

## ROLE OF STRUCTURAL HYDROGEN IN THE REDUCTION AND REOXIDATION OF IRON IN NONTRONITE

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**Abstract**—The effects of reduction and reoxidation of octahedral Fe<sup>3+</sup> on the exchange of structural hydrogen in nontronite were determined using tritium (<sup>3</sup>H) as a label element. The uptake of H from the surrounding solution of nontronite suspensions increased as the reduction of structural Fe<sup>3+</sup> increased. Similarly, the loss of H from the structure increased as the reduction increased. The results are generally consistent with a reduction mechanism involving the loss of structural OH, leaving the affected Fe sites with less than six-fold coordination. The attenuation of increased negative charge on the clay layer, however, was less than predicted by such a mechanism.

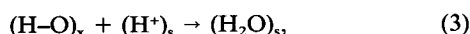
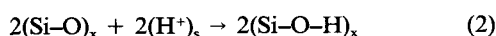
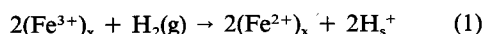
During the reoxidation of reduced nontronite in suspension, about one-third of the H remaining as part of the structure following reduction was lost, whereas twice that amount of H was incorporated into the structure from the surrounding solution. A reoxidation mechanism is proposed whereby H<sub>2</sub>O from the surrounding solution is incorporated into the mineral structure followed by the elimination of a hydrogen ion, returning the Fe to six-fold coordination. This mechanism implies the reversibility of Fe reduction in nontronite.

**Key Words**—Hydrogen, Nontronite, Oxidation, Reduction, Structural sites, Tritium.

### INTRODUCTION

Changes in the oxidation state of Fe in the octahedral sheets of clay minerals have a pronounced effect on the physical and chemical properties of the clay. Color (Anderson and Stucki, 1979), swelling (Foster, 1953, 1955; Stucki *et al.*, 1984c), layer charge (Stucki and Roth, 1977; Stucki *et al.*, 1984b), weathering (Farmer *et al.*, 1971), and unit-cell dimension (Radoslovich, 1962; Ross and Rich, 1973) vary with a change in Fe oxidation state. Although some of the effects of changes in the oxidation state of Fe are well documented, the specific mechanism or mechanisms by which these effects occur are undetermined.

On the basis of their work with the amphibole crocidolite and the clay minerals chamosite and nontronite, Addison and Sharp (1963) proposed the following mechanism for the reduction of Fe<sup>3+</sup> in dioctahedral clay minerals:

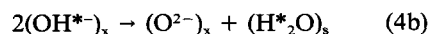
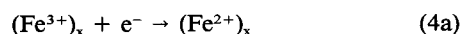


where x, g, and s denote the solid, vapor, and solution phases, respectively, and Si–O and Si–O–H refer to apical oxygens shared by the tetrahedral and octahedral sheets.

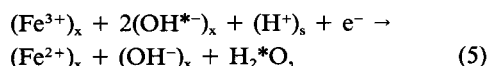
Eq. (1) deals with the interaction between structural Fe<sup>3+</sup> and the reducing agent H<sub>2</sub>. This reduction reaction occurs at 370°C (Addison and Sharp, 1963). Eqs. (2) and (3) describe the simultaneous addition of protons

to the tetrahedral “oxide” oxygens, without the elimination of water, and to the octahedral “hydroxyl” oxygens, resulting in the elimination of water.

Using the hydrogen isotope deuterium (D) as a label to follow similar “oxide-hydroxide” conversions in reduced nontronite at lower temperatures, Roth and Tullock (1973) observed that: (1) the number of structural OH groups decreased during reduction, (2) reduction at room temperature brought about complete H/D exchange in the structural OH groups, and (3) oxidation of reduced nontronite restored the original OH content without complete exchange of all the structural H. Based on these observations, they proposed the following stepwise reaction mechanism for the reduction of structural Fe<sup>3+</sup> in nontronite:



which can be written as the half-cell reaction



where \* identifies protons initially part of the clay mineral structure. Eq. (4a) involves the transfer of an electron from the reducing agent to structural Fe<sup>3+</sup>, and Eq. (4b) represents the simultaneous condensation of structural OH. The water molecule formed diffuses into solution, and the structural oxide formed in Eq. (4b) reprotoxates (Eq. (4c)). This mechanism accounts

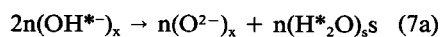
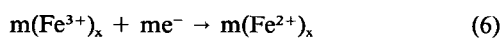
Table 1. Diagrammatic representation of the pathways studied.

