

Chapter 8

PROPERTIES AND BEHAVIOUR OF IRON IN CLAY MINERALS

Because iron (Fe) is the fourth-most abundant element in Earth's crust (6% of mass), next to oxygen, silicon, and aluminium, its ubiquitous presence in clays and clay minerals should be no surprise. It is, in fact, an intimate part of many processes occurring in natural ecosystems. Murad and Fischer [1988] reviewed the many pools of iron that exist in nature and discussed the geobiochemical cycle of iron (summarized briefly in Figure 8.1), illustrating how it is transformed from one pool to another. They pointed out the many connections within and between the mineral or inorganic phases of iron and its organic or biological phases in the environment. The number and complexity of these interactions are great, so a complete discussion of the significance of terrestrial iron would fill many volumes. In this chapter emphasis is placed on a description of the phases in which iron occurs in clay minerals and the properties and behaviours it imparts to them by virtue of its susceptibility to oxidation and reduction (redox) reactions. As is evident from Figure 8.1, redox is a pathway that is common to several of the inter-pool transformations and thus exerts much influence on terrestrial ecosystems.

An expanded treatise on iron in soils and clay minerals was published previously by Stucki et al. [1988], which reviewed the chemistry, detection, and characterization of iron in oxides, carbonates, sulfides and sulfates, phyllosilicates, agricultural soils, hydromorphic and lateritic soils, and pedogenic processes. It also touched on the role of microorganisms in determining the fate of iron in soils and sediments. Since that work was published, numerous advancements have been made in understanding and characterizing structural iron in smectites, especially in relation to redox processes. Advancements have also been made in the study of iron in other phyllosilicate minerals such as kaolinite and mica.

The effects of structural iron on clay properties was reviewed by Stucki [1988] and Stucki and Lear [1989]. Since that work was published, little new has come to light regarding the overall effect of structural iron on clay properties, but much has been learned about the effects brought about by changes in its oxidation state [Stucki et al., 2002]. The current chapter will focus largely on the latter phenomena.

8.1 PHASES OF IRON IN CLAYS

Iron-bearing clays are ubiquitous in nature; in fact, the presence of iron in the structure of smectites is clearly the rule rather than the exception. They may form through natural or synthetic processes [Stucki, 1988; Badraoui and Bloom, 1990; Boiabid et al., 1991; Aoki and Kohyama, 1991; Badaut et al., 1992; Decarreau et al., 1992; Martin et al., 1992; Grauby, 1993; Grauby et al., 1993; Grauby et al., 1994; Petit et al., 1995; Martin et al., 1998; Giresse and Wiewiora, 2001]. Stucki [1988] illustrated the classification scheme for iron-bearing smectites, for which nontronite is the dioctahedral end member. A number of different nontronites have been studied by various workers, and they vary in their total iron contents and in some fine detail of their properties [Koster et al., 1999; Gates et al., 2002]. The supply of many of these samples is dwindling, but a new source that is less limited was recently discovered in Australia [Keeling et al., 2000] and reports of its characteristics are now beginning to emerge [Gates et al., 2002; Frost

et al., 2002a,b]. Montmorillonite also contains structural iron, but to an extent of about 3% by weight compared to about 20% or more in nontronite.

Iron may occur in both the octahedral and tetrahedral sheets of 1:1 and 2:1 clay minerals, and in the gibbsite/brucite sheet of 2:1:1 minerals. Iron can also exist as a compensating-ion on the clay exchange complex [Yamagishi, 1982; Diamant et al., 1982; Helsen and Goodman, 1983; Johnston and Cardile, 1985; Coyne and Banin, 1986; Thompson and Tahir, 1991; Hirt et al., 1993; Choudary et al., 1994; Ebitani et al., 2002; Letaief et al., 2002] or be placed in pillars between the 2:1 layers [Bergaya and Barrault, 1990; Bergaya et al., 1991; Rightor et al., 1991; Mody et al., 1993; Komadel et al., 1994; Mishra and Parida, 1998; Wasserman and Soderholm, 1998; Chirchi and Ghorbel, 2002]. In natural soils, iron (hydr)oxides (usually Fe^{3+} forms) are commonly precipitated or adsorbed to the clay surfaces or admixed as a separate phase [Murad, 1987, 1988; Schwertmann, 1988a,b]. Minerals containing Fe^{2+} are also important, such as vivianite [Nembrini et al., 1983; Hansen and Poulsen, 1999], siderite [Loeppert, 1988], and pyrite [van Breemen, 1988b,c]. In sulfur rich and oxidizing environments, jarosite is commonly formed [van Breemen, 1988a,b,c]. Green rust is a mixed-valent iron mineral that has attracted much recent interest [Murad and Taylor, 1984; Hansen, 1989; Cuttler et al., 1990; Koch and Morup, 1991; Schwertmann and Fechter, 1994; Genin et al., 1998; Hansen and Poulsen, 1999; Erbs et al., 1999; Lee and Batchelor, 2002] and appears to be a highly reactive iron phase in some soils and sediments. Characterizing the distribution of iron among these various phases and crystallographic sites is both a challenging and a rewarding endeavor, and one in which more effort and investigations are warranted.

8.1.1 Phase Identification

After reviewing the many studies published on the subject of iron phase identification, one concludes that identifying the location of iron with respect to the general phases (e.g., oxide, phyllosilicate) is more readily accomplished than pin-pointing the exact site in which it is located (e.g., cis-,trans-octahedral, tetrahedral, exchanged). The mixing of iron (hydr)oxides with iron-bearing smectites is readily observed using Mössbauer spectroscopy (Figure 8.2a), in which the iron (hydr)oxides are identified by the component peaks of a six-line pattern and the silicate iron is identified from the main central doublet at about 0.3 mm/s and the additional feature located at about 2.2 mm/s. The six-line features of the (hydr)oxides are readily distinguished from silicate structural Fe^{3+} and Fe^{2+} , especially if the Mössbauer spectra are obtained at liquid He temperature (4.2 K) where all iron oxides are magnetically ordered but the iron in the silicate is not. The Mössbauer spectrum may also be used to establish the identity of iron oxides that may be present by examining the Mössbauer hyperfine parameters (isomer shift, quadrupole shift, and magnetic hyperfine field) [Murad, 1987, 1988, 1998; Murad et al., 1990; Rancourt, 1998].

The complete separation of these various phases as a pure component by either a chemical or physical separation treatment is highly unlikely, if not impossible. The iron (hydr)oxide can, however, be effectively removed by the CBD reductive dissolution treatment (citrate-bicarbonate-dithionite as described by Mehra and Jackson [1960]), and this is evident in the Mössbauer spectrum by disappearance of the six-line pattern (Figure 8.2b). Removal of only the poorly crystalline, or more readily soluble, iron oxide phases can also be carried out using various methods such as ammonium oxalate or dilute HCl extractions [Borggaard, 1988]. Complete separation or removal of the iron oxide phases by chemical means without in some way altering the remaining phases is, with current practice, unlikely; but, the importance of such

cross-cutting effects on the other phases may be of limited significance compared to the advantages attained by removal of the iron. Alternatively, a certain level of refined physical separation can be accomplished by successive and repeated particle-size fractionations [Manceau et al., 2000a]. The latter approach is non-specific for iron, so it also removes much of the other, non-iron phases such as quartz, which may have been present in a finely divided form. A possible disadvantage of this physical separation is that the resulting particle-size fraction of the recovered clay phase is much less than 2 μm .

8.1.2 Distribution between Octahedral and Tetrahedral Sites

Iron may be distributed randomly or clustered in the octahedral sheet, with the latter occurring normally in the iron-rich smectites. Theoretically, however, clustering could also occur in iron-poor smectites; but, magnetic susceptibility measurements [Schuette et al., 2000] of oxidized and reduced Upton montmorillonite (total iron = 3% by weight) found only paramagnetic ordering, which means that the iron ions are too far apart to interact with one another; and no intervalence electron transfer band is observed in partially reduced montmorillonite. Strong interactions are, on the other hand, observed in the iron-rich smectites. These two methods, i.e., magnetic susceptibility and visible absorption spectroscopy, combined with partial reduction of structural iron, provide a convenient method to determine the distribution of iron ions relative to one another.

