



ENVIRONMENTAL RESEARCH BRIEF

Oxidation-Reduction Mechanisms in Iron-Bearing Phyllosilicates

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Abstract

Oxidation-reduction reactions of structural iron in smectite clay minerals were studied with respect to reduction reaction mechanisms and effects on physical-chemical properties of the clay. The purpose of these studies was to assess the implications of redox chemistry at mineral surfaces on transport, transformation, and bioavailability of redox-sensitive metal pollutants. Reducing agents selected were dithionite ($S_2O_4^{2-}$), sulfide (S^{2-}), thiosulfate ($S_2O_3^{2-}$), hydrazine (N_2H_4), ascorbic acid ($C_6H_8O_6$), hydroquinone ($C_6H_6O_2$), and sodium oxalate ($Na_2C_2O_4$). Clay samples were prepared as aqueous suspensions of <2- μm particle-size fractions of Na-saturated, freeze-dried ferruginous smectite. The reductive strength of each reducing agent was determined by measuring the resultant level of Fe(II) in the clay crystal using either a photo-colorimetric method or Mössbauer spectroscopy. Heats of reaction were used with $S_2O_4^{2-}$, S^{2-} , and $S_2O_3^{2-}$ to further determine the extent of redox reaction. The role of free radicals in the reduction process was measured using electron spin resonance (ESR) spectroscopy.

Results revealed that the order of reduction potential for the various agents was $S_2O_4^{2-} > S^{2-} > C_6H_8O_6 > S_2O_3^{2-} > C_6H_6O_2 \approx C_2H_2O_4$. Free radical activity was found only in the reaction with dithionite and was assumed to be due to the sulphydryl ($SO_2^{\cdot-}$) free radical. The free radical was labile in pure solution, but its lifetime increased at least two-fold in the presence of the clay. The signal from the clay- $S_2O_4^{2-}$ suspension may, in fact, be only partially attributable to $SO_2^{\cdot-}$. Reduction by this highly reactive agent may induce electron hopping within the clay crystal itself, which could also be reflected in the persistent signal from the clay. When free radicals or unpaired electrons

are involved in the reducing processes, the following steps may occur: a) the active free radical (e.g., $SO_2^{\cdot-}$) approaches the clay surface and transfers an electron to structural Fe(III), reducing it to Fe(II); b) because of this initial reduction, the crystalline structure is energetically destabilized by an excess negative charge, causing partial dehydroxylation, which, in turn, energetically activates point defects, such as tetrahedral aluminum (Al) sites, within the clay crystal; c) excess electrons at point defects may pass to structural Fe(III), reducing it. These processes continue until all structural Fe(III) is reduced.

At least two types of reducing agent were identified based on their reducing mechanism, namely, those with and those without free radical activity. The number of steps involved in the reduction process depends on the reduction potential of the reducing agent. Measurements of rheological characteristics of oxidized and reduced clay suspensions indicated that structural Fe(II) increases the attractive bond energies between clay particles. The type of bonding between particles is uncertain; hydrogen bonding may make an important contribution. The effects of microbial reduction and interactions with clay minerals were reviewed.

Background

The risk that metal cations pose to the global ecosystem depends largely on their activity in porous media, which can be calculated only if the true exposure levels of the cations to biota are known. Exposure is determined by the transport, transformation, and bioavailability characteristics of the metal cation, which in turn depends on speciation. The fate of redox-active pollutants in porous media are governed by solubility and adsorption processes, but modifications also occur due to redox reactions in the solid-liquid interface. These effects are governed by the thermodynamic energy of redox couples and

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by the rates at which reactions proceed. Solid surfaces in the media create a unique chemical environment that influences both the energetics and the kinetics of reactions among chemical components.

Knowledge of the solution concentration or activity of metals alone is insufficient to provide a complete model of exposure because, in this interfacial region, two phenomena occur that are absent in solution. First, the solid surfaces become an active participant, as both reactant and product, in the chemical reactions. Second, chemical constituents in solution come under the influence of van der Waals, electrostatic, hydration, and possibly other forces that alter their total potential energy or reactivity. Accurate definition of speciation thus requires an understanding of the processes and forces that are operating in the interface, in terms of both the participants and the rates of reaction. When this understanding is achieved, the capability to model and predict more successfully the behavior of percolating ions in porous media will be greatly enhanced.

The purpose of this study was to characterize more fully the physical-chemical properties and processes that occur when iron-rich clay minerals undergo reduction and reoxidation. Redox reaction mechanisms in phyllosilicate clay minerals were studied with respect to the free radical activity, heat of reaction, and effect on clay interlayer forces. Several reducing agents representing a wide range of reduction potentials and free radical activities were compared, and the redox interactions between clays and microorganisms were reviewed. The project also produced a publication containing a detailed review of the thermodynamic basis of redox reactions in clays (Stucki *et al.*, 1992).

