

REDUCTION OF STRUCTURAL IRON IN FERRUGINOUS SMECTITE BY FREE RADICALS

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Abstract—The oxidation state of structural iron greatly influences the physical-chemical properties of clay minerals, a phenomenon that may have significant implications for pollutant fate in the environment, for agricultural productivity, and for industrial uses of clays. Knowledge of redox mechanisms is fundamental to understanding the underlying basis for iron's effects on clays. Past studies revealed that the extent of Fe reduction varied depending on the reducing agent used, but this variation may not have been a simple function of the reduction potential of the reducing agent. The objective of this study was to identify the relationship between the Fe reduction mechanism and free radical activity in the reducing agent. Several reducing agents and their mixtures with the Na-saturated, 0.5 to 2 μm size fraction of ferruginous smectite (SWa-1) were analyzed by electron spin resonance (ESR) spectroscopy to determine the presence of unpaired electrons or free radicals. Only $\text{Na}_2\text{S}_2\text{O}_4$ exhibited paramagnetic free-radical behavior with a signal at about $g = 2.011$, which was attributed to the sulphoxylate ($\text{SO}_2^{\cdot-}$) free radical. The free radical was labile in aqueous solution, and the ability of $\text{Na}_2\text{S}_2\text{O}_4$ solution to reduce structural Fe in the smectite decreased with age of the solution and paralleled the disappearance of the free radical signal in the ESR spectrum. The paramagnetic species was preserved and enhanced if $\text{Na}_2\text{S}_2\text{O}_4$ was added to the clay suspension, indicating that either the clay surface stabilized the $\text{SO}_2^{\cdot-}$ radical or the additional unpaired electrons were produced in the clay structure.

Key Words—Clay, Dithionite, Electron spin resonance spectroscopy, ESR, Hydrazine, Iron, Reduction, Smectite, Sulfide, Thiosulfate.

INTRODUCTION

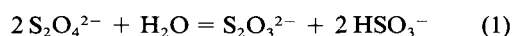
The reduction of structural Fe in smectite clay minerals has been the subject of numerous investigations (see reviews by Stucki, 1988, and Stucki and Lear, 1989), each having a primary goal of understanding the underlying redox mechanism. The redox state of the clay and knowledge of how to control or exploit it are of great importance to agriculture, industry, and the environment because of their profound effects on many physical-chemical properties of the clay (Stucki and Lear, 1989; Lear and Stucki, 1989; Komadel *et al.*, 1990; Khaled and Stucki, 1991; Stucki and Tessier, 1991).

In these studies, a number of different reducing agents were employed, but the precise electron transfer mechanism and the basis for differences in the reducing power of the various agents have yet to be identified. The most commonly used reducing agent was sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$), which has a standard electrode reduction potential, E° , of approximately -1.12 V (Lide, 1992). The potency of $\text{Na}_2\text{S}_2\text{O}_4$ as a reducing agent for

clays was demonstrated by Komadel *et al.* (1990), who used it to reduce virtually all of the structural Fe in nontronites. But hydrazine (N_2H_4 , or its conjugate acid N_2H_5^+ if hydrated), which has an E° of -0.94 V (Douglas *et al.*, 1983), 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).

Why should these two reducing agents behave so differently with respect to Fe reduction in the clay when their reduction potentials are similar? And why is the $\text{S}_2\text{O}_4^{2-}$ anion better able to approach the negatively charged clay surfaces than are the neutral or cationic hydrazine species? Rozenson and Heller-Kallai (1976a) hypothesized that reduction of Fe-rich smectites by $\text{S}_2\text{O}_4^{2-}$ occurs at the mineral edges, which may be more electrostatically inviting to an anion than are negatively charged basal surfaces. But because total reduction can be achieved with $\text{S}_2\text{O}_4^{2-}$ (Komadel *et al.*, 1990), reason suggests that this reducing agent must access the basal surfaces in order for electrons to move to all of the Fe located in the octahedral sheets. This is only a negative argument, however, and fails to explain how the $\text{S}_2\text{O}_4^{2-}$ anion overcomes the like-charge electrostatic repulsion at the basal surfaces.