A discussion about how iron is distributed between the cis (M2) and trans (M1) octahedral sites in 2:1 dioctahedral smectites has been going on for many years, and it continues; but, some things are now more clear. A rule that continues to be generally accepted is that the more iron-rich the layer, the more vacant the M1 sites (centrosymmetric structure, sometimes referred to as trans-vacant); and, conversely, the more iron-poor, the more populated the M1 sites (non-centrosymmetric structure). In other words, nontronite and ferruginous smectite are largely if not completely trans-vacant, whereas montmorillonite contains some Fe^{3+} in the M1 sites. These conclusions are based on a variety of spectroscopic and structural measurements, including x-ray diffraction, selected area diffraction, Mössbauer, and infrared [Tsipursky et al., 1978; Bookin et al., 1979; Besson et al., 1981, 1983; Drits et al., 1981; Tsipursky and Drits, 1984; Dainyak et al., 1984a,b, 1992; Dainyak and Drits, 1987; Muller et al., 1997].

The least reliable method for this purpose is Mössbauer spectroscopy. Soon after its advent as a tool in iron clay chemistry, the curve fitting of its absorption spectrum almost always required two doublets for octahedral Fe^{3+} in order to obtain a proper match of experimental and theoretical spectra. The temptation was to assign these two doublets of slightly different quadrupole splitting to the cis and trans sites (e.g., [Goodman et al., 1976; Rozenson and Heller-Kallai, 1977; Goodman, 1978; Russell et al., 1979; Heller-Kallai and Rozenson, 1981]). This spectral interpretation has since been suggested to be a great over-simplification of a Mössbauer spectrum, and spectral fittings using a distribution of quadrupole splittings are now becoming the preferred practice. Rancourt and co-workers [Rancourt, 1989, 1994a,b, 1998; Rancourt et al., 1993, 1994a,b] thoroughly discussed the analytical and experimental requirements if Mössbauer spectroscopy is to be used for the identification of specific site symmetries.

While the strictly centrosymmetric structure of oxidized (unaltered) nontronite is widely accepted, magnetic susceptibility measurements of a series of nontronites raised some doubt regarding the complete absence of Fe^{3+} in M1 sites. Lear and Stucki [1990] and Schuette et al. [2000] reported magnetic susceptibility of five nontronites, ranging in total iron content from

about 18% to 24% iron by weight. In every case these nontronites exhibited frustrated anti-ferromagnetism, meaning that the inverse susceptibility versus temperature plots failed to reveal the characteristic cusp at the magnetic ordering temperature as seen with ferripyrophyllite [Coey et al., 1983], and instead continued downward as occurs when magnetic frustration occurs [Ballet and Coey, 1982; Coey, 1988]. The cusp is expected if the structure is strictly centrosymmetric. Manceau et al. [2000a] offered alternative explanations for each of these nontronites that reconcile these aberrant data with the other structural observations; but, since the data are rather uniform and the explanations are non-uniform, further studies of the magnetic interactions in iron-bearing smectites appear to be warranted in order to understand these inconsistencies better.

The vibrational energy of structural OH groups reveals the presence of octahedral iron, as pointed out by Stubican and Roy [1961a,b,c] and Farmer and Russell [1964, 1966, 1967], and again more recently by Robert and Kodama [1988], Bishop et al. [2002], Madejova et al. [1992, 1994, 1995], and Petit et al. [1999]. If Fe^{3+} is present, the shift is to lower frequency. Reduction of Fe^{3+} to Fe^{2+} causes an even further shift to lower frequency [Stucki and Roth, 1976; Fialips et al., 2002a,b; Lee et al., 2005]. If used in combination with other structural information, such as EXAFS [Manceau et al., 2000b; Li et al., 2003, 2005], and by extending the range of analysis to both the mid- and near-infrared regions of the spectrum, this method would add further detail that may be helpful in distinguishing local coordination symmetry for structural iron.

Much less is known about the amount, chemistry, and behaviour of tetrahedral iron than of octahedral iron in smectites. Tetrahedral iron evidently is always in the trivalent state, since no case of tetrahedral Fe^{2+} has been reported in phyllosilicates and its ionic radius is too large for that site. The historical or traditional approach for calculating structural formulas first places excess Al^{3+} in the tetrahedral sheet, then Fe^{3+} if required to satisfy the Si^{4+} deficit. This assignment order is arbitrary [Luca and Cardile, 1989; Luca, 1991a,b; Luca and Maclachlan, 1992; Manceau et al., 2000a; Gates et al., 2002] and creates the potential for underestimating the amount of tetrahedral iron; so, published formulas using this approach should be viewed skeptically insofar as the tetrahedral iron content is concerned.

Conclusive, quantitative evidence for the substitution of Fe^{3+} for Si^{4+} in tetrahedral sites continues to be rather elusive, but some progress has been made over the past two decades. An early strategy for measuring tetrahedral Fe^{3+} was proposed by Osthaus [1953, 1956], which was based on the premise that the rate of dissolution of octahedral cations was greater than of tetrahedral cations. He found two slopes in the plot of time versus the amount of iron released during HCl dissolution. Tetrahedral iron was estimated by extrapolating the lesser rate to time zero. Komadel and co-workers, however, found that the rates of dissolution of octahedral and tetrahedral cations are the same [Cicel et al., 1990; Komadel et al., 1993, 1996, 1998; Tkac et al., 1993, 1994; Madejova et al., 1993, 1998; Komadel, 1999]. Cardile [1989] and Luca and Maclachlan [1992] also questioned the validity of Osthaus's approach. The underlying premise for the selective dissolution method has, thus, been discounted and alternative methods for assigning tetrahedral iron must be found.

Cardile [1989], Cardile and Slade, [1987], Johnston and Cardile [1985, 1987], Luca [1991a,b], and Luca and Cardile [1989] proposed that Mössbauer spectroscopy can be used to identify tetrahedral iron by emphasizing the small shoulder on the low energy side of the main central peak in dioctahedral, iron-rich smectites. This is done by saturating the smectite with a high charge density cation such as Ca^{2+} , then dehydrating at 300 °C to bring about an interaction between the interlayer cation and the tetrahedral iron. By this method, the tetrahedral Fe^{3+} content of Garfield nontronite was estimated to be about 9% (Johnston and Cardile [1985]) and

of ferruginous smectite (SWa-1) about 5% (Luca and Cardile [1989]). The author (J. W. Stucki, unpublished results) was able to reproduce Luca and Cardile's [1989] Mössbauer spectra for Ca-exchanged, dehydrated ferruginous smectite SWa-1, but x-ray absorption near-edge spectroscopy (XANES) failed to verify that this sample contains tetrahedral iron ([Manceau et al., 2000a]. Of the four nontronites (ferruginous smectite, SWa-1; Pannamint Valley; Garfield; and Hohen Hagen, NG-1) studied by Manceau et al. [2000a] using XANES, conclusive evidence for tetrahedral iron was found in only the NG-1 sample. Its level was very high at about 17% of total iron. In the case of the other two nontronites (Panamint Valley and Garfield), the Mössbauer (J. W. Stucki, unpublished data) and XANES results were consistent in indicating no tetrahedral iron. Other workers have also found XANES to be a useful method to help sort out the site occupancy questions of structural iron [Dyar et al., 2001, 2002].

Gates et al. [2002] performed an in-depth analysis of the tetrahedral Fe^{3+} content of fourteen different nontronites and ferruginous smectites using near infrared, XANES, polarized EXAFS, and XRD methods. They concluded that the tetrahedral Fe^{3+} contents for these respective samples were: (1) ferruginous smectites, none; (2) Manito nontronite (API #33-b), 3%; (3) Bingham nontronite, 6.5%; (4) Garfield, approximately 3% (except the oriented powder method gave a value of 10.5%); (5) Hohen Hagen (NG-1), 16.5%; (6) Spokane, 15.3%; (7) Clausthal Zellerfeld, 19.8%, (8) N Au-1, 1.9%; (9) N Au-2, 7.6%; (10) Mountainville, Pennsylvania, 5.8%; and (11) Tasmania, 10.8%. As these results indicate, the amount of tetrahedral Fe^{3+} can be rather substantial. Using these data, calibrations of other methods, including Mössbauer spectroscopy, may be possible.

Sherman and Vergo [1988] observed in nontronites a ${}^6\text{A}_1 \rightarrow {}^4\text{E}_1, {}^4\text{A}_1 ({}^4\text{G})$ electronic transition for tetrahedrally coordinated Fe^{3+} that occurs at 429-434 nm in the visible spectrum. Since this is a Laporte-allowed ligand-field transition, its absorption coefficient is 10 to 100 times that of octahedral Fe^{3+} , potentially making it an excellent indicator for even small amounts of tetrahedral iron. Surprisingly, this is a method for distinguishing tetrahedral Fe^{3+} that has received no further attention; but, with the application of suitable curve-fitting techniques, it could very well provide a wealth of untapped information.