Methods

The <2- μm particle-size fraction of ferruginous smectite SWa-1 (Source Clays Repository of The Clay Minerals Society, Columbia, Missouri) was Na-saturated, washed free of excess salts to approximately 10^{-3} M Na, and freeze dried. Twenty-five- to 30-mg portions of the freeze-dried clay were then resuspended for subsequent reduction treatments generally by mixing with 37.5 ml of high-purity H_2O (18 Mohm cm^{-1} resistivity) and 2.5 ml of citrate-bicarbonate buffer (1 part 0.3 M $\text{Na}_2\text{C}_6\text{O}_6 \cdot 6\text{H}_2\text{O}$ and 8 parts 1 M NaHCO_3). The mixture was shaken gently overnight. The citrate-bicarbonate (CB) buffer was used in order to maintain near-neutral pH and thereby minimize acid dissolution of the clay during treatment with $\text{Na}_2\text{S}_2\text{O}_4$. In some experiments, however, only high purity H_2O was used. Structural Fe in the clay was reduced at room temperature (nominally 25°C), for time periods ranging from 1 to 57 hr, by reagent-grade reducing agents. Those used were sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$), sodium sulfide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$), sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$), hydrazine (N_2H_4), ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$), hydroquinone ($\text{C}_6\text{H}_6\text{O}_2$), and sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$). Iron(II) and total Fe were measured quantitatively by the photo-colorimetric method of Komadel and Stucki (1988), or semi-quantitatively by Mössbauer spectroscopy.

Electron spin resonance (ESR) spectra were obtained at room temperature using a Bruker ESP 300 (X-band) ESR spectrometer equipped with both liquid and solid sample cells. Each reducing agent was analyzed in the solid phase and in solution with either high purity H_2O or CB buffer solution. ESR spectra of the clays also were obtained after resuspension, but in the absence of reducing agent. Each reducing agent then was added to the suspended clay to bring the Na concentration in suspension to 0.01 M, and the mixture was immediately loaded into the ESR liquid cell. ESR spectra were obtained after various time intervals up to 57 hr.

The resonance peak position in each ESR spectrum was expressed in terms of the value of g , which was calculated from the magnetic field intensity (H) using the relation

$$g = \frac{h\nu}{\beta H} \quad (1)$$

where h is Planck's constant, ν is the microwave frequency with which the sample was irradiated while the magnetic field was varied (for an X-band ESR spectrometer, the value of ν is about 9 GHz), and β is the Bohr magneton ($= 9.2741 \cdot 10^{-21}$ erg gauss $^{-1}$).

Line intensity is an important characteristic of an ESR spectrum and can be a qualitative indicator of spin concentrations if relaxation and saturation effects are absent. According to Vedrine (1980), the spin populations directly determine the magnetic susceptibility, χ_o , to which the line intensity, I , is proportional according to the relationship

$$I \propto \chi_o = \frac{1}{3kT} g^2 \beta^2 N_o \bar{J}(\bar{J} + 1) \quad (2)$$

where \bar{L} , \bar{S} , and \bar{J} ($= \bar{L} + \bar{S}$) are, respectively, the orbital, spin, and total angular momenta of the electron; N_o is the number of unpaired spins; k is Boltzmann's constant; T is the absolute temperature; and g is the "so called" electron free-spin g -factor. In the present study, all of the terms on the right side of Equation 4, except N_o , were assumed to be constant. The intensity of the ESR signal thus was assumed to be directly proportional to N_o and was obtained by integrating the area under the pre-derivative spectrum.

For rheological measurements, clay suspensions were prepared as above but treated only with $\text{Na}_2\text{S}_2\text{O}_4$, Na_2SO_4 (sodium sulfate), or NaCl (sodium chloride). Shear stress vs. shear rate for different treatments were made using a Fann rotational viscometer (Model 35, Fann Instrument Corp., Houston, TX) at 25°C . During these measurements, the R1-B1 rotor-bob combination was used with a spring having a constant of 0.2 or 0.5. When the oxidation of the structural iron was a factor, the measurement was made inside an inert-atmosphere glove box.

Enthalpy, or heat of reaction, was measured using a Calvet microcalorimeter in the laboratory of Dr. Philip F. Low at Purdue University, using the techniques described by Gan (1990) and by Gan and Low (1992).

