

REDUCTION AND REOXIDATION OF NONTRONITE: QUESTIONS OF REVERSIBILITY

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Abstract—Redox cycles are common in nature and likely have a profound effect on the behavior of soils and sediments. This study examined a key component of redox cycles in smectites, namely, the reoxidation process, which has received little attention compared to the reduction process. Unaltered (oxidized) and reoxidized ferruginous smectites (nontronites) were compared using infrared and Mössbauer spectroscopies, and thermal gravimetric analysis. The infrared and thermal gravimetric data revealed that the structural OH content of reduced-reoxidized clay is about 15 to 20% less than in the original (oxidized) sample, indicating that the structure remains partially dehydroxylated even after reoxidation. Mössbauer spectra of reoxidized samples consisted of larger quadrupole splitting for Fe(III) doublets than in the unaltered samples, suggesting that the environment of Fe(III) is more distorted after the reduction-reoxidation treatment.

Key Words—Dehydroxylation, Ferric, Ferrous, Hydroxylation, Infrared spectroscopy, Iron, Mössbauer spectroscopy, Nontronite, Oxidation, Reduction, Reoxidation, Smectite, Thermal gravimetric analysis, X-ray diffraction.

INTRODUCTION

Oxidation-reduction reactions are common in nature, and are believed to be a primary mechanism for the weathering of rocks and minerals (Walker 1949, Scott and Amonette 1988, and references therein), and in determining the properties of clays, soils, and sediments (Chen *et al* 1987, Stucki and Lear 1989). The dominant octahedral cation in nontronites and ferruginous smectite is Fe; and in some nontronites Fe occupies a fraction of the tetrahedral sites (Goodman *et al* 1976, Cardile 1987, 1989, Cardile and Johnston 1985, 1986, Luca 1991, Luca and Cardile 1989). It is the only major element in the smectite structure that potentially may exist in two relatively stable oxidation states, Fe(II) and Fe(III), and a change in its oxidation state *in situ* alters the physical and chemical properties of the clay (Stucki 1988, and references therein, Komadel *et al* 1990, Stucki and Tessier 1991, Khaled and Stucki 1991, Gates *et al* 1993).

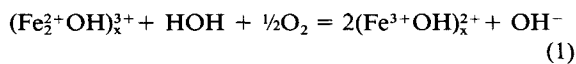
Many of aforementioned studies have shown the effects of structural Fe reduction on the properties of dioctahedral smectites, but only a few have addressed the issue of reversibility of the reduction reaction (Rozenon and Heller-Kallai 1976, Russell *et al* 1979, Lear 1984, Komadel *et al* 1990, Stucki and Lear 1989). Because redox cycles occur naturally in soils and sediments as a result of various alternating ambient conditions, such as wetting and drying, better insight into the reversibility of reduction reactions, i.e., the reoxidation process, is fundamental to a complete understanding of natural processes in the environment.

Using sodium dithionite as a reducing agent in a buffer solution containing citrate and bicarbonate, and purging the reaction vessel with N₂ gas, Komadel *et al* (1990) reduced 92% of the structural Fe in nontronite sample NG-1. They studied the path of reduction, followed by reoxidation with O₂ gas, using visible absorption spectroscopy, and discovered that the rate and level of reduction increased with temperature and with the amount of reducing agent added. They also found that the color of the reoxidized sample was similar to the pale yellow observed in the original, unaltered clay.

If unbuffered sodium dithionite is used, some of the structural Fe is dissolved (Rozenon and Heller-Kallai 1976, Stucki and Roth 1977), thus rendering the process irreversible with respect to the structural Fe composition. Rozenon and Heller-Kallai (1976) successfully reduced only about 39% of the structural Fe in ferruginous smectite SWa-1, but noticed a distinct black color in the sample and that extensive dissolution of structural Fe (>20%) had occurred. Stucki and Roth (1977) noticed a similar, but transient, black color in unbuffered dithionite treatments. The color likely arises from the formation of FeS as Fe(II) dissolved from the clay reacts with sulfur products from dithionite decomposition and disproportionation. A yellow-orange product is observed if a sample reduced in unbuffered dithionite is reoxidized with 5% H₂O₂ (Rozenon and Heller-Kallai 1976), which provides further evidence that structural Fe is liberated in the process, otherwise the color would be closer to the original pale-yellow. The Mössbauer spectrum for Fe(III) in a sample reoxidized in this manner is characterized by much