8.2 METHODS FOR IRON REDUCTION

Structural iron in the octahedral sheet of smectites is clearly more difficult to reduce than iron in (hydr)oxides because it is located at a distance of several Å from the point of closest approach (basal surfaces) by any reducing agent. How this gap is overcome is unknown and is at the source of understanding the electron transfer process. Many different reducing agents have been tried (summarized in Table 8.1), including hydrazine, hydrogen gas, and hydrogen sulfide, but the two most commonly used agents are dithionite and bacteria. Hydrazine may be effective in low-iron smectites, but it is a poor reductant of iron-rich smectites. Following are more details about the two most-used methods.

8.2.1 Dithionite

Most studies of the variable oxidation states of iron in smectites have focused on the use of sodium dithionite as the reducing agent in citrate-bicarbonate buffered suspensions. The dithionite method is based on the procedure of Mehra and Jackson [1960], which was devised to remove iron oxides from soils, as modified by Roth et al. [1968, 1969], Stucki and Roth [1977],

and Stucki et al. [1984b] for smectites.

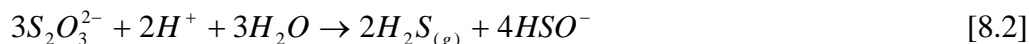
The method for dithionite reduction typically involves preparation of the smectite suspension in an 8:1 (vol:vol) 0.3 M Na-citrate:1.0 M Na-bicarbonate buffered (C-B) solution in a septum-capped reaction tube, heating the suspension to 70 °C with continuous purge of O₂-free N₂ gas, addition of Na-dithionite as the salt (solid phase), and reaction for up to four hours. The suspension is then cooled to room temperature and washed under inert-atmosphere conditions to remove excess dithionite and establish a background solute concentration. The temperature, time, and ratio of dithionite to smectite all contribute to determining the extent of reduction. If the amount of dithionite to be added becomes too large, it may overcome the buffering capacity of the C-B buffer. Amonette [2003] calculated that the buffering capacity must be at least 4 protons per dithionite molecule. The N₂ purge greatly advances the level of reduction by removing the gaseous products from the otherwise closed reaction vessel [Komadel et al., 1990].

Inert-atmosphere conditions should include the removal of O₂ from exchange solutions by boiling while purging with O₂-free N₂, then exchanging solutions without exposing either the reaction system or the exchanger solution to the atmosphere. This is accomplished in the author's laboratory using a Controlled Atmosphere Liquid Exchanger (updated version of apparatus described by Stucki et al. [1984b]).

The dithionite anion, S₂O₄²⁻, when placed in aqueous solution, undergoes two types of reaction. The first is the irreversible disproportionation into thiosulfate and sulfite according to the reaction [Amonette, 2003]



These products are rather mild reductants and, in fact, are ineffective in reducing structural iron in smectite (Gan, Stucki, and Bailey, unpublished results). Thiosulfate in acid solution further disproportionates to



where the hydrogen sulfide gas produces a pungent and easily recognizable odor. While these reactions are rather slow, they do render a solution of dithionite ineffective as a reductant of structural iron in smectite within a few hours [Gan et al., 1992]. The decreased pH resulting from this reaction also creates an environment in which the smectite will dissolve, releasing Fe²⁺ ions into solution. The hydrogen sulfide will then react with Fe²⁺ to produce FeS, a black precipitate. These problems, along with the problem of dissipation of S₂O₄²⁻ reduction capacity with time in aqueous solution, are addressed in the dithionite-reduction methods by preparing the clay in a pH-buffered solution including a chelate for Fe²⁺ (e.g., citrate) and by adding S₂O₄²⁻ as the solid salt rather than as a solution. The pH is thus maintained at a circum-neutral value while any dissolved Fe²⁺ is kept in solution and the reduction reaction is allowed to proceed before significant disproportionation occurs. Recent preliminary studies in the author's laboratory (Ribeiro and Stucki) indicate that the concentration of bicarbonate buffer typically used (1 M) may provide too much buffering capacity for the amount of dithionite used, so the pH can increase to >9. A proper balance between dithionite and buffer must, therefore, be considered.

The second reaction of S₂O₄²⁻ in water is the reversible breaking of the S-S bond to form two sulfoxylate free-radical anions [Rinker et al., 1964]



which are very reactive toward the reduction of structural Fe^{3+} in smectites. The sulfoxylate free radical becomes the actual reductant of structural iron in smectite and is capable of reducing virtually all of the structural iron, whereas no other reductant has yet been found that will accomplish the same. Gan et al. [1992] showed a direct, linear correlation between the intensity of the EPR signal originating from the sulfoxylate unpaired electron and the level of iron reduction achieved in ferruginous smectite. They also showed that the free radical is labile with time, reinforcing the need to add the dithionite as the solid-phase salt rather than as a solution.

Dithionite has been used effectively to create spatially fixed reduced zones in sub-surface aquifers at the Hanford site, Washington, for the purpose of intercepting and chemically reducing contaminants such as Cr^{6+} and nitroaromatics [Amonette, 2003]. The use of microorganisms as an alternate reductant has also proven effective.

8.2.2 Bacteria

Since the discovery in 1986 and 1987 by Stucki and co-workers [Stucki and Getty, 1986; Komadel et al., 1987; Stucki et al., 1987] that bacteria are able to reduce structural Fe^{3+} in clay minerals, many studies have confirmed this finding and extended the range of possibilities for its exploitation. Wu et al. [1988] showed that bacteria in extracts from Chinese rice-paddy soils actively reduce smectite structural iron; and studies by Kostka et al. [1999a, 2002] and Cervini-Silva et al. [2003] reported that bacteria from a variety of origins, including well-drained and flooded soils, can reduce structural Fe^{3+} in smectite and change its physical-chemical properties.

The extent and rate of bacterial reduction varies depending on the bacterial system. The highest level of bacterial reduction of iron-rich smectite reported thus far is about 41% of the total octahedral iron, which was achieved either with an unidentified rice-paddy inoculum [Wu et al., 1988] or with the metal-reducing bacterium *Shewanella oneidensis (putrefaciens)* [Kostka et al., 1996]. The rate of reduction is greatest with *Shewanella*, achieving the half-level of reduction in only four hours. Other general types of bacteria known to reduce structural iron in clays include *Geobacter*, *Pseudomonas*, and *Bacillus* [Stucki and Getty, 1986]. The reduction of iron observed in rice paddy soils presumably is also the product of bacterial activity [Boivin et al., 2002; Favre et al., 2002a,b].

The basic method used for bacterial reduction will vary somewhat depending on the bacterium selected to perform the reduction. Some bacteria are facultative anaerobes whereas others are strict anaerobes, so the method of culture must be modified accordingly. *Shewanella* bacteria, which are the most often used bacteria [Gorby et al., 1994; Kostka et al., 1996], are facultative anaerobes and can be grown aerobically; but, in order to utilize Fe^{3+} as their electron acceptor, they must be cultured anaerobically in the presence of the clay. In the method of Kostka et al. [1996] where *Shewanella oneidensis* was used, the clay suspension was prepared in an iron-free growth medium and sterilized (either by microwave or autoclave heating). The *Shewanella* bacteria were initially cultured aerobically in a separate vessel on a minimal Fe^{3+} medium, then an inoculum of growing cells was transferred to the sterilized smectite and incubated under anaerobic conditions. After the desired incubation time, the reaction was terminated and analyses performed. Reaction termination can be either by sterilization or washing with dilute NaCl solution. The former creates a sterile system in which no further bacterial activity occurs, whereas the latter simply dilutes the concentration of bacterial cells.

Since the bacteria are still viable they will continue to grow slowly over time. While the presence of viable bacteria presents some problems with the stability of the reduction product, termination by washing is advantageous for samples with properties that are sensitive to the elevated temperatures of heat sterilization (e.g., mineral phase transformations). In this case, however, analyses would normally occur soon after washing and the presence of bacteria would be taken into consideration in the interpretation of results.

Bacterial reduction of structural iron in phyllosilicates has now been employed in a number of studies (summarized in Table 8.2) and appears to be an area of increasing interest. These studies have focused on topics varying from the effects of bacterial reduction on clay dissolution and mineral phase transformation to effects on the transformation of chlorinated aliphatics and pesticides.