Results and Discussion

Comparison of Reducing Agents

The reduction of structural iron in ferruginous smectites by different reducing agents has important implications for the behavior of redox-sensitive metals in the environment. Reducing agents used were dithionite ($\text{S}_2\text{O}_4^{2-}$), sulfide (S^{2-}), thiosulfate ($\text{S}_2\text{O}_3^{2-}$), stannous chloride (SnCl_2), hydrazine (N_2H_4), ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$), oxalate ($\text{C}_2\text{H}_2\text{O}_4$), phenol ($\text{C}_6\text{H}_6\text{O}$), and hydroquinone ($\text{C}_6\text{H}_6\text{O}_2$). Experiments were carried out at different temperatures and with different contact times between clay and reducing agent. Survey results revealed that great differences in reducing power exist among these reducing agents. Results from three of these are compared in Figure 1. In the inorganic group, $\text{S}_2\text{O}_4^{2-}$ demonstrated very strong reducing ability, whereas $\text{S}_2\text{O}_3^{2-}$ was the weakest. In the organic group, the reducing power was in the order $\text{C}_6\text{H}_8\text{O}_6 > \text{C}_6\text{H}_6\text{O}_2 > \text{C}_2\text{H}_2\text{O}_4 \approx \text{C}_6\text{H}_6\text{O}$. The reduction process sometimes involves ancillary

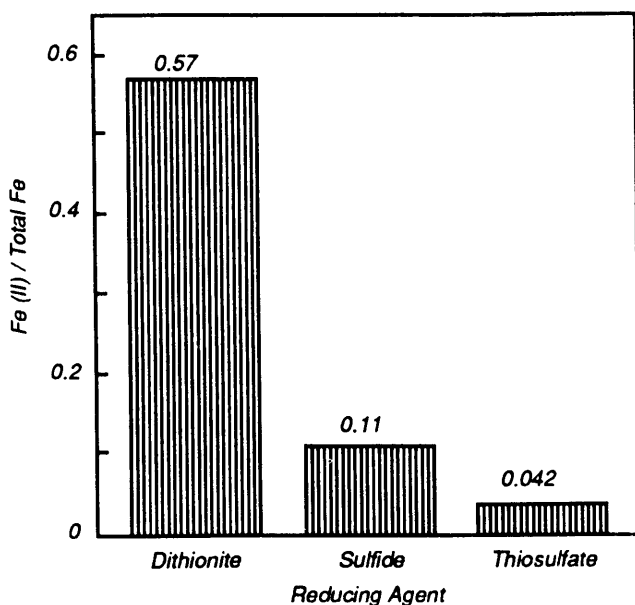


Figure 1. Reduction of structural Fe in Na smectite SWa-1 by freshly prepared 0.01 M solutions of $\text{Na}_2\text{S}_2\text{O}_4$, Na_2S , and $\text{Na}_2\text{S}_2\text{O}_3$ for 24 hr at 25°C.

reactions in the mineral structure, depending on the reducing power of the reductant.

Free Radical Activity

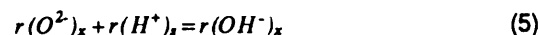
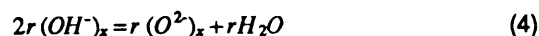
Further comparisons were made among the inorganic group of reducing agents. Figure 1 reveals the relative reducing abilities of $\text{S}_2\text{O}_4^{2-}$, S^{2-} , and $\text{S}_2\text{O}_3^{2-}$ in ferruginous smectite (SWa-1) at room temperature (25°C). Hydrazine's effect was similar to that of S^{2-} . Notice that $\text{S}_2\text{O}_4^{2-}$ is peculiar and demonstrates a much higher ability to reduce structural Fe(III) than any of the other compounds.

The standard electrode reduction potential, \mathcal{E}° , of $\text{S}_2\text{O}_4^{2-}$ is approximately -1.12 V (Vanysek, 1992). But N_2H_4 (or its conjugate acid N_2H_5^+ if hydrated), which generally reduces only about 10% of the structural Fe in these same clays (Stucki *et al.*, 1976; Rozenson and Heller-Kallai, 1976a, 1976b; Stucki and Roth, 1977; Russell *et al.*, 1979; Stucki, 1988; Stucki and Lear, 1989), has an \mathcal{E}° of -0.94 V (Douglas *et al.*, 1983). Obviously, the difference between these two reducing agents must be due to something other than their standard electrode potentials.

The ESR spectra of these same reducing agents revealed no signal from N_2H_4 , $\text{S}_2\text{O}_3^{2-}$, or S^{2-} , and a strong signal from $\text{S}_2\text{O}_4^{2-}$ (Figure 2). These results clearly indicate the presence of unpaired electrons in $\text{S}_2\text{O}_4^{2-}$ by the resonance signal centered at about $g = 2.0091$ for the solid phase and shifted to $g = 2.0113$ for the solution phase. The signals were most intense in the freshly prepared $\text{S}_2\text{O}_4^{2-}$ solutions, then decreased in intensity over time, disappearing completely after about 57 hr in the 1.0 M solution, and after less than 4 hr in the 0.01 M solution.