The $\text{S}_2\text{O}_4^{2-}$ ion disproportionates in H_2O , giving

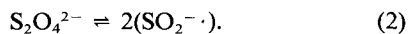


and the hydrogen ion activity of the solution increases

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rapidly to pH 2 or less, depending on the amount of $\text{Na}_2\text{S}_2\text{O}_4$ added. It also breaks down into two sulphyloxy-late ($\text{SO}_2^{\cdot-}$) free radicals by the monomerization reaction (Dunitz, 1956; van der Heijde, 1953; Lynn *et al.*, 1964; Nickless, 1968):



Hodgson *et al.* (1956) identified the paramagnetic $\text{SO}_2^{\cdot-}$ free radical species in solid $\text{Na}_2\text{S}_2\text{O}_4$ using electron spin resonance (ESR) spectroscopy, reporting a g value of 2.01. Rinker *et al.* (1959) reported ESR results from $\text{Na}_2\text{S}_2\text{O}_4$ solutions, showing that the free radical also existed in aqueous solution at $g = 2.0051$. In a preliminary experiment, Stucki and Lear (1989), upon observing the ESR signal in freshly prepared $\text{Na}_2\text{S}_2\text{O}_4$ solutions, hypothesized that the free radical could have sufficient reductive capability to reduce structural Fe from the basal surfaces of smectite in spite of the coulombic barrier. The purpose of the present study was to test the hypothesis of Stucki and Lear (1989) by establishing more definitively the relationship between free-radical behavior in the reducing agent, its ability to reduce structural Fe in ferruginous smectite, and the Fe reduction mechanism.

MATERIALS AND METHODS

The 0.5 to 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. A 25- to 30-mg portion of the freeze-dried clay was then resuspended for subsequent reduction treatments by mixing with 37.5 ml of high-purity H_2O (18 Mohm-cm resistivity) and 2.5 ml of citrate-bicarbonate buffer (1 part 0.3 M $\text{Na}_2\text{C}_6\text{O}_5 \cdot 6\text{H}_2\text{O}$ 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 1 to 57 hr by reagent-grade sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$), sodium sulfide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$), or sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$). Iron(II) and total Fe were measured by the 1,10-phenanthroline method of Komadel and Stucki (1988).

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 were also 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 was expressed in terms of the value of g , which was calculated from the magnetic field intensity (H) using the relation

$$g = \frac{h\nu}{\beta H} \quad (3)$$

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_0 , to which the line intensity, I , is proportional according to the relationship

$$I \propto \chi_0 = \frac{1}{3kT} g^2 \beta^2 N_0 \bar{J}(\bar{J} + 1) \quad (4)$$

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_0 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, which can be calculated from experimental observations using Equation 3. In the present study, all of the terms on the right side of Equation 4, except N_0 , were assumed to be constant. The intensity of the ESR signal thus was assumed to be directly proportional to N_0 and was obtained by integrating the area under the prederivative spectrum.

RESULTS AND DISCUSSION

Figure 1 reveals the relative abilities of dithionite, sulfide, and thiosulfate to reduce smectite SWa-1 at room temperature (25°C). Notice that $\text{Na}_2\text{S}_2\text{O}_4$ exhibited a much greater capacity to reduce structural Fe(III) than did either of the other compounds. This is consistent with the hypothesis of Stucki and Lear (1989) who stated that $\text{Na}_2\text{S}_2\text{O}_4$ should be a better reducing agent than any others that they studied because of its free-radical activity. Earlier studies (Rozenon and Heller-Kallai, 1976a, 1976b; Stucki *et al.*, 1976; Stucki and Roth, 1977) that compared the reductive capability of various reducing agents also provided findings consistent with the hypothesis of Stucki and Lear (1989).