H <sup>+</sup> -clay → reduced in H <sup>+</sup> OH → reoxidized in H <sup>+</sup> OH			
Pathway	H <sup>*</sup>	H <sup>*</sup>	H <sup>*</sup>
1	<sup>1</sup> H	<sup>3</sup> H	
2	<sup>3</sup> H	<sup>1</sup> H	
3	<sup>1</sup> H	<sup>1</sup> H	<sup>3</sup> H
4	<sup>1</sup> H	<sup>3</sup> H	<sup>1</sup> H
5	<sup>1</sup> H	<sup>3</sup> H	<sup>3</sup> H

for complete exchange of structural H and the decrease in hydroxyl content during reduction. The reactions shown in Eqs. (4a)–(4c) were considered to be interdependent.

If only the reduction of structural Fe<sup>3+</sup> occurred without invoking other changes in the mineral structure, the surface charge would increase linearly with Fe<sup>2+</sup> content. Roth *et al.* (1969) reported that the surface charge remained constant during reduction. Both of the proposed reaction mechanisms above maintain a constant net negative charge on the structure during the reduction of structural Fe<sup>3+</sup>.

Further studies by Stucki and Roth (1977) and Stucki *et al.* (1984b), however, indicated that the observed relationship between surface charge and Fe<sup>2+</sup> content deviates markedly from both the relationship predicted assuming no reaction other than the reduction of structural Fe<sup>3+</sup> and the relationship reported by Roth *et al.* (1969). The reaction mechanism proposed by Roth and Tullock (1973) was, therefore, modified by Stucki and Roth (1977) to account for these results. Eq. (4a) remained the same, but Eqs. (4b) and (4c) were considered to describe separate reactions which may or may not occur with the reduction of structural Fe<sup>3+</sup>. The revised mechanism can be described by the following reactions:



where the variables *m* and *n* are stoichiometric coefficients. These variables represent the extent to which Eqs. (7a) and (7b) compensate for the increased net negative charge due to the reduction of Fe<sup>3+</sup>.

If *m* > *n* = 0, the surface charge increases linearly with increasing Fe<sup>2+</sup> content, which is the relationship obtained if no reaction occurs other than the reduction of structural Fe<sup>3+</sup>. If *m* = *n*, Eqs. (6)–(7b) reduce to Eqs. (4a)–(4c), the relationship proposed by Roth and Tullock (1973) which maintains constant surface charge during reduction. Results of Stucki and Roth (1977) and Stucki *et al.* (1984b) suggest, however, that the relationship between *m* and *n* is intermediate to either of those above and varies with Fe<sup>2+</sup> content. All the

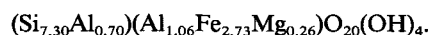
above reaction mechanisms suggest some interchange of H between the surrounding environment and octahedral hydroxyls in the clay structure.

The objective of the present study was to evaluate the reaction mechanism proposed by Stucki and Roth (1977) (Eqs. (6)–(7b)) for the reduction of structural Fe<sup>3+</sup> in nontronite by determining the relationship between the cation-exchange capacity (CEC) (which reflects the value of *m* – *n* in Eqs. (6)–(7b)) and the amount of exchange of H between the solution and the mineral structure (from which the value of *n* may be deduced). The hydrogen isotope tritium (<sup>3</sup>H) was used as a label to allow quantitative measurement of the H exchange. Reactions involving reoxidation of reduced samples were included to assess the reversibility of the reduction reaction.

## MATERIALS AND METHODS

### Material

The nontronite used in this experiment was the <2-μm fraction of reference clay SWa-1 (Source Clays Repository of The Clay Minerals Society), a ferruginous smectite from Grant County, Washington, with the basic composition (Goodman *et al.*, 1976):



The clay was Na<sup>+</sup>-saturated, dialyzed, and freeze-dried.