8.3 SURFACE INTERACTIONS WITH WATER

Smectites are well known for their affinity for water [Low, 1961, 1979, 1980, 1987], and structural Fe^{3+} and Fe^{2+} both significantly impact the smectite-water interaction. Early studies (reviewed by Stucki [1988]) indicated that the swellability of a smectite is affected by the cationic composition of the clay layer, and that the presence of octahedral Fe^{3+} has a modest but generally depressing effect on water retention capacity. A more pronounced effect is observed when the structural iron is reduced. This phenomenon was first observed by Foster [Foster, 1953, 1955], who found that the blue-gray form of Wyoming montmorillonite swelled to about half the water volume as the olive-green form, and that the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio of the blue-gray form was double that of the olive-green form. Both the Fe^{2+} content and the swelling volume of the blue-gray sample reverted to the olive-green values upon reoxidation. Nothing more was published on this subject until Egashira and Ohtsubo [1983] reported a depressing effect of structural Fe^{2+} on the swellability of smectites reclaimed from marine environments in Japan. Shortly thereafter, Stucki et al. [1984c] observed systematic changes in the swelling of several reference clay minerals reduced with pH-buffered sodium dithionite in the laboratory (Figure 8.3). Similar results have since been reported also by Lear and Stucki [1985], Yan and Stucki [1999, 2000], and Stucki et al. [Stucki et al., 2000] for dithionite-reduced smectites; and, by Gates et al. [1993] and Kostka et al. [1999a] for bacteria-reduced smectites.

Our understanding of the exact mechanism by which structural Fe^{2+} alters the hydration of clay surfaces is still incomplete, but by combining the observations of Viani et al. [1983, 1985], Yan et al. [1996a,b,c,d], Yan and Stucki [1999, 2000], Fialips et al. [2002a,b], Wu et al. [1989], Cervini-Silva et al. [2000b], and Stucki and co-workers [Stucki and Roth, 1976, 1977; Stucki et al., 2000] some interesting conclusions can be made. These studies offer convincing and self-consistent evidence that interlayer H_2O molecules interact directly with the oxygen ions which comprise the basal surfaces of the clay layers, and that this interaction is coupled with the vibrational energies of the Si-O groups in the smectite tetrahedral sheet. By virtue of this coupling at the clay-water interface, forces affecting the structure of either the adsorbed H_2O or the Si-O tetrahedra will alter clay swelling. Reduction of octahedral Fe^{3+} to Fe^{2+} does both, affecting H_2O by increasing the electron density and proton attraction at the surface oxygens (as revealed by greater Brønsted basicity) [Cervini-Silva et al., 2000b] and the Si-O tetrahedra by disrupting the crystallographic structure [Stucki and Roth, 1976; Manceau et al., 2000b; Fialips et al., 2002a,b].

Two example observations which reveal the increasing strength of interaction between

the basal oxygens and interlayer H₂O as structural iron reduction increases are given in the studies of Cervini-Silva et al. [2000b] and Yan and Stucki [1999, 2000]. Reaction of pentachloroethane with reduced smectite surfaces revealed that the parent compound was rapidly degraded to tetrachloroethene, which is a base-catalyzed dehydrochlorination reaction [Cervini-Silva et al., 2000b]. The rate of degradation increases linearly with the structural Fe²⁺ content of the smectite (Figure 8.4). The proposed mechanism of interaction is illustrated in Figure 8.5, and shows that reduction increases the attraction of basal oxygens for protons. This polarizes interlayer H₂O and increases the electron density on the aqueous oxygen ion, which, in turn, promotes the abstraction of the proton from the pentachloroethane and the α,β elimination of chlorine to yield tetrachloroethene. This reaction is direct evidence that the reduced clay surface has a greater Brønsted basicity than the oxidized surface. Degradation of the pesticide oxamyl also appears to follow a similar hydrolysis pathway in the presence of reduced smectite [Zhang, 2002].

If the surface attracts interlayer H₂O more strongly in the reduced than in the oxidized state, this should be reflected in the vibrational energies of the interlayer H₂O. Indeed, Yan and Stucki [1999, 2000] observed an increase in the vibrational energy of the H-O-H bending mode for interlayer H₂O with increasing Fe²⁺ content of the clay. An increase in the energy of this bending mode is consistent with a greater constraint being applied to the vibrational freedom of one or both of the hydrogen ions on the interlayer H₂O, which would be the case in the event of stronger interaction with the surface. Yan et al. [1996a,b,c,d] and Yan and Stucki [1999, 2000] further observed that the vibrational energy of the interlayer H₂O molecules is coupled with the vibrational energy of the structural Si-O stretching bands (Figure 8.6). This is a most remarkable observation and provides another key link in the puzzle for understanding how structural Fe²⁺ in the octahedral sheet has such a great effect on surface hydration and other surface properties.

The effects of structural iron reduction on the vibrational energy of Si-O bands was noted as early as 1976 by Stucki and Roth [1976], who observed a systematic downward shift in the Si-O vibrational energy as structural Fe²⁺ increased. This observation was confirmed and characterized more completely by Huo [1997], Yan and Stucki [1999, 2000], and Fialips et al. [2002a,b] (Figure 8.7). These shifts are consequences of rearrangements occurring in the octahedral sheet as the clay crystal attempts to compensate for the increased size of the octahedral Fe²⁺ ion compared to Fe³⁺ and to balance the increased negative charge due to iron reduction, such as by the models proposed by Manceau et al. [2000b] and Li et al. [2003, 2005]. In summary, changes in iron oxidation state alter the structure of the clay, which is reflected in the Si-O stretching vibrations which are coupled to the vibrational energy of interlayer H₂O. Through this coupling, the change in oxidation state induces a change in free energy of the interlayer H₂O, which in turn affects the swellability of the clay, as described by the following discussion.

Clay swelling or hydration occurs because the interaction between H₂O and the basal surface decreases the partial molar Gibbs free energy of bulk H₂O (\bar{G}_0) as it approaches the solid clay surface. The difference between the partial molar Gibbs free energy of clay water (\bar{G}_{H_2O}) and that of bulk water, given by $\bar{G}_{H_2O} - \bar{G}_0$, defines the potential for water to enter the interlayer from the bulk phase, i.e., the affinity of the clay surface for water, and is measured by the swelling pressure, Π , of the clay as represented by the equation [Low, 1951, 1980]

$$\bar{G}_{H_2O} - \bar{G}_0 = -V\Pi \quad [8.4]$$

where \bar{V} is the partial molar volume of the water in the clay-water system.

Since structural Fe^{2+} increases the interaction between H_2O and the clay surface, these thermodynamic arguments predict that swelling in reduced smectite should be greater than in oxidized smectite. If this is true, then why are the observed effects just the opposite [Foster, 1953, 1955; Egashira and Ohtsubo, 1983; Stucki et al., 1984b, 2000; Lear and Stucki, 1985; Gates et al., 1993]. The answer is found by comparing the studies of Viani et al. [1983] and Wu et al. [1989], who discovered that two types of interlayers are possible in swelling smectites: fully expanded and fully or partially collapsed. At any given swelling pressure, the distance between the fully expanding layers is the same, regardless of the water content of the clay at that pressure. So the differences in water content for two clays at the same swelling pressure occurs because of a difference in the fraction of layers that are fully expanded relative to the fraction that are partially or fully collapsed, rather than from the layers expanding to different distances. They described these relationships by the expression

$$\ln(\Pi + 1) = \ln \beta + \frac{\alpha}{\lambda} \quad [8.5]$$

where α and β are constants and λ is the interlayer distance. Notice that the swelling pressure, Π , is a single-valued function of interlayer distance.

Reduction of octahedral Fe^{3+} causes more of the clay layers to collapse compared to the oxidized state, thereby removing those layers from the pool of fully expanded layers [Wu et al., 1989]. The overall capacity of the clay to adsorb water on a mass basis is thus diminished. This observation compares well with other studies showing an increase in cation fixation as the reduced state of the clay increases. Chen et al. [1987] observed an increase in K fixation in agricultural soils as the amount of structural Fe^{2+} in the constituent clays increased, and Khaled and Stucki [1991], Lear and Stucki [1987], and Shen and Stucki [1994] confirmed this principle in standard reference clays, indicating that layers are indeed collapsing around these cations. The extent of cation fixation by the reduced smectite depends inversely on the hydration energy of the cation [Khaled and Stucki, 1991].

