triturated (Jackson, 1956). The samples were washed with 0.5 N NaCl and triturated a total of five times before size fractionation.

The micaceous saprolite and soils were treated with  $\text{H}_2\text{O}_2$  overnight at  $75\text{--}80^\circ\text{C}$  before size fractionation. The nontronite sample was dispersed ultrasonically in the presence of 0.5 N NaCl before fractionation. The muscovite sample was mechanically ground in an agate mortar and then subjected to fractionation. The samples were washed twice with 0.5 N NaCl followed by sieving to obtain the size fractions  $> 1000$ ,  $1000\text{--}105$ ,  $500\text{--}250$ ,  $250\text{--}105$ , and  $105\text{--}46\ \mu$  in diameter. The size fractions  $46\text{--}2$ ,  $2\text{--}0.2$ , and  $< 2\ \mu$  were obtained by centrifugation. The  $< 2\ \mu$  samples were dialyzed until free of excess NaCl and the other fractions were washed with  $\text{H}_2\text{O}$  until free of excess salt. The vermiculite and mica present in the  $500\text{--}250$ ,  $250\text{--}105$ , and  $105\text{--}50\ \mu$  fractions of the saprolite and the  $250\text{--}105\ \mu$  fraction of the soil from White Mountain were selectively concentrated by air bubbling through the sediment in contact with water and collection of the suspended material.

### *Ferrous and total iron determination*

The ferrous and total iron contents of the samples after various treatments were determined by an improved method (Roth *et al.*, 1968). Approximately 30 mg of the weighed sample was dissolved in 6 ml of 3.6 N  $\text{H}_2\text{SO}_4$  and 1 ml of 48% HF in the presence of 200 mg of 1,10-phenanthroline monohydrate (orthophenanthroline) by digestion in a boiling water bath for 30 min. The excess HF was complexed with 10 ml of 5% boric acid. The solution was transferred to a 100-ml volumetric flask, brought to volume with freshly boiled water, and mixed. The ferrous iron content was determined immediately by transference of a 10-ml aliquot to a 100-ml volumetric flask which contained 4 ml of 10% Na citrate dihydrate, the solution being diluted to volume with freshly boiled water and mixed. The absorbance was determined at  $5100\ \text{\AA}$  after 30–60 minutes.

The total iron content of the sample was determined in a 5-ml aliquot of the first solution prepared for the ferrous iron determination. The aliquot was transferred to a 100-ml volumetric flask which contained 2 ml of 10% hydroxylamine hydrochloride. Following the addition of 2 ml of 10% Na citrate dihydrate, the solution was diluted to volume with water and mixed. The absorbance was determined at  $5100\ \text{\AA}$  after 24 hr. The standard curve was prepared with appropriate aliquots of a 500-ppm  $\text{Fe}^{2+}$  solution prepared from  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ . The aliquots were taken through the digestion and chromogenic procedure.

### *Deferration treatment*

Approximately 500 mg of the previously undried, fractionated sample was Ca saturated by washing three times with 0.5 N  $\text{CaCl}_2$ . The excess salts were removed by successive washing once with  $\text{H}_2\text{O}$ , once with 50% methanol, once with 100% methanol and twice with acetone before the sample was dried. Approximately 50 mg of the Ca saturated sample was transferred to a weighed glass test tube and further dried at  $110^\circ\text{C}$  overnight and weighed. The latter sample was washed twice with 0.5 N NaCl to remove a large portion of the exchangeable Ca. The quantities of reagents in the  $\text{Na}_2\text{S}_2\text{O}_4\text{--Na citrate--NaHCO}_3$  method (Jackson, 1956) were decreased to compensate for the smaller sample size. The Na saturated sample was treated with 8 ml of the combined Na citrate– $\text{NaHCO}_3$  buffer and heated in a water bath to  $75\text{--}80^\circ\text{C}$ . 50 mg of solid  $\text{Na}_2\text{S}_2\text{O}_4$  was added to the suspension and the suspension stirred every 30 sec. for 5 min while still being heated in the water bath. A second portion of  $\text{Na}_2\text{S}_2\text{O}_4$  was added and the stirring sequence repeated. The suspension was centrifuged and the supernatant solution siphoned into a 50-ml volumetric flask. The sample was treated with a second 8-ml portion of Na citrate– $\text{NaHCO}_3$  buffer, heated, and a third portion of  $\text{Na}_2\text{S}_2\text{O}_4$  was added. The suspension was centrifuged and the supernatant siphoned into the same 50-ml volumetric flask. The sample was washed twice with 8 ml of 0.5 N NaCl and the supernatants added to the same 50-ml flask. The solution was made to volume and transferred to a polyethylene bottle and later used for Fe and Al determinations. The sample was deferrated in a plastic test tube when the extract was to be used for Si determination. The sample was Ca saturated by washing three times with 0.5 N  $\text{CaCl}_2$ . The excess salt was removed by the sequence of water-methanol-acetone washings used above. The sample was dried at  $110^\circ\text{C}$  overnight and weighed to determine the gravimetric weight loss. The above procedure will later be referred to as the first deferration

treatment. The second and third deferration treatment was accomplished by repeating the above procedure a second and third time on the same sample.

The Fe released by the deferration treatments was determined by the 1,10-phenanthroline method (Jackson, 1956). The Al and Si released was determined by the aluminon and molybdosilicic blue method, respectively (Weaver *et al.*, 1968).

#### *Deferration-oxidation treatment*

Approximately 30 mg of the weighed sample was carried through three deferration treatments before being washed once with 0.5 N NaCl and once with 0.5 N NaOAc of pH 5.0. Five milliliters of 0.5 N NaOAc of pH 5.0 and 1 ml of 30% H<sub>2</sub>O<sub>2</sub> were added to the sample and the resulting suspension was placed in a water bath at 75–80°C for 3–4 hr. The sample was washed a total of three times with 0.5 N NaCl and transferred to a 100-ml polyethylene test tube for Fe<sup>2+</sup> and total Fe determinations.

#### *CEC determination*

The flow sheet (Fig. 1) outlines the method for the determination of the cation exchange capacity (CEC). Since Ca was used as the exchangeable cation, the CEC is referred to as CaEC. Samples for CaEC determination, freshly fractionated following exfoliation, were given various pretreatments but not dried at any time until the point indicated. Sodium salts were not used in excess of 0.5 N to avoid the release of K from mica (de Villiers and Jackson, 1967) which would have freshly formed some vermiculite from the biotite present in the samples. Regardless of the various pretreatments, the samples were washed once with 0.5 N NaOAc of pH 7.0 to return the pH of the samples to approximately seven prior to CEC determination. All analytical results tabulated are the averages of duplicate determinations.

#### *Electron microscopy*

Platinum-carbon replicas (Roth *et al.*, 1967) of the samples which had been dispersed in water and dried on glass for replication were used to investigate possible changes of surface and particle morphology resulting from the various treatments. Each photograph is representative of three identically prepared specimens examined.