### Methods

Five separate reaction series or pathways were designated to study the reactions associated with reduction, reoxidation, and the combination of reduction and reoxidation of structural Fe<sup>3+</sup> in nontronite. The pathways were: (1) an unaltered nontronite reduced in a <sup>3</sup>H-labeled solution, with the major form of <sup>3</sup>H as <sup>3</sup>HO<sup>1</sup>H; (2) a tritiated nontronite, where part of the octahedral hydroxyl H was replaced by <sup>3</sup>H, reduced in an unlabeled solution; (3) an unaltered nontronite reduced in an unlabeled solution and reoxidized in a <sup>3</sup>H-labeled solution; (4) an unaltered nontronite reduced in a <sup>3</sup>H-labeled and reoxidized in an unlabeled solution; and (5) an unaltered nontronite reduced in a <sup>3</sup>H-labeled solution and reoxidized in a <sup>3</sup>H-labeled solution. Table 1 summarizes these reduction-oxidation pathways.

The reductions involved the suspension of 100 mg of nontronite sample in 30 ml of 1 M citrate-bicarbonate buffer solution in a 100 ml polycarbonate centrifuge tube. The buffer solution was prepared by combining 8 parts of 1 M sodium bicarbonate (NaHCO<sub>3</sub>) with 1 part of 0.3 M sodium citrate (Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> · 2H<sub>2</sub>O). Sodium dithionite (Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>) salt was used as the reducing agent, and the amount added to the suspensions varied depending on the oxidation state desired. The suspension was then heated in a water bath at 80°C for 15 min. The reduced samples were kept isolated from the atmosphere by an aluminum screw cap containing silicon rubber septa supported by a polyvinyl chloride

Table 2. The extent of deuteration at various conditions for select clay minerals.

Mineral	Condition	Temp (°C)	Time (hr)	Extent (%)	Reference
Nontronite	Suspension	100	24	<100	Roth and Tullock (1973)
	Suspension	150	18	100	Roth and Tullock (1973)
Montmorillonite	Film	100	1	25	Russell <i>et al.</i> (1970)
	Suspension	100	6360	26	O'Neil and Kharaka (1976)
	Suspension	100	14,040	28	O'Neil and Kharaka (1976)
	Suspension	200	1580	74	O'Neil and Kharaka (1976)
	Suspension	200	5640	82	O'Neil and Kharaka (1976)
	Suspension	350	7392	80	O'Neil and Kharaka (1976)
	Suspension	350	9024	89	O'Neil and Kharaka (1976)
	Film	350	4 <sup>1</sup>	100	Russell <i>et al.</i> (1970)
	Film	370	72	<50	Roy and Roy (1957)
Beidellite	Film	100	1	7	Russell <i>et al.</i> (1970)
	Film	400	4 <sup>1</sup>	100	Russell <i>et al.</i> (1970)
Illite	Suspension	100	6360	7	O'Neil and Kharaka (1976)
	Suspension	100	14,040	12	O'Neil and Kharaka (1976)
	Suspension	200	1580	16	O'Neil and Kharaka (1976)
	Suspension	200	5640	28	O'Neil and Kharaka (1976)
	Suspension	350	7392	64	O'Neil and Kharaka (1976)
	Suspension	350	9024	75	O'Neil and Kharaka (1976)
Kaolinite	Suspension	100	6360	6	O'Neil and Kharaka (1976)
	Suspension	100	14,040	5	O'Neil and Kharaka (1976)
	Powder	135	96	8	O'Neil and Kharaka (1976)
	Powder	170	96	16	O'Neil and Kharaka (1976)
	Suspension	200	1580	19	O'Neil and Kharaka (1976)
	Suspension	200	5640	29	O'Neil and Kharaka (1976)
	Suspension	350	7392	97	O'Neil and Kharaka (1976)
	Suspension	350	9024	95	O'Neil and Kharaka (1976)
	Film	370	72	>50	Roy and Roy (1957)
	Vermiculite	Film	350	4 <sup>1</sup>	100
Muscovite	Powder	600	700	100	Vedder and Wilkins (1969)
Biotite	Powder	500	48	100	Vedder and Wilkins (1969)

<sup>1</sup> Sample subjected to 4, 1-hr treatments.

(pvc) washer and sealed with an air-tight rubber gasket (Stucki *et al.*, 1984b). The excess salts were removed by centrifuging the suspension with a force of 35,000 *g*, decanting the supernatant using an apparatus described by Stucki *et al.* (1984a), and resuspending the pellet in degassed, 0.005 M NaCl solution. This washing procedure was repeated four times. Reoxidation of reduced clay suspensions was attained by bubbling H<sub>2</sub>O-saturated O<sub>2</sub> gas through the samples for 18 hr, approximating complete reoxidation.