The ESR spectra of solid $\text{Na}_2\text{S}_2\text{O}_4$ revealed a strong resonance at $g = 2.0091$ (Figure 2A), which persisted at $g = 2.0114$ when dissolved in 1 M solution (Figure 2B). The standard deviation for g values was approximately ± 0.0002 . The position of these ESR lines compared favorably with the values reported by Hodgson

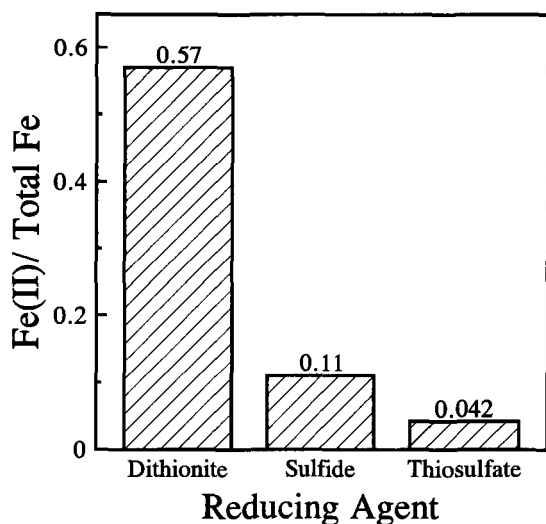


Figure 1. Reduction of structural Fe in Na smectite SWa-1 by freshly prepared 0.01 M solutions of $\text{Na}_2\text{S}_2\text{O}_4$, Na_2S , or $\text{Na}_2\text{S}_2\text{O}_3$ for 24 hours at 25°C.

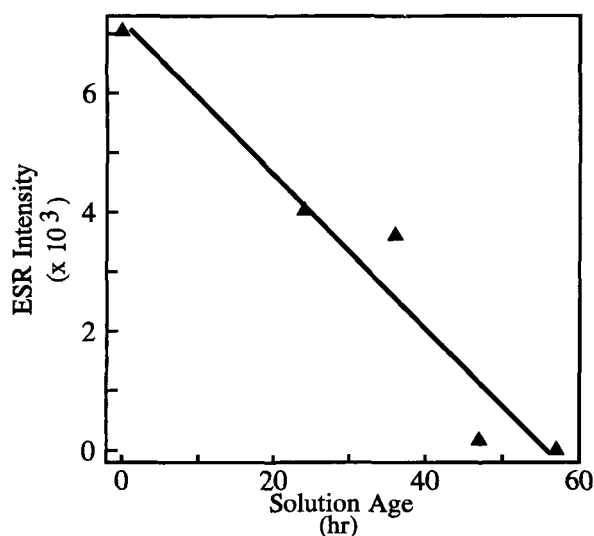


Figure 3. Effect of solution age on ESR line intensity of 1.0 M $\text{Na}_2\text{S}_2\text{O}_4$ in CB buffer.

et al. (1956) and Rinker *et al.* (1959) for the sulphoxylate ($\text{SO}_2^{\cdot -}$) free radical. The signal from the solid sample was stable with time. In solution, however, the signal was most intense in freshly prepared solutions and decreased in intensity with age until it disappeared completely after about 57 hr in the 1.0 M solution (Figure 3), and before 4 hr in the 0.01 M solution (Figure 4). The free radical, thus, appears to be unstable in solution, probably due to oxidation by dissolved O_2 (Lynn *et al.*, 1964).

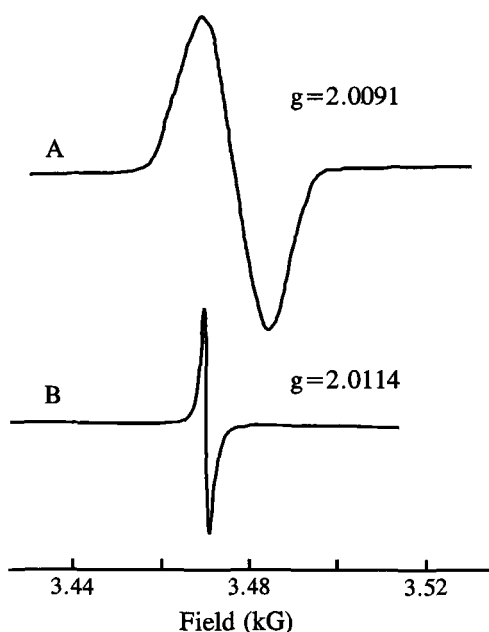


Figure 2. ESR spectra of solid (A) and 1.0 M aqueous solution (B) of $\text{Na}_2\text{S}_2\text{O}_4$.

