

NOTES

REDUCTION AND REOXIDATION OF NONTRONITE: THE DATA REASSESSED

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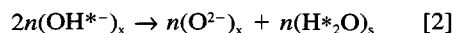
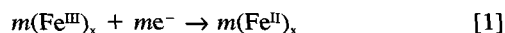
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INTRODUCTION

Redox processes in smectites and particularly in nontronites have been extensively studied and reviewed (Stucki 1988; Stucki and Lear 1990). Recently Komadel et al. (1995) reconsidered the reversibility of the redox reactions. However, despite the numerous investigations, some questions remain unanswered. The following considerations may serve as working hypotheses for further research.

It is generally accepted that nontronites contain Fe predominantly or exclusively in the trivalent state and that this Fe can be reduced and reoxidized. The extent of the reduction depends on the experimental conditions. Russell et al. (1979) demonstrated that tetrahedral Fe is preferentially reduced and dissolved by dithionite reduction. The subsequent discussion will be confined to nontronites with low tetrahedral Fe content, which were used for most of the studies reported in the literature.

Reduction of octahedral Fe(III) in nontronites is associated with loss of structural OH groups. Stucki and Roth (1977) proposed that the transfer of an electron from the reducing agent to structural Fe(III) is accompanied, or immediately followed, by loss of structural H₂O and reprotonation by H⁺ from solution. Using ³H-labeled systems, Lear and Stucki (1985) showed that loss and acquisition of structural protons occurred in the ratio of 2:1. In agreement with Stucki and Roth (1977), they inferred that the initial step is expulsion of water molecules from the structure, followed by protonation of the remaining oxygen. Lear and Stucki (1985) found that the number of hydroxyl groups lost was less than the number of Fe(III) ions reduced. Deprotonation can, therefore, only partially compensate the increase in layer charge caused by Fe(III) reduction. They proposed the scheme:



where m and n are stoichiometric coefficients, $m > n > 0$, H* denotes structural protons and the subscripts x and s refer to clay and solution phases, respectively. This model is consistent with the observed proton mobility, but some other data reported in the literature remain without plausible explanation. I shall address 3 problematic features of the literature data and of the interpretations offered.

DISCUSSION

Lack of Correlation between the Infrared Spectra of Reduced Nontronites and the Degree of Fe Reduction

Changes observed in the infrared spectra on reduction of nontronites include the following: 1) The band at 3560 cm⁻¹, which comprises all of the OH stretching vibrations, is reduced in intensity and shifted to lower frequencies; 2) The band at 1030 cm⁻¹, assigned to the principal Si-O vibrations, shifts to lower frequencies; 3) The band at about 870 cm⁻¹ assigned to Fe-OH-Al and the band at about 815 cm⁻¹ assigned to Fe-OH-Fe bending vibrations are shifted and become weak or disappear (Rozenon and Heller-Kallai 1976; Stucki and Roth 1976, 1977; Russell et al. 1979; Komadel et al. 1995). These changes are only partially reversible upon reoxidation. Whereas Fe(II) is readily reoxidized to Fe(III) and the principal Si-O band is restored to its original position, the intensity of the OH bands, and particularly that assigned to Fe-OH-Fe deformation, is not fully restored (Rozenon and Heller-Kallai 1976; Komadel et al. 1995).

The observed spectral changes are poorly correlated with the degree of Fe reduction. For example, similar

shifts of the principal Si-O band were observed for Fe(II)/Fe(III) ratios ranging from 0.8 (Rozenon and Heller-Kallai 1976) to 9 (Komadel et al. 1995) for nontronite from the same locality. The band at 870 cm^{-1} disappeared in a hydrazine-reduced sample with an Fe(II)/Fe(III) ratio of only 0.08, but persisted with reduced intensity in a dithionite-treated sample with a much higher Fe(II) content (Rozenon and Heller-Kallai 1976). Moreover, even for complete reduction of Fe(III) the proposed model predicts that an appreciable number of OH groups should persist. For example, for nontronite SWa-1, with an initial Fe(III):OH ratio of 2.73:4 and $n/m = 0.32$ (Lear and Stucki 1985), 3.12 of the 4 OH groups are expected to remain after complete reduction, according to the mechanism described by Equations [1] through [3]. Komadel et al. (1995), using a similarly buffered system and the same clay as Lear and Stucki (1985), observed no bands due to OH stretching or bending vibrations after $\sim 90\%$ reduction. Structural changes caused by the reduction of Fe may be expected to lead to shifts in position of OH bands, but are unlikely to eliminate them completely. Band shifts were the principal features of spectra of reduced samples that had been washed before drying (Stucki and Roth 1976, 1977; Russell et al. 1979).