larger QS than in the unaltered clay, and the overall absorption envelope is uncharacteristically split (Russell *et al* 1979). Further, the loss of the Fe₂OH bending vibration at 810 cm⁻¹ in the infrared spectrum upon reduction of sample SWa-1 is unrestored after reoxidation. Russell *et al* (1979) found a broader Mössbauer spectrum and less tetrahedral Fe in a nontronite from South Africa (KOE) (27% of total Fe was tetrahedral) after unbuffered dithionite reduction and reoxidation. They could reduce only 13 and 26% of total Fe in Garfield nontronite and ferruginous smectite SWa-1, respectively.

Lear and Stucki (1985) reduced as much as 80% of the total Fe in SWa-1 in citrate-bicarbonate-dithionite (CBD) solution. By measuring the change in ³H (tritium) content in the clay (as incorporated into structural OH groups) and in the surrounding aqueous solution during reduction and reoxidation with O₂, they proposed a reversible mechanism for the reduction process in which the reoxidation step was given by



where x signifies that the preceding quantity is part of the clay crystal structure. Stucki *et al* (1984b) observed reversible changes in the negative layer charge of Garfield nontronite reduced to about 55% in CBD.

The purpose of the present study was to reduce as much of the structural Fe as possible with CBD solution in three nontronites with low tetrahedral Fe content, then to compare the amount of structural OH and the symmetry of the structural Fe environment in untreated, reduced, and O₂-reoxidized samples to determine the extent to which these properties in the unaltered (oxidized) clay could be restored after reduction and reoxidation.

MATERIALS AND METHODS

The clays used were nontronites NG-1 (Hohen Hagen, Federal Republic of Germany), SWa-1 (Grant County, Washington), and GAN (API No. 33a, Garfield, Washington). The first two samples were obtained from the Source Clays Repository of the Clay Minerals Society, Columbia, Missouri; the last from Wards Natural Science Establishment, Rochester, New York. Each nontronite was fractionated to <2-μm, Na⁺-saturated, washed free of excess salts to approximately 10⁻⁴ M, and freeze-dried. The magnetic Fe-oxide fraction was removed from sample NG-1 by the method of Lear *et al* (1988). The compositions of these clays were published elsewhere (Goodman *et al* 1976, Schneiderhöhn 1965), and none contains any significant amount of structural Fe(II) in the original state.

Twenty-five mg of sample was suspended in 2.5 ml of citrate-bicarbonate buffer solution and diluted with 37.5 ml of water in an inert-atmosphere reaction vessel

(Stucki *et al* 1984a). The atmosphere within the vessel was maintained by inserting two needles: one carried the purge gas (N₂ during reduction, O₂ during reoxidation) deep into the suspension, whereas the other served as a vent. Purge gas was flow-regulated and H₂O-saturated. Continuous flow of N₂ protected the suspension from contact with O₂ in the air and from sedimentation, and swept gaseous reaction products (unspecified, but may include H₂S) out of the system, thus enabling the reaction to proceed to a point close to complete reduction. The temperature of the reaction mixture was maintained at 348 K by placing the lower 2/3 of the reaction vessel into a constant-temperature water bath.

Iron was reduced by briefly removing the cap from the reaction vessel and adding 50 mg solid sodium dithionite (Na₂S₂O₄) directly to the clay suspension. After about 90 minutes the purge gas was changed to O₂ to effect reoxidation.