## RESULTS AND DISCUSSION

### *Iron oxide, alumina, and silica released by deferration treatment*

Chemical analysis of the extract from the deferration treatment revealed that the amount of Fe<sub>2</sub>O<sub>3</sub> released generally decreased with subsequent

Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>–Na citrate–NaHCO<sub>3</sub> treatments (Table 1). The nontronite and muscovite samples were exceptional in that approximately the same amount of Fe<sub>2</sub>O<sub>3</sub> was released with each treatment. The iron released from the nontronite was attributed to a small amount of decomposition of the nontronite and its ferruginous chlorite impurity (Alexiades and Jackson, 1967) by the deferration treatment. Rather high amounts of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> were also released from nontronite (Table 1).

There was a tendency for the amount of Fe<sub>2</sub>O<sub>3</sub> released to increase in the smaller particle size fractions of the vermiculites and soils. The micaceous saprolite was an exception to this trend, the percentage of Fe<sub>2</sub>O<sub>3</sub> released becoming less with a decrease in particle size.

The amounts of Al<sub>2</sub>O<sub>3</sub> released by the deferration treatments followed the same general pattern as the amounts of Fe<sub>2</sub>O<sub>3</sub> released (Table 1). The percentage of Al<sub>2</sub>O<sub>3</sub> released by the deferration treatment was generally less than the percentage of Fe<sub>2</sub>O<sub>3</sub> released, with the exception of muscovite for which the reverse was true. The amount of Al<sub>2</sub>O<sub>3</sub> released by the second and third deferration treatments was less than that released by the first deferration treatment.

The change in percentage of SiO<sub>2</sub> released in the several deferration treatments was small relative to the change in percentage of Fe<sub>2</sub>O<sub>3</sub> released (Table 1). This may indicate that each deferration treatment partially desilicated the samples involved in this study to the extent of generally less than 1 per cent by weight. An exception was the nontronite, with which a significant decomposition of the sample is evident. The extent to which the decomposition of the nontronite is attributable to the ultrasonic treatment is not known. The amount of SiO<sub>2</sub> released by three deferration treatments of all samples appeared to be only poorly correlated with the percentage of Fe<sub>2</sub>O<sub>3</sub> and/or Al<sub>2</sub>O<sub>3</sub> released (Table 1).

There was a high correlation ( $r = 0.97$ ) between the percentage of Al<sub>2</sub>O<sub>3</sub> and the percentage of Fe<sub>2</sub>O<sub>3</sub> released by the three deferration treatments from all of the vermiculite size fraction and from the  $> 2 \mu$  size fraction of the saprolite and soils (Fig. 2). The least square regression equation (Fig. 2) for this population of samples showed that the amount of Al<sub>2</sub>O<sub>3</sub> released was approximately ten per cent of the Fe<sub>2</sub>O<sub>3</sub> released.

A large amount of Al<sub>2</sub>O<sub>3</sub> relative to Fe<sub>2</sub>O<sub>3</sub> was released from the  $< 2 \mu$  fractions of the saprolite, soils, and nontronite and from 2 to 0.2  $\mu$  muscovite. These samples appeared to constitute a separate population as shown by their position well above the least square regression line for a plot of the amount of Al<sub>2</sub>O<sub>3</sub> vs. Fe<sub>2</sub>O<sub>3</sub> released by three

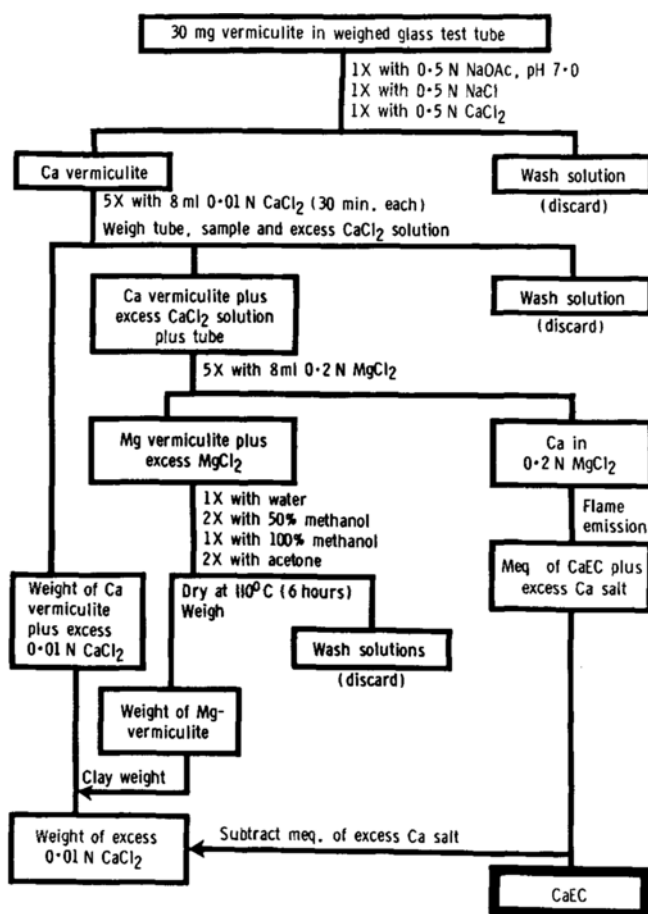


Fig. 1. Flow sheet for the determination of cation exchange capacity (CaEC) of various size fractions of vermiculites and soils.

deferration treatments of vermiculites and  $> 2 \mu$  saprolite and soils (Fig. 2). This release of relatively larger amounts of  $Al_2O_3$  by  $Na_2S_2O_4$ -Na citrate- $NaHCO_3$  treatment of  $< 2 \mu$  fractions might well be characteristic of naturally occurring clay sized samples, which may have a somewhat different mineralogical composition.

#### Water content of sesquioxide coatings

The sum of the oxides,  $Fe_2O_3$ ,  $Al_2O_3$ , and  $SiO_2$ , extracted by the  $Na_2S_2O_4$ -Na citrate- $NaHCO_3$  treatments of vermiculites, saprolite, soils, nontronite, and muscovite was always less than the gravimetric weight loss resulting from these treatments (Table 1). This difference has been attributed to loss of water that had been associated with the sesquioxides released by the deferration treatment (Roth *et al.*, 1968). This difference would also in-

clude any non-determined material that was associated with the sesquioxides and any sample material that was lost during the deferration treatments. A plot of this difference, that is, the percentage gravimetric weight loss minus the percentage of total oxides released, versus the percentage of total oxides released, revealed a strong correlation for the vermiculites,  $r = 0.96$  (Fig. 3). A much lower correlation was obtained for the saprolite, soils, nontronite, and muscovite,  $r = 0.49$ . The Y-intercept value, 0.78 per cent for the vermiculites, gives an estimate of the average undetermined constituents released and mechanical sample loss during the deferration treatments (Fig. 3). The least square regression equation,  $Y = 0.78 + 0.35X$ , for this population of vermiculite samples indicated that the total oxides released by the deferration treatments may have contained approximately