Another consequence of the increased interaction between reduced smectite surfaces and interlayer H_2O is that the hydration energy of the surfaces exposed to H_2O should increase, even though the net water holding capacity can decrease for the reasons just explained. Stucki et al. [2000], in a study of the effects of organic cations on clay swelling, demonstrated that this is indeed the case. The quaternary ammonium cation trimethylphenyl ammonium (TMPA^+) was exchanged onto the oxidized and reduced smectites, then the water retention curve was obtained. Water retention curves were also obtained for the Na-exchanged analogs (Figure 8.8). Remarkably, in comparing the water contents of Na-oxidized, Na-reduced, TMPA^+ -oxidized, and TMPA^+ -reduced smectites, all at the same applied swelling pressure, they found that the TMPA^+ -reduced sample held the most water! How can this be, since TMPA^+ is largely a hydrophobic cation (notice that it depresses the water content when the clay is in the oxidized state)? A plausible explanation is that this cation prevents the clay layers from collapsing upon iron reduction, and thereby allows their surfaces to become hydrated and to participate in swelling, whereas with Na as the exchanged cation the collapse occurs and their swelling is precluded. The

reduced clay surface then is apparently much more attractive to H₂O than is the oxidized surface because its water content exceeds that of even the Na-oxidized form of the smectite (fully expanded state with no collapsed layers) , leading to a conclusion that the hydration energy of the reduced surfaces far exceeds that of the oxidized surfaces, consistent with the enhanced interaction between basal oxygens and adsorbed H₂O. The dominant hydrating force in the interlayer, moreover, is not the interlayer cation, but the clay surface itself.

If the reduced clay surface is more highly hydrated than the oxidized surface, or that its hydration energy is greater, one would expect the adsorbed water to be held with greater energy. MacKenzie and Rogers [1977], using differential thermal analysis (DTA), observed that the hydration energy of a Fe²⁺-containing clay is more complex than the oxidized analog (also see discussion by Stucki [1988]). Huo [1997] and Fialips et al. [2002a,b], using infrared spectroscopy, discovered in reduced smectite a H₂O phase that was more resistant to dehydration than in the oxidized smectite, and the intensity of the O-H stretching bands from this H₂O phase increased as the extent of structural Fe²⁺ increased (Figure 8.9). These observations are consistent with more strongly bound H₂O.

Iron reduction also affects the hydraulic conductivity through a clay-water paste. This is a property of compacted clay that is related to both clay-water interactions and to the texture or fabric of the clay matrix, and studies have shown that it may either increase or decrease upon structural iron reduction, depending on the order in which the sample was reduced and compacted. Shen et al. [1992] observed a decrease in the hydraulic conductivity of reduced ferruginous smectite that was compacted onto a membrane filter, as compared to the unaltered or oxidized form. This decrease in hydraulic conductivity was attributed to the particles of the reduced smectite having a smaller aspect ratio (thicker and of more limited lateral extent) (see [Stucki and Tessier, 1991]), which enables them to form a more dense matrix upon compaction.

If, however, the smectite is first compacted, then reduced by percolation of a pH-buffered dithionite solution, the hydraulic conductivity actually increases. Shen et al. [1992] explained this behaviour as being due to the strong interlayer attractive forces that are asserted when structural iron is reduced, causing the superimposed layers to collapse and, to a certain extent, rotate in the a-b plane to form a less turbostratic stacking order. The latter was reported previously by Stucki and Tessier [1991], who observed an increased order in the electron diffraction patterns upon structural iron reduction. When these actions of layer rotation and collapse occur in a previously compacted gel, the movement of particles creates voids between them that gives rise to meso pores with greater conductivity than the micropores in a highly compacted smectite. These studies were carried out using sodium dithionite as the reducing agent, but the phenomena of layer collapse and rotation have also been observed in bacteria-reduced smectites [Kim et al., 2003], indicating that such processes affecting hydraulic conductivity could well be occurring in natural or engineered clay barriers.

8.4 CLAY-ORGANIC INTERACTIONS

The discovery that reduction of structural iron activates smectite surfaces with respect to chlorinated aliphatics [Gorby et al., 1994] and pesticides [Xu et al., 1996] has opened an exciting new area of investigation into clay-organic interactions. Pesticides, chlorinated aliphatics, and nitroaromatics have thus far been investigated (Table 8.1). Pesticides studied include atrazine, alachlor, trifluralin, oxamyl, chloropicrin, dicamba, and 2,4-D. These studies are significant because they demonstrate that the interaction mechanism between the smectite and the pesticide

involves much more than mere sorption to the clay surface. The pesticides, with the exception of 2,4-D, react with reduced clay surfaces much more extensively than with oxidized or reduced-reoxidized surfaces, and degradation products are observed (examples given in Figures 8.10 through 8.12). Atrazine (Figure 8.10), for example, partially degrades to hydroxyatrazine when reacted with reduced ferruginous smectite [Xu et al., 2001], but no products are observed by HPLC when it is reacted with the oxidized (unaltered) or reduced-reoxidized form of the same smectite. A similar phenomenon occurs with alachlor [Xu et al., 2001; Kocherginsky and Stucki, 2000], except the degradation products are many and have yet to be fully identified. Chloropicrin (trichloronitromethane) is transformed to the di- and mono-chloro forms [Cervini-Silva et al., 2000a] by reductive dechlorination (Figure 8.11). Oxamyl converts to either the hydrolysis product, oxamyl oxime (OO), or to the reduction product, N,N-dimethyl-1-cyanoforamide (DMCF), depending on the solution pH. Smectites in any oxidation state will promote the hydrolysis product, but the rate of degradation is greatly accelerated by the reduced smectite [Zhang et al., 2005]. Specific degradation products from trifluralin (Figure 8.12) and dicamba are still unidentified [Tor et al., 2000; Sorensen et al., 2003].

Clearly, the reduced smectite acts as a reducing agent with most of the pesticides studied, either eliminating -Cl or -NO₂ groups. But in the case of oxamyl a hydrolysis product is also observed, indicating that reduced clay surfaces, in addition to catalyzing redox activity, also promote pH-catalyzed reactions. This is consistent with results from chlorinated alkanes (see below).

The extent to which the reduced smectite degrades the pesticide varies from one pesticide to the other. As mentioned above, 2,4-D seems to be unaffected by the smectite, regardless of oxidation state, and only a small fraction of alachlor [Kocherginsky and Stucki, 2000; Xu et al., 2001] and dicamba are affected. Oxamyl [Zhang et al., 2005], chloropicrin [Cervini-Silva et al., 2000a], and trifluralin [Tor et al., 2000], on the other hand, are almost completely degraded by the reduced smectite (Figures 8.11 and 8.12) but little affected by the oxidized smectite.

The effect of reduced smectites on organics is not limited to pesticides. Studies have reported the dechlorination of chlorinated aliphatics [Gorby et al., 1994; Rodriguez et al., 1999; Cervini-Silva et al., 2000a; Cervini-Silva et al., 2000b; Nzungung et al., 2001; Cervini-Silva et al., 2001; Cervini-Silva et al., 2002; Cervini-Silva et al., 2003] and the reduction of nitroaromatics [Yan and Bailey, 2001; Hofstetter et al., 2003] by reduced smectites. Gorby et al. [1994] found that tetrachloromethane reacts with dithionite-reduced Panther Creek bentonite to yield tri- and dichloromethanes by step-wise hydrogenation. The reaction rate increased if Fe(0) was combined with the smectite. Whether the enhanced reaction rates can be attributed to structural Fe²⁺ in the smectite is, however, in question because: (1) when the sample was washed with HCl to remove sulfides and Fe²⁺, its reactivity with CCl₄ was greatly diminished, (2) reactivity of the clay was restored if Fe²⁺ was added back as an exchanged cation, and (3) the interaction mechanism for admixing with Fe(0) is unknown. The authors stated that the products are consistent with other proposed reaction pathways [Kriegman-King and Reinhard, 1994] for degradation of polyhalogenated methanes by reduced-sulfur compounds. Similar results were found for degradation of trichloroethene. All of these tests apparently were conducted using a heterogeneous clay system rather than with just the pure smectite.

Nzungung et al. [2001] also reported that dechlorination of trichloroethene is faster in a heterogeneous system than with pure reduced smectite. The heterogeneous system tested was smectite + dithionite. In the absence of dithionite the smectite failed to promote the dechlorination of trichloroethene, whereas dithionite alone at approximately the same pH was

effective. The most effective combination, however, was dithionite combined with the smectite. Comparison of different smectites found the rate of dechlorination to be greater with montmorillonite than with ferruginous smectite. They attributed these differences in smectite behaviour to a difference in available interlayer surface area due to greater layer collapse in the ferruginous sample, but more work is needed to clarify the relative roles of smectite and dithionite.