Selected reduced and reoxidized samples were freeze-dried and analyzed for Fe(II) and total Fe using the 1,10-phenanthroline method of Komadel and Stucki (1988), and Mössbauer spectroscopy. Reduced samples were handled by the method of Stucki *et al* (1984a). The solute concentration in some reoxidized samples was decreased by washing with water to 10⁻⁴ M. For infrared and thermal gravimetric analyses, five portions of each nontronite were reduced and reoxidized in parallel to obtain more than 100 mg of reoxidized sample. The suspensions of these parallels were combined after the last washing and air-dried at room temperature. After grinding to <0.2 mm, the powder was used for infrared (IR) spectroscopic and thermal gravimetric (TG) analyses. Infrared spectra were obtained using a Perkin-Elmer 983 G spectrometer and KBr pellet-technique (200 mg KBr + 0.2 mg sample). The assignment of the bands follows Farmer (1974). Thermogravimetric curves were obtained on 100-mg samples in static air using a Derivatograph thermoanalyzer (manufactured by Magyar Optikai Művek, Budapest), heated at a rate of 10 deg (K) min⁻¹. Mössbauer spectra were obtained at 90 K using a Ranger Scientific MS-900 spectrometer equipped with a Technology Systems cryostat and analyzed with a least-squares computer program assuming Lorentzian line shapes.

RESULTS AND DISCUSSION

High levels of reduction were achieved with all three nontronites investigated (Table 1). The slight discrepancy between values for Fe(II) and Fe(III) obtained from colorimetric and Mössbauer methods could be caused by partial reoxidation of the samples when they were transferred from the freeze-dryer to the Mössbauer sample holder, and/or by unequal recoil-free fractions of Fe(II) and Fe(III) (Amonette *et al* 1994). Reoxidation or failure to use an open system for re-

Table 1. Fe(II)/Total Fe ratio in reduced nontronites calculated from Mössbauer spectra (MS) and from chemical analyses (CA).

Nontronite	Fe(II)/Total Fe (%)	
	MS	CA
NG-1	86	92
SWa-1	89	94
GAN	84	90

duction probably contributed to the small Fe(II) values in reduced nontronite GAN reported by Cardile *et al* (1987) and Murad (1987) (0 and 16% of total Fe, respectively).

Mössbauer spectra of the untreated samples were taken at 90 K in the velocity range $\pm 10 \text{ mm s}^{-1}$ to identify other Fe phases possibly present in the samples. All three clays showed magnetic sextets with hyperfine fields ranging from 47.4 to 47.9 T, in addition to the paramagnetic doublets. These values are typical of poorly-crystallized goethite. Goethite was also identified in these three nontronites by Murad (1987) and Lear *et al* (1988). The relative areas of the magnetic sextets were 9% in NG-1 (8% by Lear *et al* 1988), 3% in SWa-1 (2.9% by Murad 1987), and 8% in GAN (4.6% by Murad 1987). Recall that sample NG-1 initially also contained maghemite, which was removed by a hand magnet (Lear *et al* 1988).

Mössbauer spectra of untreated, reduced, and reoxidized SWa-1, in the velocity range $\pm 4 \text{ mm s}^{-1}$, are given in Figure 1. These spectra are typical of the other smectites studied. The reoxidation was rapid and complete—less than 0.2% of total Fe was found as Fe(II) in all three reoxidized nontronites. Peaks attributable to Fe(II) were absent from both the untreated and reoxidized samples, whereas in the reduced sample 88% of the absorption area was due to Fe(II). The spectra of untreated and reoxidized nontronites were fitted with two Fe(III) doublets, neglecting the inner two lines of goethite sextets and the tetrahedral Fe content. The parameters of the spectra are listed in Table 2. The isomer shift (IS) of all doublets is in the range 0.32 to 0.36 mm s^{-1} , which is typical for octahedral high-spin Fe(III). The quadrupole splittings (QS) of the reoxidized samples were larger than the untreated ones (Table 2, Figure 1), indicating that the symmetry sur-

Table 2. Mössbauer parameters of untreated and reoxidized nontronites.