Table 1. Percentage of Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> released by Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>-Na citrate-NaHCO<sub>3</sub> treatments

Size fraction (μ)	Weight per cent of untreated sample												Total of oxides released	Total gravimetric weight loss
	Fe <sub>2</sub> O <sub>3</sub>			Al <sub>2</sub> O <sub>3</sub>			SiO <sub>2</sub>			Total of oxides released	Total gravimetric weight loss			
	Deferration			Deferration			Deferration							
First	second	third	First	second	third	First	second	third	First	second	third	Total of oxides released	Total gravimetric weight loss	
1000-105	0.1	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.3	1.5
105-46	0.1	0.0	0.1	0.0	0.1	0.0	0.1	0.0	0.1	0.0	0.0	0.0	0.4	0.9
46-2	0.2	0.1	0.1	0.0	0.0	0.0	0.1	0.1	0.1	0.1	0.1	0.1	0.7	1.4
< 2	0.6	0.2	0.2	0.1	0.1	0.1	0.5	0.4	0.4	0.4	0.4	0.4	2.6	5.9
> 1000	1.0	0.3	0.2	0.1	0.1	0.1	0.1	0.3	0.2	0.3	0.2	0.2	2.3	3.6
1000-105	0.7	0.1	0.1	0.1	0.0	0.0	0.0	0.2	0.1	0.2	0.1	0.1	1.3	3.2
105-46	0.6	0.2	0.1	0.1	0.1	0.1	0.2	0.3	0.2	0.3	0.2	0.2	1.9	3.0
46-2	1.7	0.4	0.2	0.1	0.1	0.1	0.3	0.6	0.4	0.6	0.4	0.4	3.9	5.2
< 2	3.4	1.3	0.8	0.3	0.2	0.2	0.2	2.0	1.5	2.0	1.5	1.5	9.8	14.7
> 1000	0.1	0.1	0.1	0.0	0.0	0.0	0.1	0.1	0.1	0.1	0.1	0.1	0.6	1.7
1000-105	0.2	0.1	0.1	0.1	0.0	0.0	0.2	0.1	0.1	0.1	0.1	0.1	0.9	2.1
105-46	0.4	0.2	0.1	0.1	0.1	0.0	0.3	0.2	0.2	0.2	0.2	0.2	1.6	2.4
46-2	0.6	0.2	0.2	0.1	0.1	0.0	0.5	0.3	0.2	0.3	0.2	0.2	2.2	3.3
< 2	1.2	0.5	0.3	0.2	0.1	0.1	0.9	0.8	0.4	0.8	0.4	0.4	4.5	6.5
1000-105	6.4	0.5	0.3	0.5	0.2	0.1	0.4	0.3	0.1	0.3	0.1	0.1	8.8	12.7
105-46	7.5	0.5	0.4	0.5	0.1	0.1	0.5	0.3	0.2	0.3	0.2	0.2	10.1	14.7
46-2	11.1	0.6	0.4	0.8	0.2	0.2	0.7	0.2	0.2	0.2	0.2	0.2	14.4	19.7
< 2	13.6	0.8	0.6	1.1	0.4	0.3	1.1	0.7	0.7	0.7	0.7	0.7	19.3	26.6
500-250	16.3	0.4	0.2	1.4	0.1	0.1	0.4	0.1	0.1	0.1	0.1	0.1	19.1	25.9
250-105	14.8	0.3	0.1	1.3	0.1	0.1	0.4	0.1	0.1	0.1	0.1	0.1	17.3	21.0
105-50	10.4	0.2	0.1	1.1	0.1	0.1	0.3	0.1	0.1	0.1	0.1	0.1	12.5	17.7
50-2	1.0	0.1	0.1	0.3	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.1	2.2	4.6
< 2	2.1	0.2	0.3	0.9	0.6	0.6	0.3	0.6	0.6	0.6	0.7	0.7	6.3	11.6
250-105	1.3	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	2.4	6.2
50-2	0.9	0.1	0.1	0.2	0.1	0.1	0.3	0.2	0.2	0.2	0.2	0.2	2.2	4.9
< 2	6.4	0.4	0.3	1.2	0.6	0.5	1.3	0.9	0.9	0.9	0.8	0.8	12.4	18.9
50-2	1.0	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.2	0.1	0.1	2.0	7.9
< 2	2.1	0.5	0.4	0.6	0.4	0.3	1.4	1.0	1.0	1.0	0.8	0.8	7.5	13.4
< 2	2.9	2.7	2.7	0.4	0.5	0.5	2.9	3.5	3.5	3.5	3.9	3.9	20.0	25.6
2-0-2	0.2	0.1	0.2	0.9	0.5	0.3	0.8	0.4	0.4	0.4	0.2	0.2	3.6	8.2

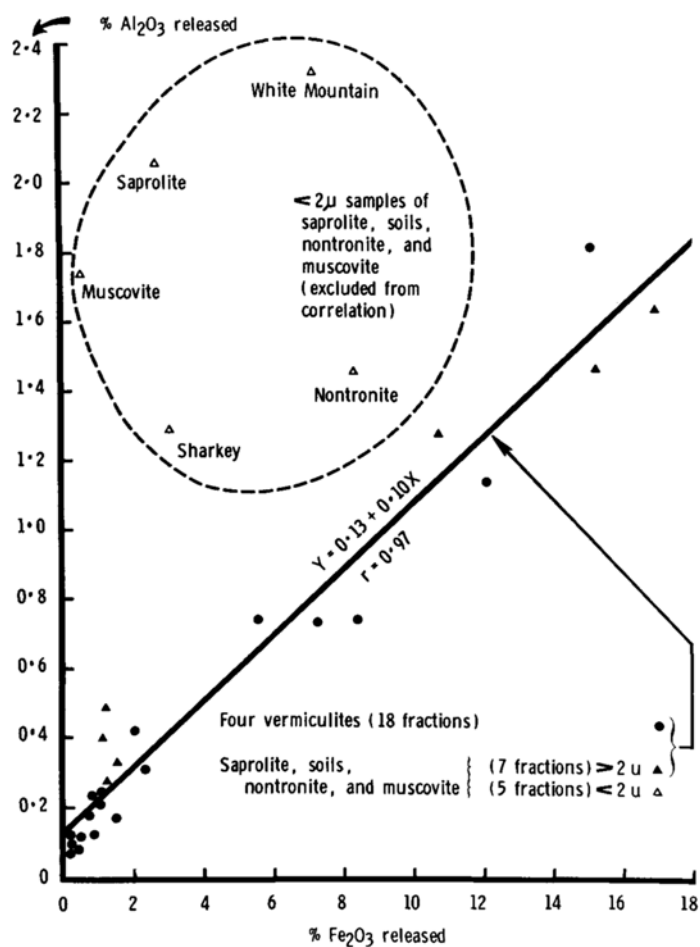


Fig. 2. Plot of  $\text{Al}_2\text{O}_3$  vs.  $\text{Fe}_2\text{O}_3$  released by a total of three  $\text{Na}_2\text{S}_2\text{O}_4$ - $\text{Na}$  citrate- $\text{NaHCO}_3$  treatments of vermiculites, sapolite, soils, nontronite and muscovite.