Treatment of 25 mg samples of smectite SWa-1 with 25 ml of aged $\text{Na}_2\text{S}_2\text{O}_4$ solutions always reduced less structural Fe than the addition of an equivalent amount of solid $\text{Na}_2\text{S}_2\text{O}_4$ directly to the clay suspension (Table 1), and the reductive activity of $\text{Na}_2\text{S}_2\text{O}_4$ solution decreased sharply with the age of solution (Table 1). The fresh 0.01 M solution produced a Fe(II) to total Fe ratio of 0.115; whereas, the reduction ratio dropped to 0.013 if the solution was aged 4 hr before combining with the clay. In the 1 M solution, the Fe(II) : total Fe ratio decreased from 0.837 to 0.014 if the solution was aged first for 57 hr. The resulting correlations between ESR peak intensity and reducing capacity of dithionite (as measured by the Fe(II) to total Fe ratio achieved in the clay) (Figure 5) indicate a direct relationship between $\text{SO}_2^{\cdot -}$ concentration and reducing ability of the reagent.

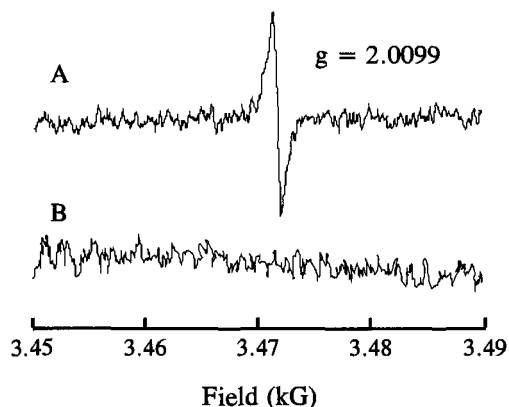


Figure 4. ESR spectrum of 0.01 M $\text{Na}_2\text{S}_2\text{O}_4$ in CB buffer: A) fresh, B) after 4 hr.

Table 1. Reduction of 25 mg of sample SWa-1 at room temperature by 10 ml of Na₂S₂O₄ solution aged for different times.

Na ₂ S ₂ O ₄ concentration (moles/liter)	Age of solution (hr)	Fe(II)/total Fe
0.01	0	.115
	4	.013
1.0	0	.837
	24	.605
	48	.318
	57	.014

A previous study found that the level of Fe reduction in clays depends on the amount of Na₂S₂O₄ added (Stucki *et al.*, 1984a). The initial concentration of freshly prepared Na₂S₂O₄ in H₂O or CB buffer also affects the ESR peak intensity, as illustrated in Figure 6. Solution in H₂O gives a slightly different response compared to solution in CB buffer (Figure 6). Based on Equation 4, these results clearly indicate that the number of unpaired spins or unpaired electrons in solution increases as the initial concentration of Na₂S₂O₄ increases.

No ESR signal was observed in any of the other reducing agents used in this study, indicating that the reduction mechanism by these reducing agents differs from that of Na₂S₂O₄ in that unpaired electrons are insignificant in the reaction.

The ESR spectrum of the freeze-dried SWa-1 sample (not shown) reveals the presence of a paramagnetic species in the clay structure at $g = 2.0202$, but the signal disappeared if the clay was suspended in H₂O or CB buffer, probably due to the strong adsorption of microwave energy by water. The origin of this signal is uncertain, but could result from a defect site in the clay. No signal from structural Fe, which should occur at about $g = 4$ (McBride *et al.*, 1975), was evident because of strong magnetic relaxation effects among the Fe ions.