Nontronite	Peaks	IS		QS		IS		QS	
		NG-1		SWa-1		GAN			
		mm/s							
Untreated	1;4	0.34	0.75	0.33	0.78	0.35	0.67		
	2;3	0.35	0.26	0.34	0.28	0.35	0.23		
Reoxidized	1;4	0.35	1.18	0.33	1.17	0.36	1.17		
	2;3	0.32	0.55	0.33	0.55	0.34	0.55		

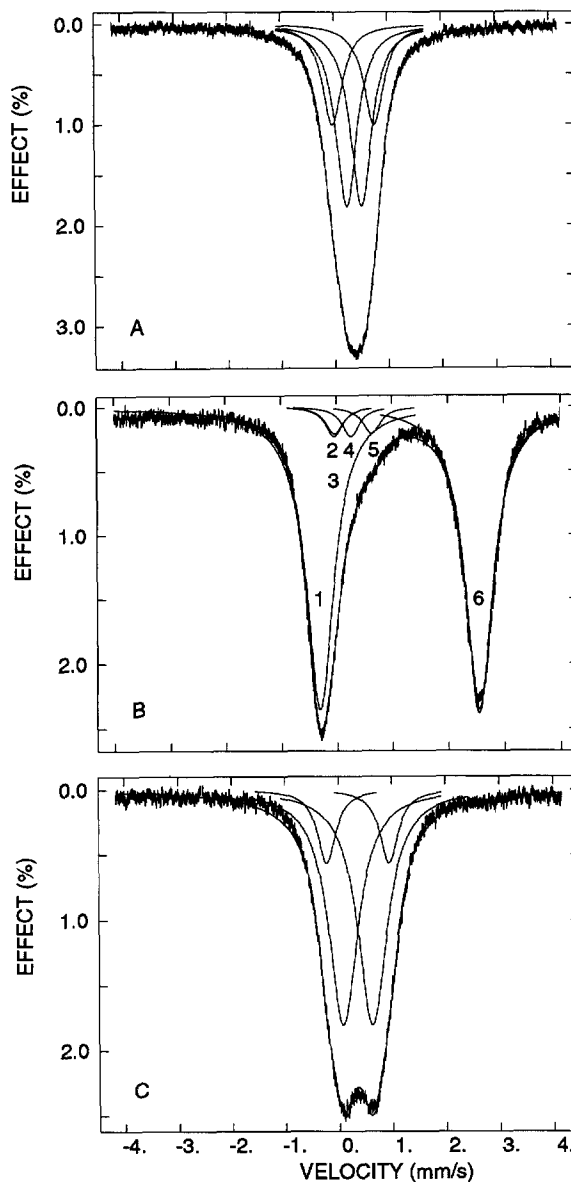


Figure 1. Mössbauer spectra of unaltered (A), reduced (B), and reoxidized (C) nontronite SWa-1 at 90 K. Peaks 1 and 6 in (B) are assigned to Fe(II), all others in (A), (B), and (C) are assigned to Fe(III).

rounding Fe(III) was decreased in the reduction-reoxidation process. Heller-Kallai and Rozenson (1980) observed similar broadening in spectra of heated SWa-1; after one hour at 400°C, their spectrum consisted of two doublets having the same IS of 0.38 mm s^{-1} , which value is similar to those of the reoxidized samples reported in Table 2, but QS doubled.

Infrared spectra of untreated, reduced, and reoxidized NG-1 and SWa-1 are given in Figure 2. This region is characterized by a band at 3556 and at 3545 cm^{-1} in the untreated NG-1 and SWa-1, respectively