35 per cent by weight of water which was stable at a temperature of  $110^\circ\text{C}$ . The amorphous hydrated oxide gels present in tropical soils may contain as much as 300 per cent water under field conditions (Sherman *et al.*, 1964).

#### *Micromorphology of particle surfaces*

Electron microscopic examination of platinum-carbon surface replicas of thirteen of the deferrated samples, dried from water suspensions on glass, revealed small particulate material with high relief on the particle surfaces (Figs. 4b and 4e). Such material was not present on the particles given  $\text{H}_2\text{O}_2$  treatment alone (Figs. 4a and 4d). This particulate material appeared on samples that released very small amounts of  $\text{Fe}_2\text{O}_3$  on deferration (105-46  $\mu$  vermiculite from Transvaal; Table

1; Fig. 4d). Subsequent treatment with  $\text{H}_2\text{O}_2$  in 0.5 N  $\text{NaOAc}$  of pH 5.0 removed the particulate material (Figs. 4c and 4f). Analysis of the extract from the subsequent  $\text{H}_2\text{O}_2$  treatment revealed just a trace of iron (equivalent to  $< 1\text{-mole Fe}/100\text{g}$  of sample). Analysis for total sulfur (Chaudhry and Cornfield, 1966) in some of the deferrated samples which showed the particulate material after deferration revealed no significant amount of sulfur above that found in the original oxidized sample. The material present on particle surfaces of some deferrated samples was thought to be ferrous sulfide, but because the quantity of this material was very small, it was not possible to confirm its chemical composition. This material was probably present only on the outside surfaces of the particles, since its presence on the extensive interlayer



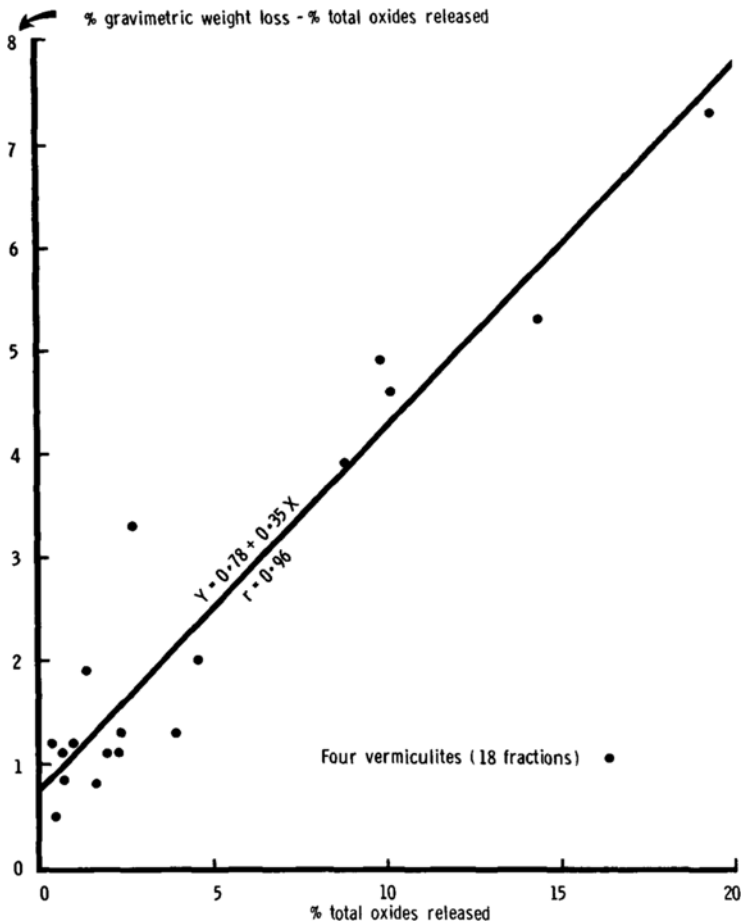


Fig. 3. Plot of the difference between the gravimetric weight loss and total oxides released versus the total oxides released by three deferration treatments of vermiculites.

surfaces would have been expected to bring the quantities into range of the analytical methods.

Electron micrographs of platinum-carbon surface replicas of vermiculite samples revealed colloidal material on the surface of the particles that was removed by treatment with  $\text{Na}_2\text{S}_2\text{O}_4$ -Na citrate- $\text{NaHCO}_3$  (Fig. 5), a result similar in principle to the cleaning effects noted with Colorado vermiculite (Roth *et al.*, 1967, 1968). With the Utah vermiculite more colloidal coating material appears to have been removed from around the particles of the  $< 2 \mu$  fraction (Figs. 5c and 5d; arrows on Fig. 5d point to vermiculite particles on a glass substrate) than from the surface of  $> 1000 \mu$  particles (Figs. 5a and 5b). Little coating material was present on the  $1000$ - $105 \mu$  fraction of Montana vermiculite to be removed by the treatment (Figs. 5e and 5f). The chemical analyses of the deferra-

tion extract of these samples (Table 1) concur in that the percentage of total oxides released from these fractions of the Utah and Montana vermiculites were 9.8, 2.3 and 0.9 per cent, respectively.

The coatings on the surface of the micaceous vermiculite particles (such as Fig. 4a) showed no evidence of crystallinity by X-ray diffraction analysis. The crystallization of the iron oxide in the coating may have been prevented by the presence of approximately 10%  $\text{Al}_2\text{O}_3$  by weight. This interpretation is analogous to that with 10-20 per cent of the iron in lepidocrocite replaced by aluminum, which caused a marked decrease in crystallinity to X-rays (de Villiers and van Rooyen, 1967). These workers also pointed out that an aluminum-substituted, lepidocrocite-like compound may occur in oxisols without being sufficiently crystalline for detection by X-ray diffraction techniques.

The presence of organic matter may also affect the crystallization of iron oxides (Schwertmann, 1966), and the ionic environment, particularly the presence of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , may direct the crystallization toward hematite (Schellmann, 1959; Taylor and Graley, 1967).

A scrolling phenomenon on vermiculite surfaces has been reported (Raman and Jackson, 1964). The tube-like structures on the cleavage of deferrated Utah vermiculite (arrows, Fig. 5b) may be scrolls. The latter structures have high shadows and occur at the margin of the layers on the original electron micrograph, whereas the scrolling reported by Roth *et al.* (1967) appears to result from tearing of the layers.