When $\text{S}_2\text{O}_4^{2-}$ was added to the clay suspension, making the final Na concentration 0.01 M, a moderately strong ESR signal was evident initially (Figure 3A), then after 4 hr the signal became even stronger than that of the pure $\text{Na}_2\text{S}_2\text{O}_4$ solution of the same concentration (0.01 M) (Figure 3B). The signal per-

sisted for up to 9 hr of contact between clay and $\text{Na}_2\text{S}_2\text{O}_4$, which was more than double its lifetime in pure $\text{Na}_2\text{S}_2\text{O}_4$ solution. Hence, the concentration of free radicals from the $\text{Na}_2\text{S}_2\text{O}_4$ solution was preserved and enhanced if added to the clay. Apparently, the SWa-1 initially reacted with SO_2^\cdot which donated an electron to the clay; but as the reaction proceeded, unpaired electrons were produced within the clay crystal structure, giving rise to the persistent signal in Figure 3B. This explanation is consistent with earlier studies (Stucki *et al.*, 1984b; Lear and Stucki, 1985; Stucki and Lear, 1989) that strongly indicated, based on layer charge measurements, that some of the Fe is reduced by a source of electrons (Z) within the clay structure. Aluminum-substituted tetrahedral sites may provide such a source of high-potential electrons due to the lower-valent tetrahedral cation. This step would have occurred only after sufficient Fe(III) was reduced by SO_2^\cdot to either activate or catalyze the movement of internal electrons to structural Fe(III). This process would be similar to the reaction proposed by Stucki and Lear (1989):



where subscripts x and s denote clay and solution phases, respectively; Z is an unidentified electron donor located within the clay crystal, which may be the Al-substituted tetrahedral

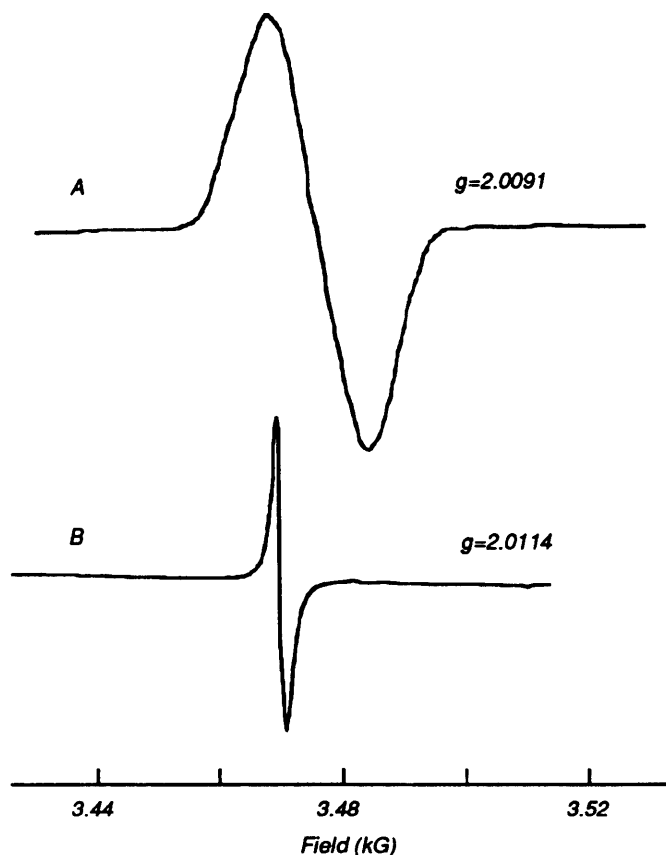


Figure 2. ESR spectra of solid (A) and 1.0 M aqueous solution (B) on $\text{Na}_2\text{S}_2\text{O}_4$.

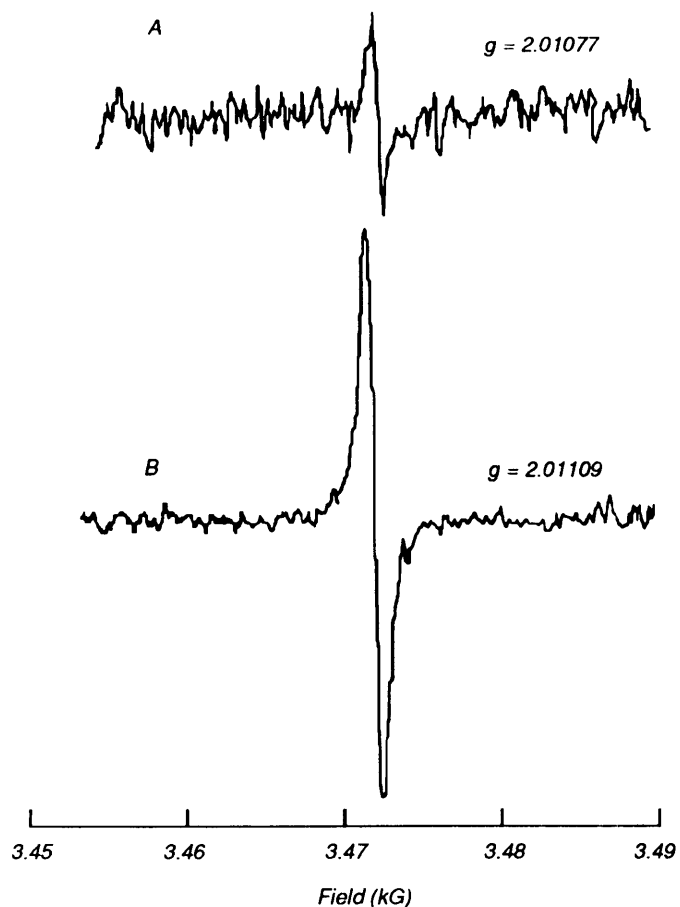


Figure 3. ESR spectra of 0.01 M $\text{Na}_2\text{S}_2\text{O}_4$ in smectite SWa-1 suspension: A) fresh, B) after 4 hr.