The observed lack of reactivity of the pure smectites with the chlorinated alkene may, on the other hand, be attributed to the fact that the primary mechanism for dechlorination of chlorinated aliphatics is hydrolysis or dehydrochlorination, which may be rather difficult with the trichloroethene, since it already possesses one double bond. Pentachloroethane can degrade either by a reductive dechlorination pathway, which produces trichloroethene, or by a dehydrochlorination pathway, which yields tetrachloroethene. When reacted with dithionite- or bacteria-reduced smectite, it degrades via the dehydrochlorination pathway rather than the reductive dechlorination pathway [Cervini-Silva et al., 2000b, 2003]. No further degradation of the tetrachloroethene was observed. Other chlorinated alkanes also appear to follow this same pathway [Cervini-Silva et al., 2003] in the presence of pure smectite.

Nitroaromatic compounds (NAC), including nitrobenzene, acetylnitrobenzene, and trinitrotoluene can be reduced by chemically reduced smectite. Nitrobenzene is converted to aniline when reacted with reduced ferruginous smectite (SWa-1) or Upton montmorillonite [Yan and Bailey, 2001]. Reaction kinetics revealed extensive conversion by SWa-1 within the first 40 hrs; then it leveled to a small non-zero slope and after 500 hrs reduction was still increasing slightly. The rate was slower with Upton and the extent of degradation was less. Adsorption of nitrobenzene to the clay surfaces was unaffected by the iron oxidation state; but aniline adsorption was significantly depressed by iron reduction. Interestingly, the amount of structural Fe^{2+} actually participating in the reaction (as a fraction of total Fe) was rather low (< 40% in SWa-1 and 10% in Upton). Perhaps the reaction occurs primarily at clay layer edges.

Hofstetter et al. [2003] investigated the reactivity of different forms of iron in and on smectites for transforming acetylnitrobenzene to the corresponding aniline. The isomers 2- and 4-acetylnitrobenzene have different selectivities for the clay interlayers, namely, the para (4-) isomer is planar and is easily sorbed between smectite layers, whereas the cis (2-) isomer sorbs only to the edge surfaces. These properties were exploited to probe the reactivities of structural Fe^{2+} , edge-complexed Fe^{2+} , and exchanged Fe^{2+} toward reductive amination to the corresponding anilines. Hectorite was used as the non-structural iron control. Results revealed that exchanged Fe^{2+} has no reactivity toward NAC reduction, but both edge-complexed and structural Fe^{2+} were effective in producing the aniline product. The observed fraction of total Fe^{2+} that participated in the process was similar to that of Yan and Bailey [2001], providing further indication that NAC reduction may occur primarily at the edge surfaces.

Further investigations of the reactions of redox-modified clay minerals with organic compounds are in progress and are greatly needed. Little is known about the reduction potential of reduced smectite, except that it must lie somewhere between the reduction potentials of chloropicrin and pentachloroethane, since it reduces the former but not the latter. Organic compounds may be effective probes of the surface characteristics of the reduced smectite, revealing properties such as effective pH and reduction potentials. The specific site on the clay surface, i.e., edge versus basal surface, where organic reactions take place is also an area that needs much further study.

The toxicity of pesticides to mammals, which are obviously non-target organisms for

pesticides, can be greatly altered by exposing the pesticide to reduced-iron smectites. Sorensen et al. [2004, 2005] compared the mammalian toxicity of four different pesticides (alachlor, oxamyl, 2,4-D, and dicamba) before and after treatment with either oxidized or reduced smectite, and found that the oxidized smectite had no effect on toxicity, but the reduced smectite significantly decreased the toxicity of alachlor and oxamyl, increased the toxicity of dicamba, and had no effect on the toxicity of 2,4-D. The redox state of smectites, from either natural or imposed processes, may, therefore, be an important factor in determining or manipulating the risks associated with pesticides in the environment.

8.5 LAYER CHARGE, CATION EXCHANGE, AND CATION FIXATION

The layer charge is one of the most important properties of smectite clay minerals, and is susceptible to modification in situ by reduction of structural Fe^{3+} to Fe^{2+} . The isomorphous substitution of Fe^{3+} in the octahedral sheet of the phyllosilicates of course invokes no change in layer charge, and in the tetrahedral sheet it has the same effect on charge as does Al^{3+} substitution for Si^{4+} ; but, reduction of Fe^{3+} to Fe^{2+} in a dioctahedral structure is reflected in an increase in the negative surface charge. Stucki and co-workers found that the layer charge increases upon iron reduction; but, the increase is less than predicted by the structural Fe^{2+} content [Stucki et al., 1984a]. This difference in measured layer charge compared to the apparent number of electrons added to the clay crystal has led to further investigations of potential ancillary reactions, such as concomitant protonation or dehydroxylation, and has motivated numerous discussions regarding the complete reduction reaction mechanism. These discussions are presented in more detail in Section 8.6.

An increase in layer charge is accompanied by an increase in cation exchange capacity, as well as an increase in the ability of the smectite to fix interlayer cations. Stucki et al. [1984b] reported a steady increase in cation exchange capacity as iron reduction progressed in nontronite, which has been confirmed by others for dithionite-reduced smectites [Lear and Stucki, 1985; Khaled and Stucki, 1991; Gates et al., 1996], bacteria-reduced smectites [Kostka et al., 1999b; Gates et al., 2000], and rice-cropped vertisols [Favre et al., 2002a,b]. Lear and Stucki [1985] further observed that a small fraction of the exchangeable Na^+ becomes non-exchangeable, or fixed, during the reduction process, which could be due to the complete or partial collapse of smectite layers [Wu et al., 1989].

Heller-Kallai [1997] pointed out, however, that the layer charge in these studies may have been underestimated due to the explicit assumption that Na^+ was the only interlayer cation and accounted for all of the layer charge. She argued that, even though the citrate-bicarbonate buffer and dithionite reducing solutions were comprised of only the Na salts, the documented dissolution of aluminium from the smectite [Stucki et al., 1984b; Leite et al., 2000] during the reduction process could have led to formation of complex Al-citrate cations. Perhaps these cations could then be preferentially exchanged onto the clay surface in place of some of the Na^+ . The fact that the ratios of dissolved silicon, aluminium, and iron in solution after reduction differed from the ratios in the clay structure was offered as potential evidence to support this hypothesis. She further suggested that cation fixation could occur by the complex Al-citrate cation blocking the exchange of Na and other interlayer cations, thus providing an alternative mechanism for cation fixation which does not require the complete collapse of superimposed clay layers. Direct evidence establishing the existence of the complex Al-citrate cation and its potential to fix other interlayer cations, however, is still lacking. Recent observations of

collapsed layers in bacteria-reduced smectites [Kim et al., 2003] indicate that such an alternative explanation for cation fixation may be unnecessary.

The effects of iron reduction on cation fixation have significant implications for soil fertility, mineral transformations in the soil, and the fate of redox-sensitive pollutants such as Cr [Taylor et al., 2000]. Potassium is a key plant nutrient, but fertilizer recommendations for K are often inaccurate for reasons that are yet to be fully explained. Some soils exhibit K deficiencies even though the total K appears to be sufficient [Singh and Hefferman, 2002]. Chen et al. [1987] most likely found the answer, however, when they discovered that structural iron reduction leads to extensive K⁺ fixation in smectitic soils. Khaled and Stucki [1991] and Shen and Stucki [1994] verified that structural Fe²⁺ reduction in smectites does, indeed, lead to a sharp increase in the fixation of K⁺. They also observed that the amount of exchangeable K⁺ was similar in oxidized and reduced forms of the clay (Figure 8.13), and that the increased layer charge due to Fe³⁺ to Fe²⁺ reduction was manifested primarily in the pool of fixed K.

The potential for this process to remove large amounts of K from the plant-available pool in the soil is made dramatically apparent by the following calculation for a rather typical agricultural soil.