Changes in infrared spectra similar to those observed for reduced nontronites occurred upon deprotonation of smectites, which was either effected by heating with alkali halides (Heller-Kallai 1976) or by exposing nontronite or ferruginous smectites to alkali metal hydroxide solutions under ambient conditions (Russell 1979; Heller-Kallai and Rozenon 1981). Structural protons combine with the anions of the reagents and charge balance is maintained by the cations.

Rozenon and Heller-Kallai (1976) reduced nontronite at alkalinities ranging from pH 5.6 to pH 11.8 in unbuffered dithionite or hydrazine solutions or with hydrazine vapor and dried the unwashed samples. Stucki and co-workers (1976, 1977, 1984, 1985, 1988, 1989, 1990, 1991, 1995) used citrate-bicarbonate (CB) buffered solutions to maintain a slightly alkaline pH (Mehra and Jackson 1959) during dithionite (CBD) reduction. However, when unwashed samples were evaporated to dryness for infrared spectroscopy in the study by Komadel et al. (1995), the pH could no longer have been restricted to the buffer region. It can be concluded that all of the unwashed, dried, reduced nontronites were exposed to high alkalinities. In such samples, deprotonation of structural OH groups, in addition to dehydroxylation, is expected to reduce the intensity of OH absorption bands or to eliminate them completely, as was observed by Komadel et al. (1995).

It appears that the changes in the infrared spectra are due to 2 concurrent processes: reduction of Fe(III) and concomitant changes, and deprotonation in an alkaline environment. Changes in the spectra of washed

samples can be attributed entirely to reduction of Fe(III), whereas both processes occur in the unwashed samples.

The hypothesis that deprotonation occurs upon reduction of structural Fe(III) receives support from pH measurements of unbuffered alkaline dithionite solutions: pHs of 8.1 and 11.8 before reaction with nontronite were decreased to 6.8 and 7.5, respectively, by the reaction (Rozenon 1975).

The concept that deprotonation can occur independently from Fe reduction has important implications for any integrative approach to the interpretation of experimental data. Some of the infrared and Mössbauer spectra were recorded on unwashed dried samples. In contrast, other measurements, for example the determination of surface charge (Stucki et al. 1984), were performed on samples that had been thoroughly washed. The good agreement between Fe(II)/Fe(III) values obtained by wet chemical and Mössbauer analyses of unwashed samples (Komadel et al. 1995) shows that the oxidation state of Fe is independent of the method of sample preparation, if suitable precautions are taken to avoid reoxidation. Infrared spectra, however, reflect loss of hydroxyl groups due to both reduction of Fe(III) and deprotonation and will be affected by the method of sample preparation. Only data derived from spectra of washed samples can therefore be expected to be compatible with the model represented by Equations [1] through [3].

Discrepancy between the Observed Cation Exchange Capacity (CEC) of Reduced Nontronite and that Predicted by the Model

Equations [1] through [3] predict an increase in surface charge of smectites with increasing Fe reduction. Lear and Stucki (1985) showed that the ratio n/m remained constant throughout the range of Fe reduction examined. The surface charge was therefore expected to rise linearly, but this was not observed. Both the total amount of Na^+ in the digested sample (Stucki et al. 1984) and the CEC, measured as the amount of Na^+ exchangeable by Li^+ (Lear and Stucki 1989), increased less than predicted by the model, reached a maximum and decreased before complete reduction of Fe was achieved. Stucki and Lear (1990) suggested 2 possible explanations: either Equations [2] and [3] are not valid and proton mobility is due to some other process, or an electron donor source somewhere within the clay crystal neutralizes the additional positive charge.