Fe<sup>2+</sup> and total Fe were determined as described by Stucki (1981) with the exception of increasing the time of photochemical reduction of the Fe<sup>3+</sup>-phenanthroline complex to 48 hr. The <sup>3</sup>H content was determined by dehydroxylating a sample of dry clay material at 700°C for 1 hr, exceeding the required temperature for complete dehydroxylation of nontronite (Heller-Kallai and Rozenson, 1980; Serratos, 1960).

The dehydroxylation apparatus consisted of a Vycor tube connected to a vapor-collection loop. The clay sample was placed in the tube and the entire apparatus was evacuated to about 130 Pa. The Vycor tube was heated in a tube furnace for 1 hr, and the water vapor given off as the nontronite sample dehydroxylated was

collected in the vapor trap cooled to liquid nitrogen temperature. The vapor trap was then isolated from the rest of the system and flushed with 12 ml of liquid scintillation cocktail (18 g diphenyloxane (ppd), 2250 ml xylene and 750 ml Triton X-114). The amount of <sup>3</sup>H collected in the exuded water vapor was determined using a Packard Tricarb liquid scintillation spectrometer.

*Pathway 1.* Following the reduction of the nontronite sample in an aqueous solution containing <sup>3</sup>H and the removal of the excess salts, the pellet was resuspended in 10 ml of 0.005 M NaCl. About 4 ml of the suspension was transferred onto a 0.025- $\mu$ m pore-size Millipore filter in a N<sub>2</sub>-purged environmental chamber using a gas-tight syringe (Stucki *et al.*, 1984a). After flowing N<sub>2</sub> gas through the chamber for 24 hr, the dried clay film was removed and analyzed for Fe<sup>2+</sup>, total Fe, and <sup>3</sup>H.

*Pathway 2.* The unaltered nontronite was tritiated by suspending 100 mg of sample in 10 ml of 0.005 M NaCl solution and 2 ml of <sup>3</sup>H stock solution (about 5 × 10<sup>6</sup> disintegrations per minute/ml) in a hydrothermal bomb and heating at 125°C for 24 hr. This

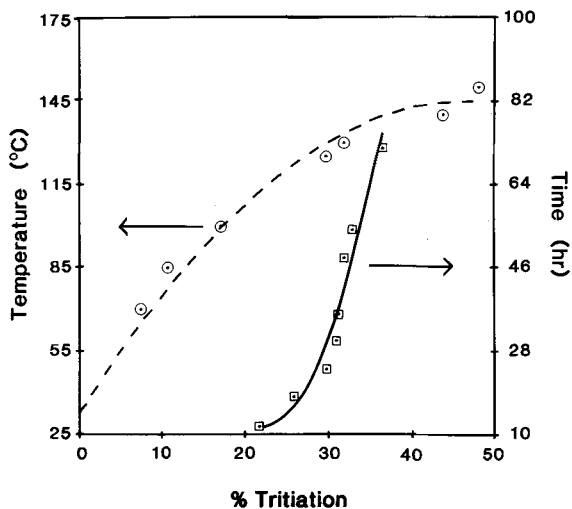


Figure 1. Amount of hydrogen replaced by tritium for nontronite suspended in  $^3\text{H}$ -labeled solution. Left-hand curve involves sample treated at various temperatures for 24 hr. Right-hand curve is for sample treated at  $125^\circ\text{C}$  for various periods of time.

process resulted in about 26% of the structural hydrogens being replaced by those from solution, based on the amount of tritium assimilated into the structure. This time and temperature was chosen based on previous deuteration studies (McAulliffe *et al.*, 1947; O'Neil and Kharaka, 1976; Roth and Tullock, 1973; Rouxhet, 1970; Roy and Roy, 1957; Russell *et al.*, 1970; Vedder and Wilkins, 1969) which indicated that H/D exchange within the mineral structure is appreciable only at temperatures exceeding  $100^\circ\text{C}$  (Table 2), and on our own study of the effects of temperature and time on the extent of tritiation of structural hydroxyls (Figure 1). Higher temperatures were avoided to minimize the risk of further structural alteration of the clay. After heating, the suspension was transferred to a 50-ml centrifuge tube, washed three times with 30 ml of 0.005 M NaCl to remove nonexchanged  $^3\text{H}$ , and freeze-dried. About 10 mg of the freeze-dried sample was analyzed for  $^3\text{H}$ , and the remaining portion ( $\sim 85$  mg) was reduced in an unlabeled solution. A clay film was produced as in pathway 1 and analyzed for  $^3\text{H}$ ,  $\text{Fe}^{2+}$ , and total Fe.