If solid Na₂S₂O₄ was added to the clay suspension, making the final Na concentration 0.01 M, the moderately strong ESR signal was evident initially (Figure 7A), then after 4 hr the signal became even stronger than that of the pure Na₂S₂O₄ solution of the same concentration (0.01 M) (Figure 7B). The signal persisted for up to 9 hr of contact between clay and Na₂S₂O₄, which was more than double its lifetime in pure Na₂S₂O₄ solution. Hence, the concentration of free radicals from the Na₂S₂O₄ solution was preserved and enhanced if added to the clay (compare Figures 4B and 7B).

Several possible explanations exist for this observation. One is that the clay promotes the monomerization of the S₂O₄²⁻ ion, i.e., drives the reaction in Equation 2 to the right. But this seems unlikely because that action should increase the reduction potential of the system, and the level of reduction actually reached

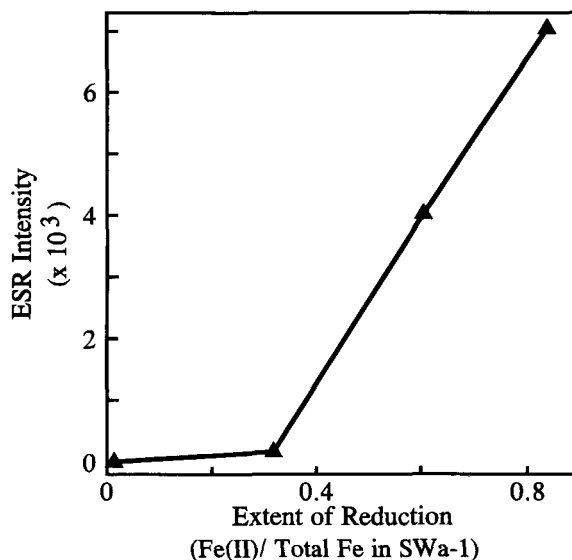
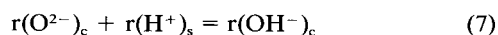
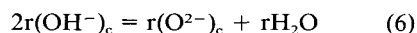
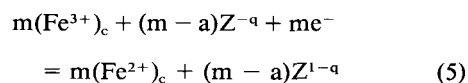


Figure 5. Relation between ESR intensity and the capacity of 1.0 M Na₂S₂O₄ solution to reduce structural Fe in C-B buffered smectite SWa-1 at 25°C (1 ml Na₂S₂O₄ solution/mg smectite).

a maximum in less than 1 hr, while the free radical was present for nearly 9 hr. The system thus failed to maintain a strong reduction potential over time, even though the paramagnetic signal was present.

Another explanation may be that the SWa-1 initially reacted with SO₂^{-·}, which donates an electron to the structural Fe in the clay; but as the reaction proceeds, unpaired electrons are produced within the clay crystal structure, perhaps at defect sites, that give rise to the persistent signal in Figure 7B. This explanation would be 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 electrons due to the lower-valent tetrahedral cation. This step occurs only after sufficient Fe(III) is reduced by SO₂^{-·} either to activate or to catalyze the movement of internal electrons to structural Fe(III). Because the electron is captured by the Fe, the signal eventually disappears. This process would be similar to the reaction proposed by Stucki and Lear (1989)