A considerable amount of the colloidal coating material present on the surface of micaceous particles from the White Mountain soil was removed by the deferration treatment (Figs. 6a and 6b). Lifting of layers frequently produces a blister-like configuration (arrows, Fig. 6b) on micaceous vermiculite particles from the White Mountain soil. Most of the amorphous material (not unlike the coatings on the vermiculites) present around the  $< 2 \mu$  particles of the Sharkey clay soil was removed by the  $\text{Na}_2\text{S}_2\text{O}_4$ -Na citrate- $\text{NaHCO}_3$  treatment (Figs. 6c and 6d). Electron micrographs of replicas of the nontronite sample before and after deferration revealed little change in the typical morphology of the clay particles (Figs. 6e and 6f).

#### *Structural iron valence changes*

The structural iron content of Transvaal and Montana vermiculites was essentially constant between various particle size fractions (Table 2). The structural iron content increased in the  $< 2 \mu$  size fraction of Utah vermiculite, whereas there was a trend for it to decrease with smaller size fractions in the Wisconsin vermiculite. The structural iron contents were considerably higher in the  $> 50 \mu$  size fractions from the micaceous saprolite and the White Mountain soil (Table 2). The fractions from the latter two sources were selectively concentrated by the air elutriation technique.

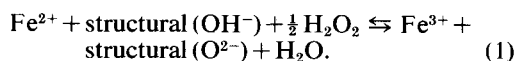
Approximately 20 per cent of the total structural iron in the oxidized Transvaal, Utah, and Montana vermiculites and 10 per cent in the oxidized Wisconsin vermiculite was in the form of ferrous iron (Table 2). The ferrous iron increased to 30-60 per cent of the total structural iron in the deferrated Transvaal, Utah, and Montana vermiculites and a larger relative amount of iron reduction occurred in the smaller size fractions. The ferrous iron in the deferrated Wisconsin vermiculite increased to approximately 45 per cent of the total structural iron. The structural  $\text{Fe}^{2+}$  content of the deferrated sample was returned to approximately that of the

oxidized sample by treatment of the deferrated sample with  $\text{H}_2\text{O}_2$  at pH 5. Similar trends in the change in valence of structural iron occurred in the saprolite, soils, nontronite, and muscovite samples (Table 2).

The actual content of structural  $\text{Fe}^{2+}$  in variously treated samples might have been affected by sulfur compounds or by residual  $\text{H}_2\text{O}_2$ . Various sulfur compounds, if present, might have reduced some  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  during the  $\text{Fe}^{2+}$  determination. Residual  $\text{H}_2\text{O}_2$ , if present, might have oxidized some  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  during the  $\text{Fe}^{2+}$  determination. In a test, the amount of structural  $\text{Fe}^{2+}$  in an oxidized sample to which colloidal sulfur (prepared from  $\text{Na}_2\text{S}_2\text{O}_4$  in water) was added, remained essentially equal to that found in the same sample without colloidal sulfur. In a further test with samples after oxidation with  $\text{H}_2\text{O}_2$ , the amounts of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  were identical in both the samples washed but undried and those dried at  $110^\circ\text{C}$  (to remove traces of  $\text{H}_2\text{O}_2$ ). Since no apparent increase in total sulfur was evident in the deferrated samples (unpublished data), and since no evidence was found for residual  $\text{H}_2\text{O}_2$  in the oxidized and the deferrated-oxidized sample, it was concluded that the reciprocal changes in the structural  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  contents on deferration by  $\text{Na}_2\text{S}_2\text{O}_4$  and oxidation by  $\text{H}_2\text{O}_2$  were real.

#### *Cation exchange capacity variations*

Although  $\text{H}_2\text{O}_2$  treatment of the deferrated samples reoxidized most of the structural  $\text{Fe}^{2+}$  that had been reduced by the  $\text{Na}_2\text{S}_2\text{O}_4$ -Na citrate- $\text{NaHCO}_3$  treatments (Table 2), the CEC of the deferrated samples was not significantly affected (Table 3). The reversible change in valence of structural iron without an equivalent change in the CEC may involve the simultaneous oxidation (or reduction) of structural  $\text{Fe}^{2+}$  (or  $\text{Fe}^{3+}$ ) and deprotonation (or protonation) of structural hydroxyls as represented in the following equation:



The structural  $\text{O}^{2-}$  or  $\text{OH}^-$  formed, serves to maintain electrostatic neutrality as the balance between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  varies. Other investigators of the oxidation of structural  $\text{Fe}^{2+}$  in hydroxylated silicates have suggested similar mechanisms for maintaining charge balance. Two studies involved heating chamosite in the presence of oxygen, with conclusions drawn from the weight loss on heating (Brindley and Youell, 1953) or from the amount of  $\text{H}_2\text{O}$  formed (Addison and Sharp, 1963). Another investigation involved the artificial weathering of micas, with conclusions drawn from the decrease