**Pathway 3.** A 100-mg nontronite sample was reduced in an unlabeled solution. After the fourth washing, the reduced pellet was resuspended in about 40 ml of 0.005 M NaCl. Using the decanting apparatus, about 30 ml of the suspension was transferred to a 100-ml centrifuge tube that had been preweighed and purged with  $\text{N}_2$ . The remaining reduced suspension was centrifuged, the supernatant was decanted, and the gel was analyzed for  $\text{Fe}^{2+}$  and total Fe. The centrifuge tube containing the transferred solution was reweighed and 1 ml of the  $^3\text{H}$  stock solution was added. The transferred suspension was then reoxidized, washed three

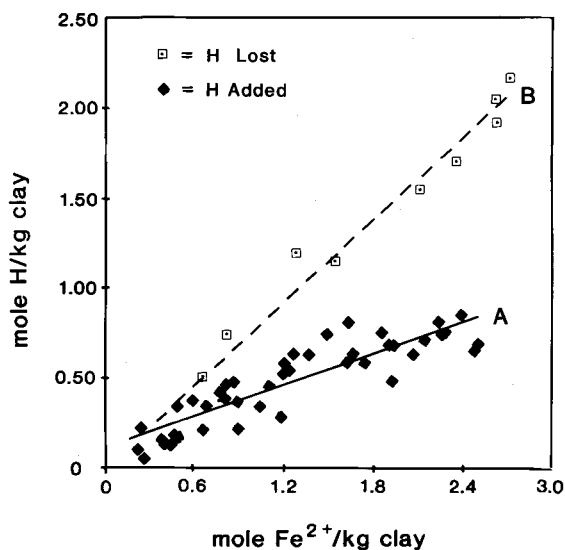


Figure 2. Changes in structural hydroxyl-H content during reduction of nontronite.

times with 0.005 M NaCl to remove nonexchanged  $^3\text{H}$ , and freeze-dried. The freeze-dried powder was analyzed for  $\text{Fe}^{2+}$ , total Fe, and  $^3\text{H}$ .

**Pathway 4.** One hundred milligrams of nontronite was reduced in a  $^3\text{H}$ -labeled solution. Following the final washing, a clay film was prepared as in pathway 1. A portion of this reduced film was analyzed for  $\text{Fe}^{2+}$ , total Fe, and  $^3\text{H}$ . The remainder ( $\sim 35$  mg) was resuspended in 20 ml of 0.005 M NaCl, reoxidized, and centrifuged, and the supernatant was decanted. The resulting pellet was resuspended in 10 ml of distilled, deionized  $\text{H}_2\text{O}$ . This suspension was freeze-dried and analyzed for  $\text{Fe}^{2+}$ , total Fe, and  $^3\text{H}$ .

**Pathway 5.** A 100-mg nontronite sample was reduced in a  $^3\text{H}$ -labeled solution. After the fourth washing, a reduced clay film was produced as described in pathway 1. A portion of the clay film was analyzed for  $\text{Fe}^{2+}$ , total Fe, and  $^3\text{H}$ . The remaining film was resuspended in 20 ml of 0.005 M NaCl and 1 ml of  $^3\text{H}$  stock solution, then reoxidized. This reoxidized suspension was washed three times in NaCl to remove nonexchanged  $^3\text{H}$ , freeze-dried, and analyzed for  $\text{Fe}^{2+}$ , total Fe, and  $^3\text{H}$ .

The surface charge was determined on a series of reduced gels as described by Stucki *et al.* (1984b).