Assumptions: A soil with medium texture having 15% clay content, of which 2/3 is smectite (10% of soil by weight is smectite)
 Iron content of the smectite is 3% by weight (a typical montmorillonite)
 Approximate weight of a hectare-furrow slice of soil is 2·10⁶ Kg
 Extent of reduction is only 20% of total iron [generally consistent with Favre et al., 2002b]
 K fixation in Upton montmorillonite at this level of reduction is about 0.1 meq/g clay = 0.0047 Kg K₂O/Kg clay [Shen and Stucki, 1994]

Calculation:

$$K(\text{fixed}) = \frac{0.0047 \text{ Kg K}_2\text{O}}{\text{Kg smectite}} \cdot \frac{1 \text{ Kg smectite}}{10 \text{ Kg soil}} \cdot \frac{2 \cdot 10^6 \text{ Kg soil}}{\text{Hectare} - \text{Furrowslice}} = \frac{940 \text{ Kg K}_2\text{O Fixed}}{\text{Hectare}}$$

This is an extremely large amount of K to cycle between the plant-available and the plant-non-available pools in the soil due to changing redox conditions! A typical fertilizer recommendation for K, based on conventional soil tests in the State of Illinois, is about 50 to 100 Kg K₂O/Hectare (Theodore R. Peck, personal communication). The very modest level of redox cycling used in the above calculation proves that the potential for K fixation due to iron reduction in the soil absolutely overwhelms the practical ability to amend the soil with K fertilizers. If the observations by Favre et al. [2002a,b] and Chen et al. [1987], i.e., that the effects of redox processes in smectites on cation exchange capacity are manifested in the field as well as in the laboratory, also apply to cation fixation, then the above calculation presents a significant understanding and a challenge for modifying soil management practices, especially under conditions where the soil experiences alternate flooding (reducing) and draining (oxidizing) through rainfall or irrigation practices. These results of Chen et al. [1987] and Favre et al. [2002b] from soil clays and of Shen and Stucki [1994] from Wyoming montmorillonite confirm that K⁺ fixation due to iron reduction is a general phenomenon in smectites that extends beyond the iron-rich forms.

Cation fixation as a consequence of iron-reducing conditions may also affect other

cationic nutrients in the soil such as Ca^{2+} , Cu^{2+} , Zn^{2+} (Figure 8.13), and NH_4^+ [Scherer and Zhang, 2002]. Because the charge density of NH_4^+ is similar to that of K^+ , the behaviour of these two cations in smectites is often regarded as being similar. Ammonium should, therefore, also have a high susceptibility for fixation. Evangelou and co-workers [Lumbanraja and Evangelou, 1990, 1992, 1994; Evangelou et al., 1994; Barbayiannis et al., 1996] found significant correlations between the fixation of these two ions in agricultural soils, suggesting that their tendencies toward fixation are indeed similar. Scherer and Zhang [2002] subsequently identified a clear link between the amount of NH_4^+ fixed in periodically flooded rice paddy soils and the oxidation state of structural Fe^{2+} in the clay minerals. Shen and Stucki (unpublished results) observed that the behaviour of NH_4^+ in redox-modified ferruginous smectite is in fact similar to that of K^+ , as illustrated in Figure 8.14. The general trend appears to be that the extent of fixation is inversely proportional to the hydration energy of the cation [Khaled and Stucki, 1991].

The reversibility of the fixation process of these cations is an important factor in determining the fate of the nutrient and the nature of the clay mineral. If fixation is even partially irreversible, cycles of iron reduction and reoxidation could be an important mechanism for the sequestering of plant nutrients into a low-availability form and for the conversion of smectite to illite in natural environments [Eslinger et al., 1979]. The feasibility for iron redox cycling to be a significant force in converting the smectite to a more illitic form was investigated by Shen and Stucki [1994], who measured the amount of structural Fe^{2+} and fixed K^+ remaining in the reoxidized form of ferruginous smectite after passing through several redox cycles (Figure 8.15). At the end of each successive cycle, i.e., when the clay was in its oxidized or reoxidized state, the amount of K^+ that remained fixed, in spite of reoxidation, increased over the level observed at the end of the previous cycle. Similarly, the amount of Fe^{2+} that resisted reoxidation increased after each cycle. These phenomena are absent when Na is the exchanged cation during iron reduction. Surprisingly, NH_4^+ seems to be released when the smectite is reoxidized and fails to accumulate over several redox cycles (Shen and Stucki, unpublished results), so, in this sense, NH_4^+ is different from K^+ . This is only a preliminary result, however, and should be verified. Clearly the presence of K promotes the irreversible collapse of some smectite layers, which diminishes access to the interlayer space by the oxidizing agent (presumably O_2 in this case) and thereby impedes reoxidation of the octahedral Fe^{2+} .

The possibility that this process is active in natural soils and sediments has recently been established by the existence of collapsed layers in bacteria-reduced smectite, using an environmental cell transmission electron microscope (ED-TEM) [Kim et al., 2003]. In a related study, the transformation of smectite to illite was also proposed as a result of bacterial reduction of structural iron [Kim et al., 2004]. In those studies no overt assertion was made that the presence of K^+ during structural iron reduction was influencing the collapsing of the layers, and no redox cycling was performed; but, because the nutrient medium used in the bacterial culture contained significant amounts of K^+ [Myers and Nealson, 1988], its influence on the process should not be overlooked and could well be contributing to the observed collapsing of layers. Projecting the synergy between redox cycling and cation fixation to geologic time, one would expect many thousands of these cycles to occur in natural soils and sediments, causing a large increase in the number of collapsed layers with the attendant increases in the amount of structural Fe^{2+} and fixed K. Such a process essentially defines the conversion of smectite to illite.

The ability of exchanged K^+ to promote the irreversible collapse of smectite layers decreases the ability of the reduced smectite to react with redox-sensitive metals at the basal surfaces. Taylor et al. [2000] studied the reduction of Cr^{6+} to Cr^{3+} by reduced smectite, and

reported that the extent of Cr^{6+} reduction was decreased by 35% if the exchanged cation on the smectite was K rather than Na, which most likely is related to a decrease in the available basal surface area due to an increase in the number of collapsed layers. A similar phenomenon may occur with other redox-sensitive pollutants.

8.6 REDUCTION POTENTIALS AND REACTION WITH REDOX-ACTIVE IONS

The soil environment is filled with a host of redox-active ions and compounds, so reactions between such species and redox-modified smectites is an extremely important process contributing to the fate of such species and to the behaviour of soils and sediments. The Eh of the soil in a rice-paddy field typically can cycle from a high of about 600 mV under well aerated conditions to less than -150 mV during flooding [Boivin et al., 2002; Favre et al., 2002b]. How this reduction potential is attributed to the minerals and the bacteria is undetermined, but clearly the oxidation state of structural iron in the constituent phyllosilicates is cycled between the oxidized and reduced states under these conditions. If formal and/or effective reduction potentials were known and understood for all of these species, effective models could be developed.

The exact reduction potential for Fe^{3+} in smectites is unknown, but Amonette [2003], using theoretical considerations, estimated it to be about 0.71 V. This value is highly dependent on iron-oxygen distances and other structural distortions, making a knowledge of the reduction reaction mechanism, along with its associated structural changes, is a critical piece of information in predicting the true reduction potential. Since iron reduction undoubtedly alters the structure, estimating the surface reduction potential *a priori* is challenging to say the least. Empirical evidence does exist, however, with respect to redox reactions involving reduced smectites and redox-sensitive surface species. Among the ions or compounds that are known to engage in redox reactions with reduced structural iron in smectites are nitrate, chromium, and the pesticides (see above) chloropicrin and oxamyl. These reactions play a significant role in the fate of these compounds in the environment.

8.6.1 Redox Transformation of Nitrate

Nitrate in natural soil profiles is rapidly reduced at the boundary between the oxic and anoxic zones. The distribution of nitrate in several Danish soil profiles drops dramatically in the very narrow zone where the upper oxidized horizon meets the lower, reduced formation [Ernstsen, 1996]. Bacterial denitrification was ruled out as the mechanism controlling this process, but bacteria may play a catalytic role in restoring the reduced state of structural iron in the clay after its oxidation by the nitrate reduction reaction [Ernstsen et al., 1998]. Based on formal reduction potentials, structural Fe^{2+} in smectite should readily reduce nitrate; but, experience has shown that the reaction is more complex than simply combining these two reactants (Ernstsen, Mulvaney, and Stucki, unpublished results). Since iron (hydr)oxides are also present in the Danish soils, the hypothesis is that they serve as a catalyst in promoting the reaction. Some, but not all, of the nitrate reduction could also be attributed to reaction with green rust [Hansen and Koch, 1998].