sites as suggested above; e^- represents the reducing agent in the solution surrounding the clay crystal, and is believed to be the $\text{SO}_2\cdot^-$ free radical when $\text{Na}_2\text{S}_2\text{O}_4$ is the reducing agent; and m , r , and a are stoichiometry coefficients. According to this hypothesis, structural Fe is reduced partially by internal and partially by external reducing agents, and the reduction is accompanied by dehydroxylation and reprotonation reactions. Lear and Stucki (1985) determined that two of the stoichiometry coefficients are linearly related, viz., $r = 0.32 m$, but the value of a has yet to be determined.

The point of contact between the clay and the reducing agent is still unknown. The same arguments of coulombic repulsion against the $\text{S}_2\text{O}_4^{2-}$ anion approaching the negatively charged basal surfaces also apply to the $\text{SO}_2\cdot^-$ free radical anion, except perhaps the high reactivity of the free radical would overcome the coulombic repulsion energy barrier. Like-charge collisions where one is a free radical are not unusual, however (Neta *et al.*, 1988). Alternatively, the free radical may react at the edges of clay layers, setting up a conduction pathway through the layer to internal Fe ions. Such a process is conceivable in Fe-rich smectite, and may explain why Rozenson and Heller-Kallai (1976a, 1976b) observed incomplete reduction of Fe-poor montmorillonite by $\text{Na}_2\text{S}_2\text{O}_4$.

The conductivity of electrons from the layer edge through the octahedral sheet would depend heavily on the presence of the transition metal. But Lear and Stucki (1987), based on measurements of magnetic exchange interactions and of interva-

lence electron transfer, concluded that structural Fe is reduced nearly randomly within the octahedral sheet. Reduction only from layer edges would likely create a reducing front passing through the layer, creating homogeneous domains of Fe(II) and Fe(III) with a rather constant number of Fe(II)-Fe(III) pairs at the reduced-oxidized interface. Results of Lear and Stucki (1987) clearly reject this possibility in ferruginous smectite.

Heats of Reaction

The driving force for any chemical reaction is reflected totally in the partial molar Gibbs free energy, $\Delta\bar{G}$, of the reaction, which is given by the sum of the changes in enthalpy, $\Delta\bar{H}$, and entropy, $\Delta\bar{S}$, viz.,

$$\Delta\bar{G} = \Delta\bar{H} - T\Delta\bar{S} \quad (6)$$

where T is the absolute temperature. A more detailed thermodynamic treatment is provided by Stucki *et al.* (1992).

Enthalpy changes were measured for the reaction of ferruginous smectite with reducing agents $\text{S}_2\text{O}_4^{2-}$, S^{2-} , and $\text{S}_2\text{O}_3^{2-}$. As noted above, the strength of these three reducing agents is in the order $\text{S}_2\text{O}_4^{2-} > \text{S}^{2-} > \text{S}_2\text{O}_3^{2-}$. The value of $\Delta\bar{G}$, therefore, should follow the same trend. The value of $\Delta\bar{H}$ is known as the heat of reaction and can be measured experimentally with a microcalorimeter. If $\Delta\bar{S}$ is constant in all three reactions, $\Delta\bar{H}$ should reflect $\Delta\bar{G}$.

The heat of reduction reaction was found to follow the order $\text{S}_2\text{O}_4^{2-} > \text{S}_2\text{O}_3^{2-} > \text{S}^{2-}$. Compared to the levels of Fe(II) achieved, the results for $\text{S}_2\text{O}_3^{2-}$ and S^{2-} are reversed, suggesting that entropy changes are greater in the S^{2-} treatment. Further explanation of this phenomenon will require more detailed understanding of the S^{2-} -clay reaction. These results also indicate that, in addition to considering $\Delta\bar{H}$, one must not overlook the $\Delta\bar{S}$ term.

Recall that the reducing power of $\text{S}_2\text{O}_4^{2-}$ deteriorates with the age of the solution because of the lability of the sulphoxylate ($\text{SO}_2\cdot^-$) free radical, but S^{2-} and $\text{S}_2\text{O}_3^{2-}$ solutions are unaffected by time. Measurements of heats of reduction reaction using variably aged solutions revealed that $\Delta\bar{H}$ decreased with increasing age only with the $\text{S}_2\text{O}_4^{2-}$ solutions. These results, therefore, are consistent with the free radical studies that found that reducing power of $\text{S}_2\text{O}_4^{2-}$ is labile.