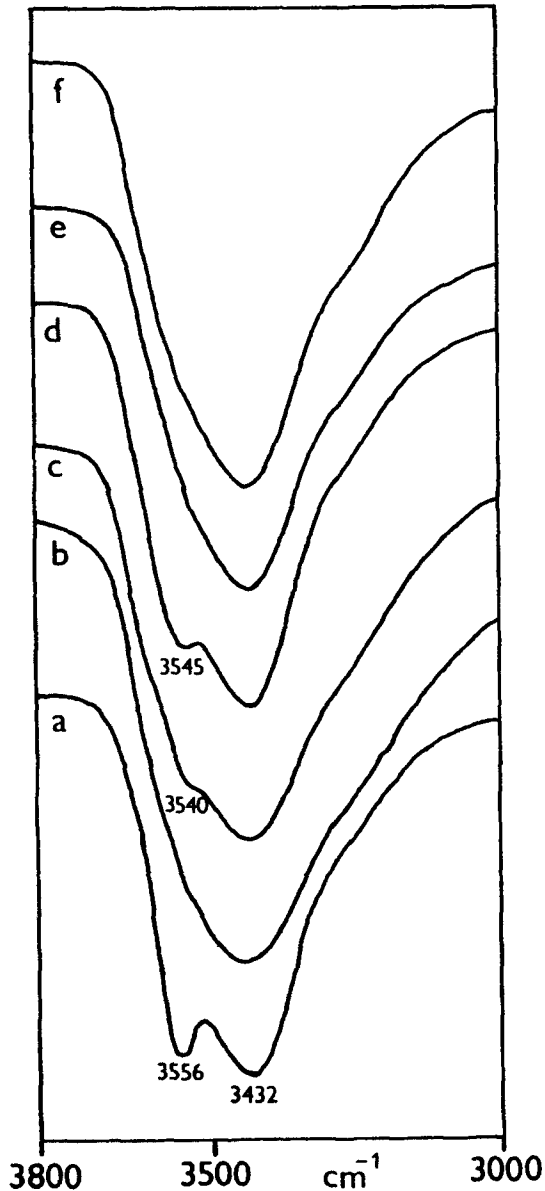


Figure 2. Infrared spectra of unaltered (a), reduced (b), and reoxidized (c) NG-1; and unaltered (d), reduced (e), and reoxidized (f) SWa-1 in the OH stretching region.

(Figures 2a and 2d). The broad absorption at about 3430 cm^{-1} is assigned to adsorbed water. The OH stretching band was lost during reduction (Figures 2b and 2e) and for NG-1 only partially restored upon reoxidation (Figure 2c), while only a weak and ill-defined inflexion could be identified in reoxidized SWa-1 (Figure 2f). Both are superimposed on the broad absorption from water.

Figure 3 shows infrared absorption spectra of untreated and reoxidized samples in the 400 to 1300 cm^{-1} region. The position of the intense Si-O stretching band

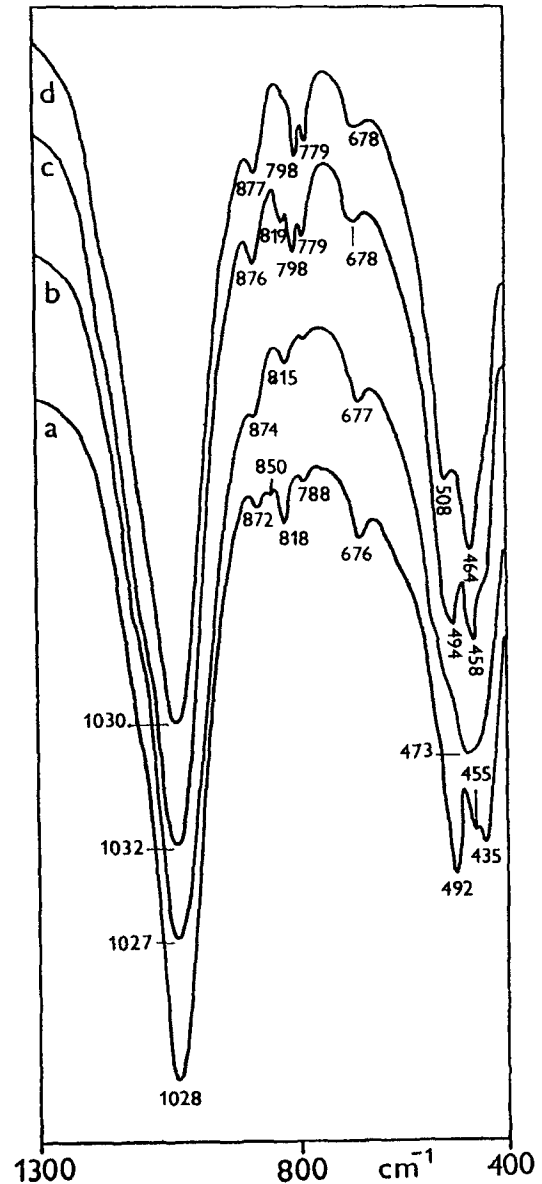


Figure 3. Infrared spectra of unaltered NG-1 (a), reoxidized NG-1 (b), unaltered SWa-1 (c), and reoxidized SWa-1 (d) in 400 to 1300 cm^{-1} region.