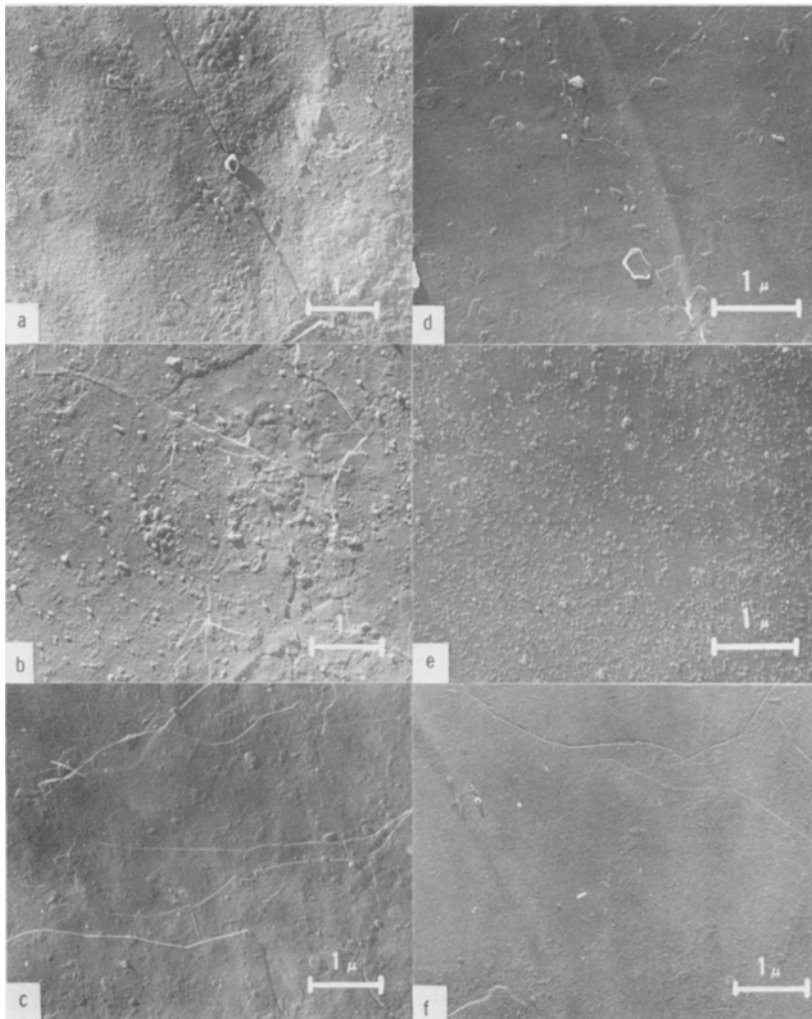


Fig. 4. Electron micrographs of platinum-carbon surface replicas of micaceous vermiculites of approximately  $100\text{--}50\ \mu$  particle size: (a) Colloidal material on micaceous surface of  $\text{H}_2\text{O}_2$  treated saprolite; (b) Particulate material on micaceous surface after deferration treatment of saprolite; (c) Relatively smooth surface of micaceous saprolite after deferration and subsequent  $\text{H}_2\text{O}_2\text{--}0.5\ \text{N NaOAc}$  (pH 5) treatments; (d) Surface morphology of Transvaal vermiculite treated only with  $\text{H}_2\text{O}_2$ ; (e) Particulate material on the surface of Transvaal vermiculite arising from the deferration treatment; (f) Relatively smooth surface of Transvaal vermiculite after deferration and subsequent  $\text{H}_2\text{O}_2\text{--}0.5\ \text{N NaOAc}$  (pH 5) treatment.

[Facing page 260]

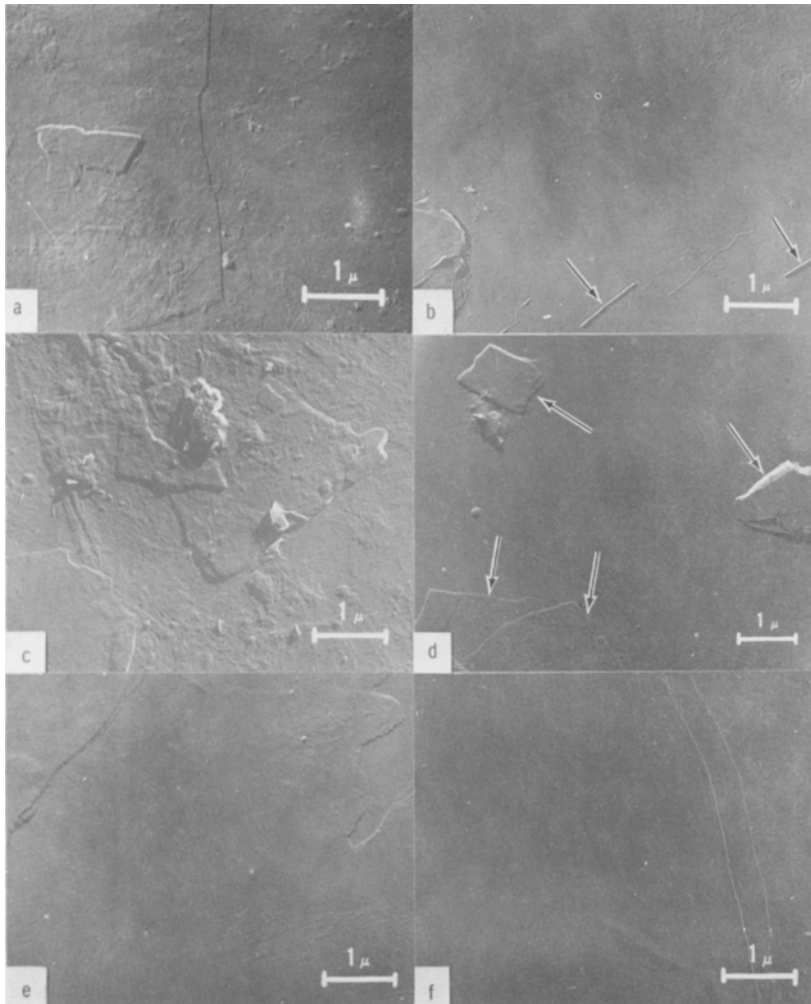


Fig. 5. Electron micrographs of platinum-carbon surface replicas of oxidized vermiculites which were smoother after subsequent deferration: (a) Oxidized Utah vermiculite,  $> 1000 \mu$ ; (b) Deferrated Utah vermiculite,  $> 1000 \mu$ . The arrows point out scrolls of the surface layer; (c) Oxidized Utah vermiculite,  $< 2 \mu$ ; (d) Deferrated Utah vermiculite,  $< 2 \mu$ . The arrows point out vermiculite particles that are present on a glass substrate; (e) Oxidized Montana vermiculite,  $1000-105 \mu$ ; (f) Deferrated Montana vermiculite,  $1000-105 \mu$ .