## RESULTS AND DISCUSSION

### Reduction

The exchange of H between the surrounding solution and the clay mineral structure during the reduction of structural  $\text{Fe}^{3+}$  is reported in Figure 2. Results from the reduction of nontronite using pathway 1 (curve A) indicate that the amount of solution H incorporated into the clay mineral structure increased as the  $\text{Fe}^{2+}$  content increased. The amount of structural H lost

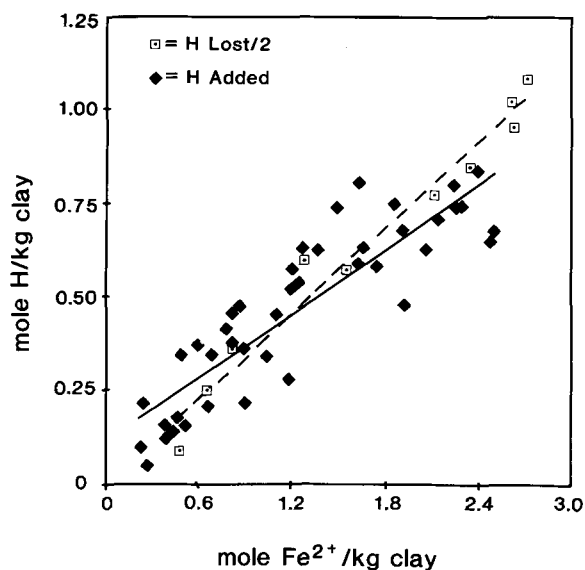


Figure 3. Relationship between loss of H as H<sub>2</sub>O and uptake of H during reduction of nontronite.

(pathway 2) also increased as the Fe<sup>2+</sup> content increased (curve B), although at a faster rate than the uptake of H from the surrounding solution. These results follow a pattern similar to previous results relating the color (Anderson and Stucki, 1979), CEC (Stucki and Roth, 1977; Stucki *et al.*, 1984b) and swelling of the Garfield nontronite (API 33a) (Stucki *et al.*, 1984c) to its Fe<sup>2+</sup> content.

The proposed mechanism for the reduction of structural Fe<sup>3+</sup> (Eqs. (6)–(7b)) predicts that the amount of structural H lost (as H<sub>2</sub>O) should be twice the amount of H assimilated into the mineral structure. Dividing the amount of structural H lost (Figure 2, curve B) causes the two curves (A and B) to coincide (Figure 3). Hence, Eqs. (7a) and (7b), i.e., the loss of structural H as H<sub>2</sub>O followed by the incorporation of solution H, have 1:1 stoichiometry and proceed sequentially as key reactions in the reduction mechanism.

Another test of the reliability of the proposed mechanism is the comparison of the predicted and observed surface charge ( $\omega$ ) as a function of  $m$ , the moles of Fe<sup>2+</sup> produced. If the values of  $m$  and  $n$  are known, the corresponding surface charge is calculable using the relation

$$\omega = \omega_0 + km(1 - n/m), \quad (8)$$

where  $\omega_0$  is the surface charge of the clay in its natural oxidation state, i.e., when no reduction has occurred;  $n$  and  $m$  are the stoichiometry coefficients in Eqs. (7a) and (7b); and  $k$  is unity, having units of charge/mole, where the units of charge are the same as for  $\omega_0$ . This relation satisfies the boundary conditions of: (1)  $\omega = \omega_0$  when  $n/m = 1$  or when  $m = n = 0$ ; and (2)  $\omega = \omega_0 + km$  when  $n = 0$  and  $m \neq 0$  (the condition when Eq. (6) is the only reaction that occurs, i.e., no charge com-

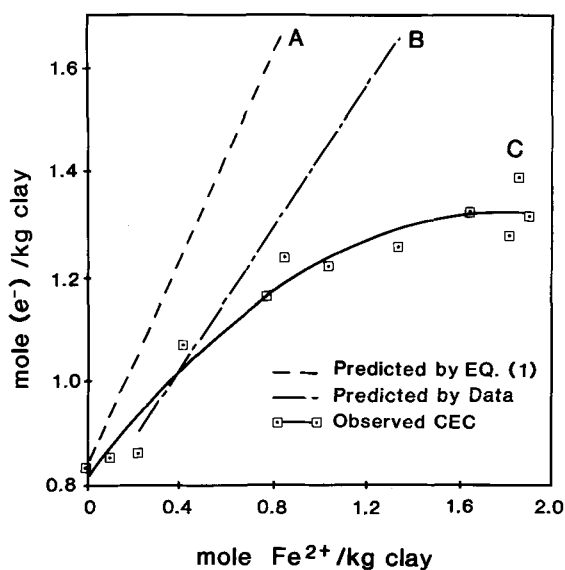


Figure 4. Surface charge predicted by Eq. (1) (curve A), predicted by the change in hydroxyl content for reduced nontronite (curve B) and observed (curve C).

ensation, and is plotted as curve A in Figure 4). From the slope of the line in Figure 3, the value of  $n/m$  from the tritiation experiments was determined to be about 0.32 and to be invariant over the range of Fe<sup>2+</sup> contents studied. Hence, Eq. (8) reduces to

$$\omega = \omega_0 + 0.68km \quad (9)$$

and the variation of surface charge with Fe<sup>2+</sup> content is linear, with a slope of 0.68k (curve B, Figure 4). This relationship is predicted by the proposed mechanism based on the tritiation results.