Microbial Reduction of Clay Fe

Microorganisms apparently also reduce structural Fe in clay minerals (Komadel *et al.*, 1987; Stucki *et al.*, 1987; Wu *et al.*, 1988). The mechanisms for microbial reduction have yet to be identified, and many questions arise as to the precise role of microorganisms in Fe redox reactions. For instance, does the reduction occur because of a membrane-bound process requiring intimate contact between clay mineral and organism, or is it due to an extra-cellular or exudate compound from the organism? Is it an aerobic or anaerobic process? What are the metabolic sequences responsible for reduction? Which organisms are most efficient? How does microbial reduction affect physical-chemical properties of the minerals and their effect on metal fate, transport, and bioavailability characteristics? Studies to answer these questions are currently underway (e.g., Gates *et al.*, 1991, 1992).

Reduction Process Schematic

The reduction mechanism(s) for Fe(III) smectites depend on the nature of the reducing agent and medium in which reduc-

tion takes place. Laboratory methods may or may not replicate actual redox processes that occur in nature but should provide insights as to the potential range of reactions that can occur. Standardization of techniques, natural variations among samples, and handling of air-sensitive clays all are factors that must be considered before valid comparisons between studies can be made. In Figure 4 is a conceptual model illustrating how the reduction potential or energy of the external reducing electron may determine the extent of Fe(II) produced and the type of ancillary processes that occur, such as those represented in Equations 3 through 5. A small amount of Fe(III) can be reduced to Fe(II) in the clay crystal by a number of reducing agents having only modest reductive capability (having energy $\approx E_1$), as indicated by the small energy barrier A. The principal effect of these agents is simply the reduction of Fe(III) to Fe(II), with a concomitant increase in layer charge and probably a decrease in the crystal lattice stabilization energy because the dioctahedral structure naturally prefers trivalent octahedral cations.

Further reduction by agents having greater reductive capabilities (having energies $\geq E_2$ or E_3), such as the $SO_2^{\cdot-}$ free radical, invokes a dehydroxylation process as indicated by energy barrier B. Dehydroxylation was reported by Roth and Tullock (1973) and Stucki and Roth (1976), based on infrared spectral information, and by Lear and Stucki (1985) based on tritium exchange between structural OH in the clay and H_2O in the surrounding solution. These changes in the clay crystal, combined with the high electron energy of the free radical, eventually surmount energy barrier C, which mobilizes electrons already present in the clay crystal into molecular or metallic-like orbitals or into semiconductor-like conductivity bands. The de-

localized electrons then are captured by Fe(III), thus effecting further Fe reduction.

Because these latter electrons were initially present in the clay, the change in Fe(II) content at this point is not reflected in the total layer charge of the clay, which explains the discrepancy between the predicted and the observed layer charge described by Stucki *et al.* (1984b), Lear and Stucki (1985), and Khaled and Stucki (1991). The energy barrier configuration may vary depending on the total Fe content of the clay because a low-Fe smectite, such as montmorillonite, may have a much lower metallic character than a high-Fe smectite, which would diminish the probability for the electron delocalization process represented by barrier C (Figure 4).

Experimental results presented herein may explain some aspects of why $Na_2S_2O_4$ reduces more Fe(III) in the clay structure than other reducing agents that have similar electrode reduction potentials. When unpaired electrons are involved in the reducing processes, the following steps may take place: a) the active free radicals (e.g., $SO_2^{\cdot-}$) approach the clay surface and transfer electrons to structural Fe(III), reducing it to Fe(II); b) because of this initial reduction, the crystalline structure is energetically destabilized by an excess negative charge, causing partial dehydroxylation, which, in turn, energetically activates point defects, such as tetrahedral Al sites, within the clay crystal; c) excess electrons at point defects may pass to structural Fe(III), reducing it. The processes continue until all structural Fe(III) is reduced. At least two types of reducing agent are identified based on their reducing mechanism, namely, those with and those without free radical activity.

Effects of Reduction on Interlayer Forces

Studies by Stucki *et al.* (1984c), Chen *et al.* (1987), Khaled and Stucki (1991), and Stucki and Tessier (1991) indicated that Fe reduction increased attractive forces between clay layers, but the exact nature of these is still unknown. Shear stress measurements in the present study indicate that hydrogen bonding may be an important factor. Oxidized and reduced clay suspensions were placed in a rotational viscometer, which measured the shear stress (s) as a function of the shear rate (σ). Results were then plotted according to the relation

$$s = \eta_{pl}\sigma + \theta \quad (7)$$

where the slope, η_{pl} , is the plastic viscosity of the system, and the y-intercept, θ , is the Bingham yield stress. θ is a measure of the number of interacting clay particles and the strength of bonds or links that occur between them, as given by the relation

$$\theta = \frac{E_A K_i N^2}{2} \quad (8)$$

where E_A is the energy of the interparticle bond, N is the number of particles, and K_i is a constant.