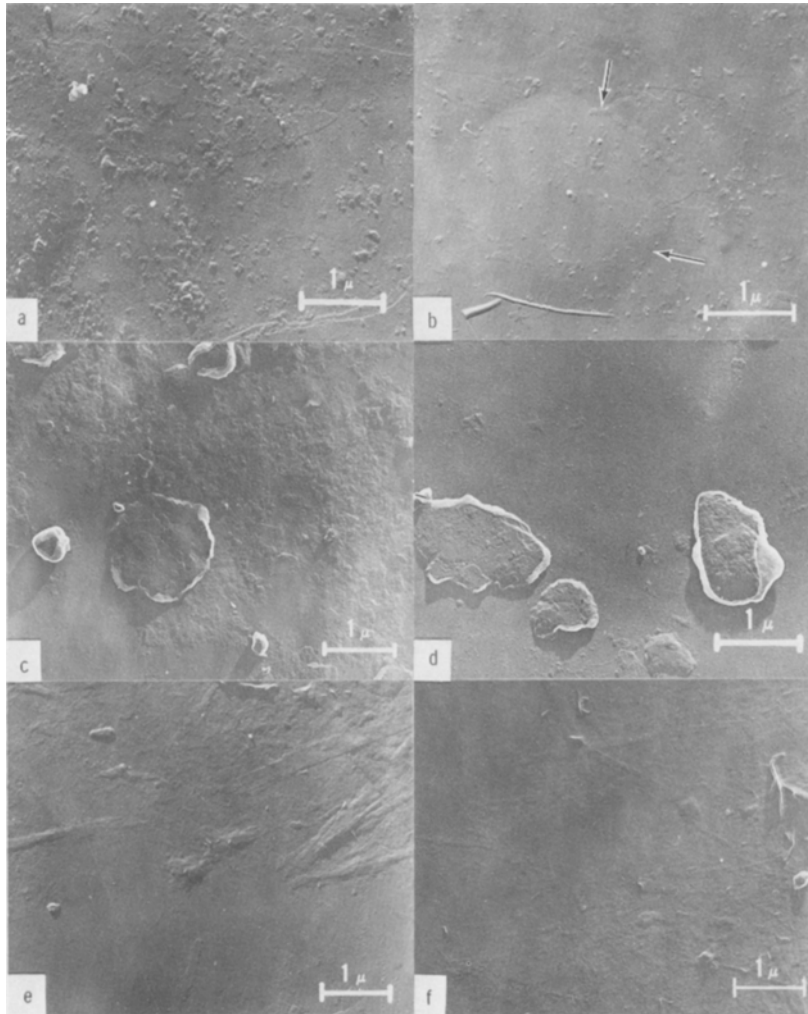


Fig. 6. Electron micrographs of platinum-carbon surface replicas of oxidized and deferrated soils and nontronite: (a) Oxidized White Mountain soil, 250–105  $\mu$ ; (b) Deferrated White Mountain soil, 250–105  $\mu$ . The arrows point out a “blister-like” configuration on the surface; (c) Oxidized Sharkey clay soil, < 2  $\mu$ ; (d) Deferrated Sharkey clay soil, < 2  $\mu$ ; (e) Oxidized nontronite, < 2  $\mu$ ; (f) Deferrated nontronite, < 2  $\mu$ .

Table 2. Content of layer structural ferrous and ferric iron of oxidized, deferrated, and deferrated-oxidized size fractions of vermiculites and soils

Size fraction ( $\mu$ )	Structural iron content (m-moles/100 g deferrated sample)								
	Oxidized			Deferrated			Deferrated-oxidized		
	Fe <sup>2+</sup>	Fe <sup>3+</sup>	Total	Fe <sup>2+</sup>	Fe <sup>3+</sup>	Total	Fe <sup>2+</sup>	Fe <sup>3+</sup>	Total
Vermiculite from Transvaal									
1000-105*	14	58	72	24	52	76	17	52	69
105-46*	15	59	74	26	49	75	19	51	70
46-2*	14	58	72	31	44	75	17	50	67
< 2*	12	54	66	37	33	70	15	50	65
Vermiculite from Utah									
> 1000	16	57	73	22	58	80	16	57	73
1000-105	16	56	72	22	54	76	18	52	70
105-46*	18	53	71	30	40	70	19	49	68
46-2*	19	55	74	34	39	73	20	53	73
< 2	29	109	138	54	81	135	27	108	135
Vermiculite from Montana									
> 1000	25	102	127	38	93	131	25	97	122
1000-105*	29	104	133	53	79	132	26	100	126
105-46*	28	101	129	59	75	134	26	101	127
46-2	30	101	131	66	65	131	26	100	126
< 2	26	101	127	74	55	129	24	100	124
Vermiculite from Wisconsin									
1000-105*	51	372	423	212	220	432	45	376	421
105-46	52	364	416	184	237	421	45	383	428
46-2	36	311	347	153	191	344	47	315	362
< 2	34	293	327	134	179	313	45	288	333
Vermiculite from micaceous saprolite (Wisconsin)									
500-250	55	261	316	96	212	308	56	259	315
250-105	56	275	331	108	217	325	67	264	331
105-50	59	245	308	116	196	312	43	276	319
50-2	36	36	72	45	26	71	32	39	71
< 2	22	66	88	37	49	86	22	69	91
White Mountain soil (California)									
250-105	32	197	229	72	160	232	36	193	229
50-2	19	69	88	37	58	95	22	67	89
< 2	24	94	118	55	78	133	24	98	122
Sharkey clay soil (Missouri)									
50-2	10	9	19	14	9	23	9	12	21
< 2	19	54	73	31	39	70	17	57	74
Nontronite (Washington)									
< 2	50	393	443	181	275	456	45	426	471
Muscovite									
2-0.2	17	41	58	27	36	63	18	43	61

\*Samples that showed roughness on deferration which was removed by subsequent H<sub>2</sub>O<sub>2</sub> treatment at pH 5.

in net negative charge of the layers, calculated from the sum of interlayer cations (Newman and Brown, 1966). The latter did not quantitatively balance the oxidation of Fe<sup>2+</sup> which had occurred. Another study involved a naturally occurring micaceous vermiculite from Colorado, with conclusions drawn from changes in the structural Fe<sup>2+</sup> content that were not accompanied by an equivalent change in CEC (Roth *et al.*, 1968). Since the mechanism

proposed for the oxidation of structural Fe<sup>2+</sup> requires that the Fe<sup>2+</sup> be regenerated in place of Fe<sup>3+</sup> by an electron-migration mechanism along the ribbon of cations, magnesium ions may block this migration (Addison and White, 1968). Any portion of the structural iron surrounded by Mg ions would be prevented from entering into the reversible change in iron valence state.

Because the oxidation of a large portion of struc-

Table 3. Cation exchange capacity of oxidized, deferrated, and deferrated-oxidized size fractions of vermiculites and soils

Size fraction ( $\mu$ )	CaEC (meq/100 g deferrated sample)		
	Oxidized	Deferrated	Deferrated-oxidized
Vermiculite from Transvaal			
1000-105	112	155	172
105-46	124	187	198
46-2	160	202	196
< 2	178	210	197
Vermiculite from Utah			
> 1000	144	161	161
1000-105	138	157	158
105-46	123	146	148
46-2	132	156	154
< 2	135	156	148
Vermiculite from Montana			
> 1000	88	112	129
1000-105	61	98	108
105-46	94	144	152
46-2	104	156	164
< 2	141	176	173
Vermiculite from Wisconsin			
1000-105	68	100	98
105-46	64	86	90
46-2	54	73	81
< 2	55	75	81
Vermiculite from micaceous saprolite (Wisconsin)			
500-250	21	25	26
250-105	20	23	24
105-50	18	22	22
50-2	7	8	8
< 2	46	61	59
White Mountain soil (California)			
250-105	44	61	61
50-2	19	23	25
< 2	52	61	61
Sharkey clay soil (Missouri)			
50-2	11	8	7
< 2	53	65	61
Nontronite (Washington)			
< 2	115	134	134
Muscovite			
2-0-2	11	16	16

tural  $\text{Fe}^{2+}$  (Table 2) did not significantly decrease the CEC of the samples (Table 3), the increase in CEC on deferration of vermiculite, saprolite, and soil samples was attributed to removal of positively charged sesquioxides which had blocked negatively charged exchange sites. The increase in CEC on deferration of the nontronite was attributed to a slight dechloritization of the ferruginous chlorite impurity (Alexiades and Jackson, 1967) present in the nontronite sample. The increase in CEC on deferration of muscovite was attributed to removal

of positively charged sesquioxides, present in the original sample or produced as a byproduct of the mechanical grinding of the sample, which had blocked approximately 30 per cent of the negatively charged exchange sites available after deferration (Table 3).

The CEC results with the several vermiculites and soils indicate that positively charged sesquioxide coatings, which are readily removed by deferration treatment, block a considerable portion of the exchange sites.