The observed surface charge as measured by total Na in the clay, however, varies curvilinearly with  $m$  (curve C, Figure 4), indicating that the  $n/m$  ratio varies over the same range of reduction. Hence, a discrepancy exists between the model and experiment. The determination of total surface charge based only on the measurement of total exchanged Na<sup>+</sup> underestimates the total surface charge if other ions are occupying exchange sites or if other charge-compensation mechanisms occur at the surface.

Alternatively, the model for the reaction mechanism may be incomplete. A consequence of Eq. (7a) is a five-fold coordination environment for either both of the Fe atoms sharing the two hydroxyls in a centrosymmetric structure or two of the three Fe atoms sharing the two hydroxyls in a non-centrosymmetric structure. Although nontronites are thought to have a non-centrosymmetric structure (Goodman *et al.*, 1976), the Mössbauer isomer shift would change with either structure if five-fold coordinated Fe sites are produced as predicted by the proposed reaction mechanism. Mössbauer studies of reduced nontronites by Russell *et al.* (1979) suggest that the environment around both the



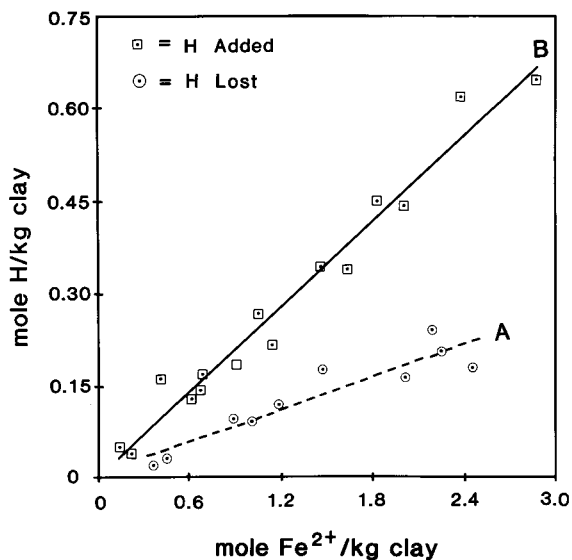


Figure 5. Changes in structural hydroxyl content during reoxidation of reduced nontronite.

$\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  is octahedral. So although the data in Figure 3 indicate that hydroxyls are eliminated from the mineral structure, some component of the reduction solution may assimilate into the mineral structure as a ligand for Fe to maintain the octahedral environment around the affected Fe atoms, and may also affect the surface charge of the mineral structure. The nontronite samples studied by Russell *et al.* (1979), however, were only mildly reduced and may have reoxidized, which would have restored the distorted Fe environments to six-fold coordination. Mössbauer studies under carefully controlled environments are needed to clarify this question.

No further conclusions can be drawn at this point, except that both the tritiation and surface-charge measurements of nontronite SWa-1 show that  $0 < n/m < 1$  over the entire range of  $\text{Fe}^{2+}$  contents studied.

#### Reoxidation

The exchange of H between the surrounding solution and the clay mineral structure during the reoxidation of  $\text{Fe}^{2+}$  was investigated for nontronite samples using pathways 3, 4, and 5. Curve B in Figure 5 represents the relationship between the amount of H assimilated into the mineral structure and the amount of  $\text{Fe}^{2+}$  reoxidized. The amount of H incorporated increased as reoxidation progressed, similar to the relationship shown above for the assimilation of H into the mineral structure during the reduction of  $\text{Fe}^{3+}$ .

Curve A in Figure 5 represents the loss of H from the mineral structure during reoxidation. Note that the rate of H loss is less than the rate of assimilation, confirming the assertion by Roth and Tullock (1973) that only part of the structural H content is exchanged during reoxidation.