near 1030 cm^{-1} appeared to be almost the same in both the unaltered and reoxidized samples. The spectra of reduced samples over this range are not shown because of interference by the absorption of CBD. However, a shift in the Si-O band from 1030 cm^{-1} in unaltered samples to about 1000 cm^{-1} upon reduction was observed, which is similar to the results of Stucki and Roth (1976) and Rozenson and Heller-Kallai (1976) who found that the position of the Si-O band shifted to about 1010 cm^{-1} upon reduction and back to about 1030 cm^{-1} after reoxidation.

Table 3. Thermal gravimetric weight loss in the range 573 to 1073 K of untreated and reoxidized nontronites.

Nontronite	Weight loss (%)	
	Unaltered	Reoxidized
NG-1	5.5	4.7
SWa-1	5.1	4.2

Deformation vibrations for M_2OH groups, where M is the octahedral cation, in nontronites occur in the range 800 to 900 cm^{-1} . The band at 818 and 819 cm^{-1} in NG-1 and SWa-1, respectively, is assigned to deformation modes of Fe_2OH groups (Figures 3a and 3c). This band is lost in the reduced samples (not shown) and is only partially restored by reoxidation (see the weak band at 815 cm^{-1} for NG-1 and only a shoulder for SWa-1, Figures 3b and 3d). The intensity of the band at 872 cm^{-1} for NG-1 and at 876 cm^{-1} for SWa-1, which arises from $FeAlOH$ deformation modes, decreased slightly from the unaltered to the reoxidized states of the clay (Figure 3).

These results indicate that the structural OH content in reoxidized samples is less than in the original, unaltered clay. This was further confirmed by TGA, which revealed a weight loss due to dehydroxylation that was about 20% less for the reoxidized samples than for the unaltered sample (Table 3).

The assignment of the weak absorption at 850 cm^{-1} for unaltered sample NG-1, which was absent for the reoxidized sample, is unclear. Stubican and Roy (1961) reported an auxiliary Fe_2OH vibration band in this range for Manito nontronite. Stucki and Roth (1976) assigned the band at 848 cm^{-1} in sample GAN to a $Fe-(OH)$ interaction, where the OH moves as a unit with respect to Fe. Goodman *et al* (1976), investigating the IR spectra of seven nontronites, also found a weak band at about 847 to 851 cm^{-1} in six of them. They assigned it to $FeAlOH$ groups. The seventh nontronite was SWa-1 with no absorption at 850 cm^{-1} and with the $FeAlOH$ band at 873 cm^{-1} . An alternative assignment of the band near 850 cm^{-1} is to a Si-O(apical) stretching vibration (Russell *et al* 1979). Its disappearance after reoxidation confirms some differences between the untreated and reoxidized NG-1. This vibration is more sensitive to changes in the octahedral layer than is the Si-O(basal) band near 1030 cm^{-1} .

Some changes upon reoxidation could be observed in the region of Si-O bending vibrations. Three absorption bands in NG-1, Si-O-Fe at 492 and 435 cm^{-1} , and Si-O-Si at 455 cm^{-1} coalesced into a broad, diffuse band at about 470 cm^{-1} after reoxidation (Figure 3). The Si-O-Fe band at 494 cm^{-1} in SWa-1 is less intense and moved to 508 cm^{-1} in the reoxidized sample, while the shoulder at about 430 cm^{-1} was lost. The Si-O-Si band at 458 cm^{-1} shifted to 464 cm^{-1} with no change in intensity (Figure 3).

CONCLUSIONS

Citrate-bicarbonate-dithionite treatment of N_2 -purged clay suspensions was a very effective method for the reduction of structural Fe in smectites, producing materials with over 90% of total Fe as $Fe(II)$. The original nontronite structure is unrestored after reduction and reoxidation, and is partially dehydroxylated.

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