## CONCLUSION

Appreciable decrease in  $\text{Fe}^{3+}$  and reciprocal increase in  $\text{Fe}^{2+}$  of micaceous vermiculites from several localities, soils, nontronite, and muscovite (containing some iron) occur under strongly reducing conditions. The  $\text{Fe}^{3+}$  content is returned to approximately its original amount by subsequent  $\text{H}_2\text{O}_2$  treatment. These results on a representative range of micaceous vermiculites and soils support a previous finding with a micaceous vermiculite from Colorado (Roth *et al.*, 1968).

The CEC increase resulting from deferration of micaceous vermiculites, soils, nontronite, and muscovite which remained through the subsequent reoxidation of structural iron, is attributed to unblocking of exchange sites that had been blocked by positively charged sesquioxide coatings. These results are similar to those obtained earlier with the micaceous vermiculite from Colorado.

Since the reoxidation of structural iron produces no significant change in the CEC, the neutralization of additional positive charge arising from the change in valence of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  may involve deprotonation of structural  $\text{OH}^-$  to  $\text{O}^{2-}$  (Equation (1)), the reactions being reversible.

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**Résumé**—La déferrisation par réduction de  $\text{Fe}_2\text{O}_3$  libre avec  $\text{Na}_2\text{S}_2\text{O}_4$  en présence de citrate de Na et  $\text{NaHCO}_3$  a entraîné une modification de 10–35 pour cent de la valence de l'ensemble du fer structurel



dans le muscovite. Un accroissement en  $\text{Fe}^{2+}$  sur la déferrisation s'est accompagnée d'une diminution équivalente en  $\text{Fe}^{3+}$ . Un traitement ultérieur avec  $\text{H}_2\text{O}_2$  a permis de réoxyder le  $\text{Fe}^{2+}$  préalablement formé. Les couches sesquioxydes sur les vermiculites micacées ont été examinées au microscope électronique. Ces couches se composaient surtout de  $\text{Fe}_2\text{O}_3$  avec environ 10 pour cent en poids de  $\text{Al}_2\text{O}_3$  et de petites quantités de  $\text{SiO}_2$ , comme l'avait déterminé l'analyse chimique des extraits de déferrisation. La capacité d'échange de cations (CEC) a marqué une hausse de 10–60 pour cent à la suite de la déferrisation des vermiculites micacées et des sols. Le traitement de l'échantillon déferrisé avec  $\text{H}_2\text{O}_2$  a restauré la teneur de  $\text{Fe}^{3+}$  à une valeur proche de celle d'origine, mais le CEC n'était pas affecté. En conséquence, l'augmentation de CEC sur la déferrisation a été attribuée à la disparition de la couche sesquioxyde à charge positive. Le changement réversible de la valence du fer structurel sans un changement similaire en CEC a été causé par la déprotonation-protonation de la structure ( $\text{OH}^- \rightleftharpoons \text{O}^{2-}$ ) en même temps que la réduction-oxydation du fer ( $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$ ) dans la couche phyllosilicate.

**Kurzreferat**—Die Enteisenung durch Reduktion von freien  $\text{Fe}_2\text{O}_3$  mit  $\text{Na}_2\text{S}_2\text{O}_4$  in Gegenwart von Na Citrat und  $\text{NaHCO}_3$  bewirkte eine Änderung im Valenzzustand von 10 bis 35% des gesamten Struktureisens in glimmerartigen Vermiculiten, Boden, Nontronit und Muskovit. Einer Zunahme an  $\text{Fe}^{2+}$  bei Enteisenung entsprach eine gleichwertige Abnahme an  $\text{Fe}^{3+}$ . Nachträgliche Behandlung mit  $\text{H}_2\text{O}_2$  führte zu Reoxydation der zuvor gebildeten Struktur- $\text{Fe}^{2+}$ .

Sesquioxydbeschichtungen auf glimmerartigen Vermiculiten wurden mit dem Elektronenmikroskop geprüft. Diese Beschichtungen bestanden vorwiegend aus  $\text{Fe}_2\text{O}_3$  mit etwa 10 Gewichtsprozent  $\text{Al}_2\text{O}_3$  und kleinen Mengen  $\text{SiO}_2$ , wie dies durch chemische Analyse der Enteisenungsextrakte erwiesen wurde.

Die Kationenaustauschleistung (CEC) stieg um 10–60% in Folge der Enteisenung von glimmerartigen Vermiculiten und Boden. Die Behandlung der enteisenen Probe mit  $\text{H}_2\text{O}_2$  stellte den  $\text{Fe}^{3+}$  Gehalt auf etwa den ursprünglichen Wert wieder her, doch die Kationenaustauschleistung war dadurch nicht berührt. Die Erhöhung der Kationenaustauschleistung bei Enteisenung wurde daher auf die Entfernung der positiv geladenen Sesquioxydbeschichtung zurückgeführt. Die umkehrbare Änderung in der Valenz des Struktureisens ohne gleichwertige Änderung der Kationenaustauschleistung wurde auf Entprotonierung-Protonisierung der Struktur ( $\text{OH}^- \rightleftharpoons \text{O}^{2-}$ ) gleichzeitig mit der Oxydationsreduktion des Eisens ( $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$ ) in der Phyllosilikatschicht zurückgeführt.

**Резюме**—Удаление путем восстановления свободной окиси железа с помощью  $\text{Na}_2\text{S}_2\text{O}_4$  в присутствии цитрата и бикарбоната натрия вызвало изменение валентного состояния от 10 до 35% всего структурного железа в слюдоподобных вермикулитах, почвах, нонтроните и мусковите. Увеличение содержания  $\text{Fe}^{2+}$  сопровождалось эквивалентным уменьшением содержания  $\text{Fe}^{3+}$ . При последующей обработке перекисью водорода структурное  $\text{Fe}^{2+}$  вновь переходило в  $\text{Fe}^{3+}$ .

Пленки полупроводников окислов на частицах слюдоподобных вермикулитов изучались с помощью электронного микроскопа. Эти пленки в основном состоят из окиси железа; в них содержится также около 10% глинозема и небольшие количества кремнезема (данные химических анализов вытяжек). Емкость катионного обмена слюдоподобных вермикулитов и почв после извлечения свободной окиси железа возрастала с 10 до 60%. Обработка образца, из которого была извлечена свободная окись железа, перекисью водорода вызывала возрастание содержания структурного  $\text{Fe}^{3+}$  до исходной величины, но емкость катионного обмена при этом не менялась. Следовательно, увеличение емкости катионного обмена при извлечении свободной окиси железа вызвано удалением пленок положительно заряженных полупроводников окислов. Обратимый характер изменения валентности структурного железа без эквивалентного изменения емкости катионного обмена объясняется потерей или приобретением структурной протонов ( $\text{OH}^- \rightleftharpoons \text{O}^{2-}$ ) одновременно с окислением или восстановлением железа ( $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$ ) в филлосиликатном слое.