Flow curves of reduced and unaltered 1% suspensions of ferruginous smectite SWa-1 are shown in Figure 5. Notice that the slope (η_{pl}) and y-axis intercept (θ) are higher for the reduced than for the unaltered sample. According to Stucki and Tessier (1991), the particles are larger in reduced compared to oxidized smectites, so for the same mass the number of particles, N , must be less in the reduced clay. Hence, by Equation (8), the particle interaction energy, E_A is stronger in the reduced clay.

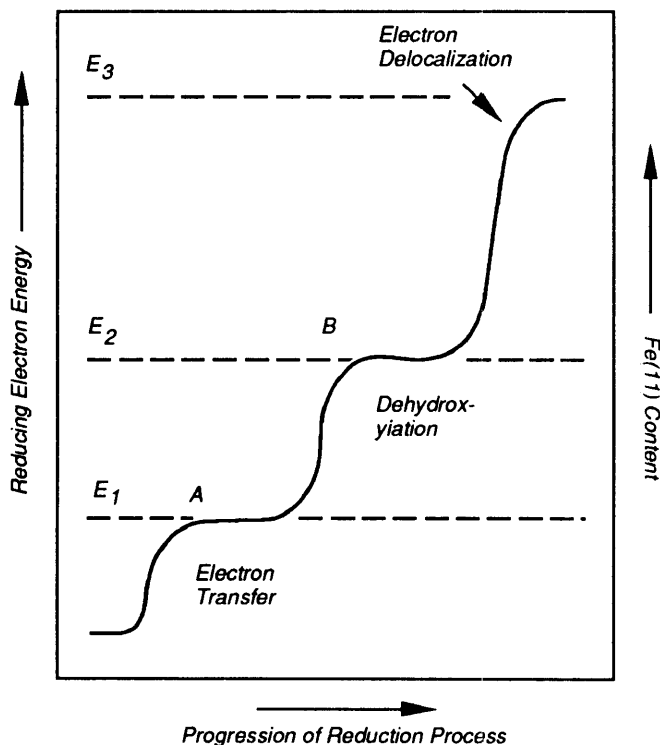


Figure 4. Conceptual model of relationships among energy of reducing electrons, structural Fe(II) content, and progression of the reduction process in ferruginous smectites.

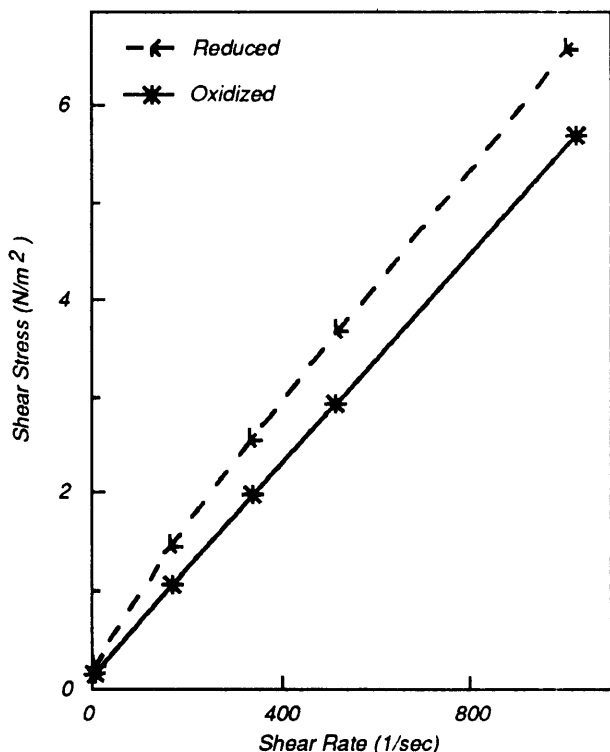


Figure 5. Flow curves of oxidized and reduced 1% suspensions of Na-nontronite (SWa-1) at 10^3 M Na^+ concentration.

Figure 6 shows the flow behavior of reduced and unaltered SWa-1 clay in 3% suspension, and compares the effects of three different anions, namely, $\text{S}_2\text{O}_4^{2-}$ (reducing agent), SO_4^{2-} , and Cl^- . The Na^+ concentration was the same in all three samples. Notice that both $\text{S}_2\text{O}_4^{2-}$ and SO_4^{2-} have greater effects than Cl^- . The difference between the $\text{S}_2\text{O}_4^{2-}$ and SO_4^{2-} may be attributed to structural Fe reduction, but the difference between the sulfate and Cl^- must be due to different anion effects. The ability of Cl^- to break hydrogen bonds is well known, so the smaller interaction energy between particles in the presence of Cl^- may be due to fewer or weaker H bonds between the particles.