The 1st alternative should be seriously considered but, as Stucki and Lear pointed out, no other satisfactory alternative has been proposed that is compatible with the data. No evidence has been presented to support the 2nd explanation. Moreover, if the clay neutralized itself, it would be difficult to explain the fixation of interlayer cations.

A 3rd explanation is that Al dissolved from the clay forms hydroxide complexes or chelates with citrate ions, which are adsorbed in the interlayers and contribute to the neutralization of the layer charge. Stucki et al. (1984) showed that CB dissolved some Si, Fe and Al from smectites. In CBD solution, the concentrations of Si and Fe increased, which demonstrates that dissolution of both the tetrahedral and the octahedral sheets was enhanced. In contrast, the concentration of Al in solution was decreased by addition of dithionite.

Aluminum forms positively charged complexes with citrate ions, which, like Al-hydroxide complexes, can be sorbed in smectite interlayers (Tee and Huang 1986). In the course of washing the reduced nontronites with dilute salt solutions and finally with water, the slightly alkaline solutions were diluted, which is expected to cause a decrease in their pH. The increase in layer charge due to Fe reduction, dilution of the solution and a lower pH are conducive to absorption of the larger, perhaps more highly charged complex Al ions in preference to the smaller, monovalent Na ions. Even if some of the complex ions were exchangeable, they would not have been detected by the method employed by Lear and Stucki (1989) for determining the CEC of reduced nontronites. Adsorption of Al complexes may also explain the apparently erratic results obtained by Stucki et al. (1984) for the concentration of Al in washings from CBD-treated nontronite.

Fixation of Interlayer Na or Other Cations without Complete Collapse of the Smectite Layers

Fixation of interlayer cations in reduced nontronites was reported for K by Chen et al. (1987), for Na by Lear and Stucki (1989) and for K, Ca, Zn and Cu(II) by Khaled and Stucki (1991). Chen et al. (1987) and Lear and Stucki (1989) attributed this phenomenon to layer collapse. This would explain fixation of interlayer cations, but Wu et al. (1989), employing X-ray diffraction and, more conclusively, Stucki and Tessier (1991), using high-resolution transmission electron microscopy, demonstrated that fully collapsed layers did not occur in CBD-treated nontronites. Fixation of cations in expanded layers is difficult to envisage, unless the cations are hydrolyzed and/or some bulky species block their exit, a situation similar to that described for the fixation of various cations including Na under the influence of organic bases (Heller-Kallai et al. 1973). The presence of positively charged Al complexes could prevent complete collapse of the layers as well as trap other cations in the interlayer space. It may be postulated that hydroxyl groups extracted from the structure or produced by the reactions of dithionite may cause hydrolysis of the trapped cations, but there is no evidence to substantiate this speculation.

The assumption that complex Al ions occur in the interlayers of dithionite-reduced nontronite is compat-

ible with the decrease in surface area measured by adsorption of ethylene glycol monoethyl ether (EGME) (Lear and Stucki 1989). Partially collapsed layers with a basal spacing of 12.6 Å (Stucki and Tessier 1991) could not accommodate more than a monolayer of EGME in the interlayers, whereas Lear and Stucki (1989) postulated a double layer for calculating the surface area.

CONCLUSIONS

If my interpretations of published data are correct, then some of the phenomena reported are artifacts of the method of sample preparation. Equations [1] through [3] were derived from experiments with unwashed samples in CB-buffered solutions. In the course of drying reduced nontronites for other experiments, the samples were exposed to more concentrated solutions, whereas upon washing the samples, the solutions were diluted. Under these conditions, the slightly alkaline pH of the systems was no longer controlled, but was either increased or decreased. Different concentrations of the supernatant with the associated changes in pH are expected to affect the reactions between the clay and the surrounding solutions.

In summary, it appears that changes in the infrared spectra of reduced, unwashed nontronite samples are only partly caused by the Fe(III) to Fe(II) conversion; the rest are due to concurrent deprotonation of hydroxyl groups in solutions that become progressively more alkaline upon evaporation. Dilution of the supernatant, with a concomitant decrease in pH, together with the higher layer charge due to Fe reduction, may increase the ion selectivity of the reduced clay for larger cations of higher charge. The presence of Al complexes in the interlayers may account for fixation of cations without complete collapse of the interlayers.

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