where subscripts c 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

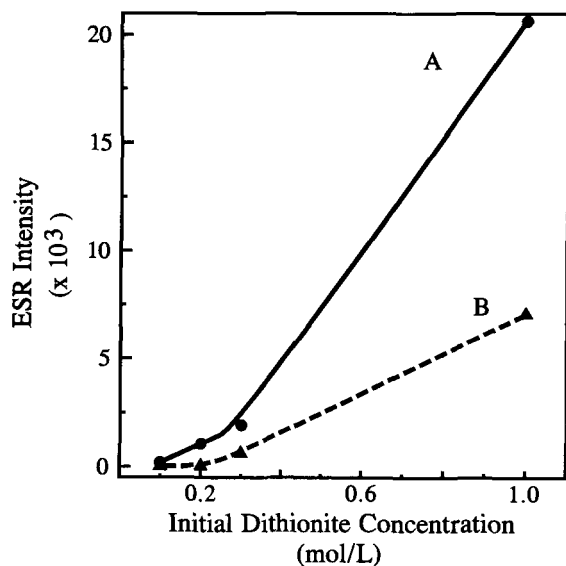


Figure 6. Effect of $\text{Na}_2\text{S}_2\text{O}_4$ solution concentration in (A) H_2O , or (B) CB buffer on ESR line intensity.

tetrahedral 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 confirmed.

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 intervalence 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

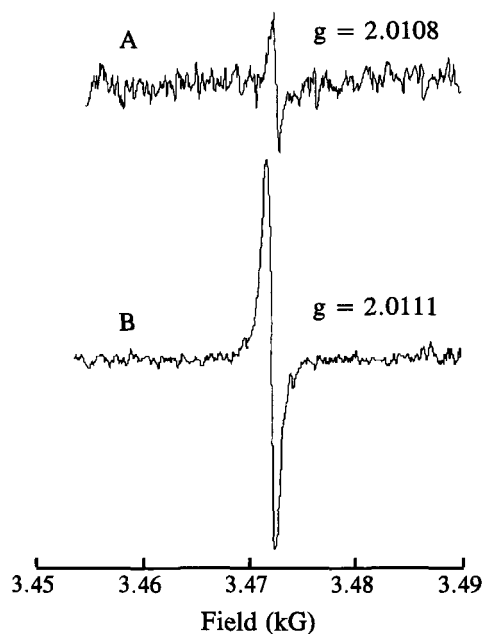


Figure 7. ESR spectra of 0.01 M $\text{Na}_2\text{S}_2\text{O}_4$ in smectite SWA-1 suspension: A) fresh, B) after 4 hr.

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.

In Figure 8 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 5 through 7. 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 (Griffen, 1992).

Further reduction by agents having greater reductive capabilities (having energies $\geq E_2$ or E_3), such as the $\text{SO}_2^{\cdot-}$ 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

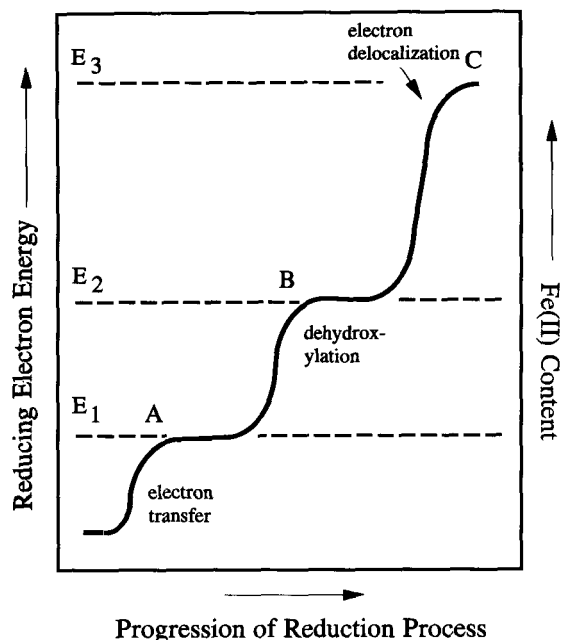


Figure 8. Conceptual model of relationships among energy of reducing electrons, structural Fe(II) content, and progression of the reduction process in ferruginous smectites.

into molecular or metal-like orbitals or into semiconductor-like conductivity bands. The delocalized 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 8).

CONCLUSIONS

Experimental results presented herein may explain some aspects of why $\text{Na}_2\text{S}_2\text{O}_4$ 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., $\text{SO}_2^- \cdot$) 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.

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