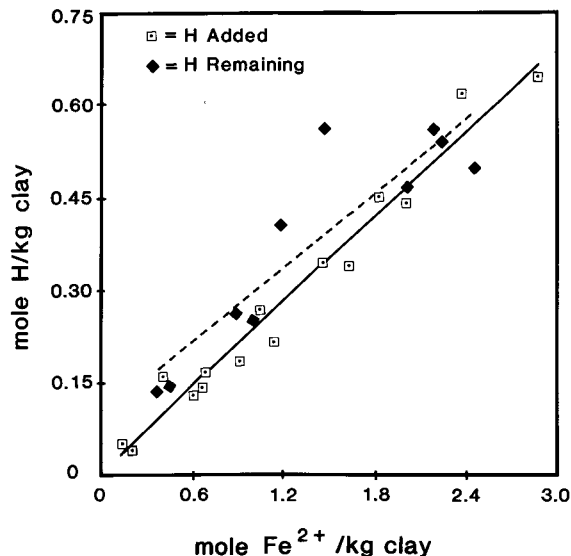
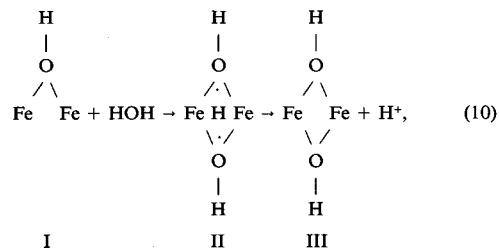


Figure 6. Uptake of solution H and amount of hydroxyl-H unaffected during reoxidation of reduced nontronite.

The amount of H incorporated into the clay mineral structure is nearly equal to the amount of H remaining as part of the mineral structure (Figure 6), which suggests the following reaction scheme:



where species I, II, and III represent the hydroxyl linkages between Fe ions in adjacent octahedral sites.  $\text{H}_2\text{O}$  from solution is assimilated into the vacancy created by the loss of structural hydroxyls during reoxidation (I  $\rightarrow$  II), followed by the elimination of a structural H (II  $\rightarrow$  III). Inasmuch as nontronite samples reduced and reoxidized via pathway 4 lost an average of about one-fourth of their  $^3\text{H}$  content, whereas samples reduced and reoxidized via pathway 3 incorporated twice that amount of  $^3\text{H}$ , an equal probability exists for any one H of the three in species II to be eliminated from the mineral structure.

The mechanism for the reoxidation of reduced nontronite was tested further by using the results from Figure 5 to predict the effect of reducing and oxidizing a nontronite sample in  $^3\text{H}$ -labeled solutions (pathway 5). These results were then compared with the actual  $^3\text{H}$  content observed for nontronite samples reduced and reoxidized in  $^3\text{H}$ -labeled solutions (Table 3). The correlation coefficient between the predicted and observed results is .95.

Table 3. Observed and predicted  $^3\text{H}$  contents for nontronite samples reduced and reoxidized in  $^3\text{H}$ -labeled solutions.

Fe <sup>2+</sup> reoxidized (mole/kg clay)	Tritium content	
	Actual (dpm/kg clay) <sup>1</sup>	Predicted (dpm/kg clay)
2.303	1487.77	1424.99
1.810	1366.70	1314.83
1.628	1257.93	1182.80
1.607	1335.54	1390.23
1.335	1253.15	1155.70
1.243	1257.93	1169.53
1.219	1114.68	1054.62
1.149	798.87	748.01
0.746	947.89	882.16
0.657	934.18	819.79
0.427	635.63	576.58
0.210	624.47	506.05

<sup>1</sup> dpm = disintegrations per minute.

The reaction mechanism proposed for the reoxidation of dithionite-reduced nontronite implies that changes occurring during reduction are reversed upon reoxidation. The reversibility of the reduction of structural Fe<sup>3+</sup> has been reported by others (Stucki and Roth, 1976; Stucki and Anderson, 1981; Stucki *et al.*, 1984b), although Rozenson and Heller-Kallai (1976) suggested that the structural changes occurring on reduction are reversible only if Al-OH-Fe associations are involved, but not if the associations are Fe-OH-Fe. The above results suggest that the structural changes which occur during reduction are reversible even if Fe-OH-Fe associations are involved.

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(Received 14 February 1985; accepted May 20, 1985; Ms. 1463)