The increase of particle interaction indicated by increasing θ and η clearly reveals that the reduction of structural Fe(III) increases the attractive forces between particles. This, in turn, likely alters the particle arrangement in the system. This supports the hypothesis that reduction of structural Fe(III) increases the proportion of collapsed layers, decreases the swelling (Stucki *et al.*, 1984a; Stucki and Lear, 1989; Wu *et al.*, 1989; Gates *et al.*, 1991), and changes the hydraulic conductivity of the system (Shen *et al.*, 1992).

These and other results from this study help us understand the colloidal properties of the oxidized and reduced samples, and lead to the following general conclusions: (1) The interaction between clay particles in aqueous suspension increases as the solid concentration increases; the sol to gel transition is found to occur at a solid to liquid concentration of 2%. (2) Stronger interaction was detected for the intermediate particle-size fraction <2 and >0.5 μm . (3) Interaction between particles increases as the Na^+ concentration increases up to 0.01 M, then

strong flocculation decreases the particle interaction energy. (4) Reduction of structural Fe(III) increases the interparticle forces as indicated by increases in θ . And, (5) the possible forces controlling the interaction energy between particles are hydrogen bonding and cation bridging.

Environmental Implications

Soil serves many functions in the environment. It acts as a geologic filter scavenging undesirable solutes from a percolating solution, or it may release previously sorbed substances back into the surrounding media depending on climatic and other conditions. The surfaces of soil minerals provide unique chemical environments that often facilitate the transformation of some chemical species to very different forms, some of which may be less desirable and more mobile, or vice-versa. Changing the surface properties of the minerals through oxidation or reduction of structural Fe will likely have a great impact on the capability of the clay interlayers to trap or sequester metal cations, which in turn will affect the bioavailability of the metal.

The chemical nature of mineral surfaces is widely recognized as one of the most significant factors contributing to the fate and behavior of contaminants, but these properties are generally considered to be unchanging during the time of contaminant exposure and reaction. The aforementioned studies clearly demonstrate, however, that mineral surface chemistry is greatly modified by changes in the oxidation state of Fe in the mineral crystal structure.

The redox activity of mineral surfaces also affect the oxidation state, and consequently the speciation and chemical behavior,

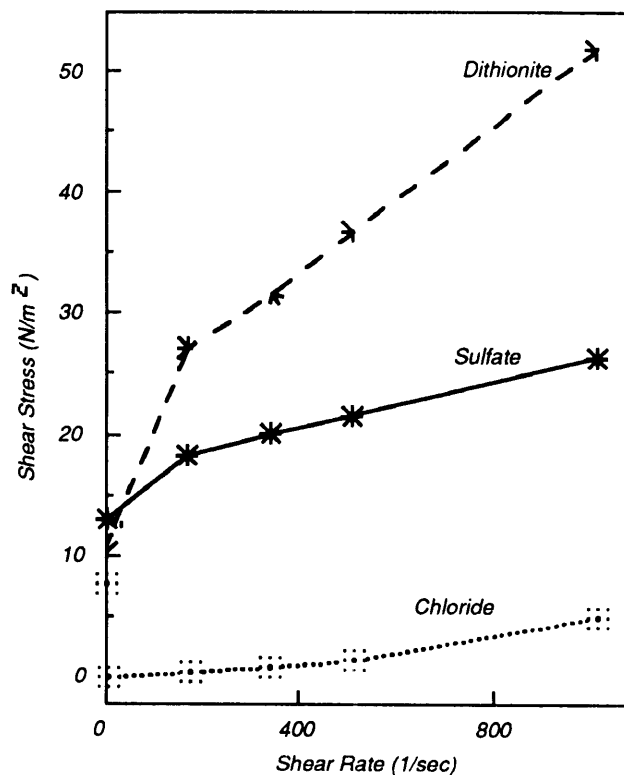


Figure 6. Flow curves of oxidized and reduced 3% suspensions of Na-nontronite (SWa-1) at 0.5 M Na^+ concentration.

of redox-sensitive metal ions in the surrounding solution. The application of such insight can be seen in the case of Cr(VI), a major environmental pollutant. Chromium may exist as Cr(VI) anion in solution (CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$). A reduced Fe clay may react with the Cr(VI) species, reducing it to Cr(III), which will either be cationic or precipitated as the oxide. By this process, Cr will be less mobile and less hazardous in the soil environment. Geochemical models, e.g., MINTEQA (Allison *et al.*, 1991), for predicting the fate and behavior of metals in the vadose zone, therefore, must account for redox transformations of the metal ion at mineral surfaces.

The exposure of soil minerals to redox-sensitive sorbates, solvents, humic materials, varying redox environments, and microorganisms may invoke surface chemical changes *in situ* over short time periods and thereby produce vital differences in the speciation and reactivity of all components in the soil-water system.

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