8.6.2 Redox Transformation of Cr⁶⁺

Reduced structural iron in smectites and other clay-mineral constituents of soils is an effective reductant for Cr⁶⁺ [Gan et al., 1996; Taylor et al., 2000], and possibly for other redox-sensitive metals of environmental concern such as U⁶⁺ and Tc⁷⁺. Gan et al. [1996] were the first to report a redox reaction between reduced smectite and Cr⁶⁺, and Brigatti et al. [2000] reported Cr⁶⁺ reduction by structural Fe²⁺ naturally present in chlorite and corrensite. No reduction occurred with unaltered (oxidized) montmorillonite. Taylor et al. [2000] found that reduced ferruginous smectite (sample SWa-1) reduces Cr⁶⁺ to Cr³⁺ with an efficiency of 79% of the idealized 1:3 ratio of Cr⁶⁺ reduced to structural Fe²⁺ oxidized. The amount of Cr³⁺ immobilized onto the clay surfaces was greatly increased if reduced smectite was used as the reductant rather than using the sequence of Cr⁶⁺ reduction in solution by dithionite followed by the addition of oxidized smectite, which confirms the important role of the reduced smectite in this process. The oxidation state of sorbed Cr was confirmed by XANES to be Cr³⁺. The extent of Cr⁶⁺ reduction is greater if the exchanged cation in the reduced smectite is Na rather than K, which indicates that the reaction occurs primarily at basal surfaces since the presence of exchanged K during structural iron reduction enhances layer collapse and decreases the amount of exposed basal surface area [Shen and Stucki, 1994].

Istok et al. [1999] investigated the possibility of reducing the iron in minerals comprising sub-surface horizons as a means for intercepting and remediating plumes of Cr⁶⁺-contaminated waters. They injected a solution of dithionite and K-bicarbonate- carbonate into wells drilled into the subsurface formation, then monitored the Cr concentration and oxidation state of ground water exiting from the formation. Analyses indicated that substantial Fe³⁺ was reduced to Fe²⁺ in the formation, and laboratory column studies revealed that the dithionite-treated sediment was capable of removing 2 mg/L Cr⁶⁺ from about 100 column pore volumes of synthetic ground water. While this experiment did not determine that the Fe²⁺ was in the structure of the constituent phyllosilicate minerals, it raises the possibility for this to be an effective in situ method for ground-water remediation.

8.7 MECHANISM FOR IRON REDUCTION

The mechanisms for structural Fe³⁺ reduction and reoxidation in smectites is only partially understood. Much progress has been made over the past two decades in learning about changes in composition and structure that accompany redox processes, but the specific pathway by which electrons penetrate the 2:1 layer is still unknown. More investigations based on quantum chemical studies of phyllosilicates, such as those performed by Peterson et al. [1979], Aronowitz et al. [1982], Bleam and Hoffmann [1988a,b], and Delville [1991], and on the theoretical discussions of Bleam [1993] and Amonette [2003] are critically needed. In fact, Bleam [1993] stated that "electron transport in transition-metal-containing phyllosoilicates" is one of the major needs for future research.

Evidence seems to reject the hypothesis that structural iron reduction occurs only at the edge surfaces of the smectite layers, and is more consistent with reduction occurring primarily at the basal surfaces. The progression of the reduction reaction in iron-rich smectite suspensions can be followed by monitoring the absorption band for the Fe²⁺-Fe³⁺ intervalence electron transfer transition observed at about 730 nm in the visible spectrum [Lear and Stucki, 1987;

Komadel et al., 1990]. This band increases linearly (Figure 8.16) until the reduction level reaches about 45% of total iron, at which point the intensity of the band levels off and then decreases. This behaviour is easily understood when one realizes that the intensity of the band is actually a measure of the number of $\text{Fe}^{2+}\text{-O-Fe}^{3+}$ entities in the octahedral sheet. In order for this band to appear, iron ions must occupy adjacent octahedral sites and be of different valence. The fact that the intensity of this band increases linearly with Fe^{2+} content is direct evidence that the number of adjacent $\text{Fe}^{2+}\text{-Fe}^{3+}$ ions also increases linearly; or, in other words, the reducing electron seeks out Fe^{3+} sites that are as far as possible from Fe^{2+} sites. Lear and Stucki [1987] described this as a random reduction with a next-nearest neighbor exclusion. This condition applies in Region I of Figure 8.16.

As the reduction reaction proceeds beyond the point where all possible $\text{Fe}^{2+}\text{-O-Fe}^{3+}$ groupings have been established, $\text{Fe}^{2+}\text{-O-Fe}^{2+}$ groups begin to form. This causes the intensity of the IT band to decrease as $\text{Fe}^{2+}\text{-O-Fe}^{3+}$ is eliminated. When the reduction process is complete, the matrix is fully comprised of $\text{Fe}^{2+}\text{-O-Fe}^{2+}$ groups and the IT band is gone. This phase of the process is observed in Region II of Figure 8.16. These changes in the iron-rich smectite are easily visible to the eye also, as the colour of the sample changes in Region I from yellow to green, then blue-green; and in Region II from blue-green to blue-gray, then to gray.

When the fully reduced smectite is reoxidized by bubbling O_2 gas through the suspension, the reoxidation process follows a similar pattern where Fe^{2+} is reoxidized to Fe^{3+} in a random pattern, with next-nearest neighbor exclusion. The intensity of the IT band increases due to formation of $\text{Fe}^{2+}\text{-Fe}^{3+}$ pairs, only this time through oxidation, and the colour reverts from gray to blue-green in Region III of Figure 8.16. In the final phase of the process, the IT band intensity decreases as the remaining $\text{Fe}^{2+}\text{-Fe}^{3+}$ pairs are eliminated by complete oxidation, as indicated in Region IV of Figure 8.16.

If reduction or reoxidation were occurring from the edge surfaces only, the semi-randomness observed in the distribution of Fe^{2+} in the octahedral sheet would require a very well ordered, two-dimensional network of octahedral iron sites through which an electron can easily pass. This possibility seems remote, although not impossible. Biotite is a phyllosilicate system in which octahedral iron is oxidized from the edges [Amonette and Scott, 1988]. In that case, an oxidizing front is observed, creating a zone of all Fe^{3+} and a zone of all Fe^{2+} , with a moving interface between the zones as oxidation proceeds. One might expect a similar model in smectites if reduction or reoxidation were occurring from the edges only, giving rise to oxidized and reduced zones with an inter-zonal interface having a relatively constant amount of mixed-valent iron sites and thus a relatively constant intensity for the IT band. This model fails to fit the observed changes in IT band intensity with Fe^{2+} content (Figure 8.16). Redox reactions at the basal surfaces, on the other hand, would have better access to the iron sites toward the center of the smectite layer and thereby produce a more random distribution of Fe^{2+} within the octahedral sheet.

Magnetic exchange interactions also reveal that iron reduction must occur in a somewhat random pattern rather than as a reducing front through the clay crystal. Schuette et al. [2000] observed that the iron in iron-rich smectites is antiferromagnetically ordered in the unaltered or oxidized state, but as iron is reduced to Fe^{2+} the exchange interaction changes to superparamagnetic or spin glass behaviour at the lowest temperatures. As temperature increases, the exchange interaction transforms to a ferromagnetic state in the reduced samples. The transition between superparamagnetic and ferromagnetic states is temperature dependent and increases linearly with increasing Fe^{2+} content in the structure. This transition is also sensitive to

isomorphous substitutions in the clay structure.

Characterizations of changes in clay structure accompanying iron reduction have been the focus of many studies, beginning with Addison and Sharp [1963]. They reduced structural iron by heating the nontronite in a H₂ atmosphere at 450 °C and proposed that the mechanism involved the protonation of both the apical oxygen ions and the structural OH groups, causing the latter to be released from the structure as H₂O and leaving Si-O-H behind. Roth and Tullock [1973], Stucki and Roth [1976], Huo [1997], and Fialips et al. [2002a,b] conducted in-depth infrared studies of reduced and reduced-reoxidized nontronite and ferruginous smectite, and found significant changes in the vibrational energies of structural OH groups, confirming (at least in part) the proposition of Addison and Sharp that reduction destabilizes the structural OH apparatus. To date no direct evidence has been reported that apical oxygen ions are protonated, but none of these studies has used the same reduction method as Addison and Sharp. Considerable evidence now exists, on the other hand, that structural OH groups are lost upon iron reduction by dithionite in aqueous solution.

Manceau et al. [2000b] noted, however, that this loss of hydroxyls occurs while the structural iron retains six-fold coordination. In order to accomplish this, while losing hydroxyls, they proposed a reorganization in the octahedral sheet to form trioctahedral domains by the migration of iron from cis to trans sites (Figure 8.17). The formation of a trioctahedral environment for structural OH may explain the appearance of the small peak at 3622 cm⁻¹ in the O-H stretching region of reduced nontronite (Figure 8.9). A similar peak was observed in Griffithite by Komadel et al. [2000], where Griffithite is a saponite with about 26% of octahedral sites being in trioctahedral configuration. Li et al. (2005) offered an alternative interpretation of polarized EXAFS observations that allows for explanation in which the protonation of structural OH is protonated by H⁺ in solution to form structural H₂O, which is also consistent with six-fold coordination and the infrared spectra.

Drits and Manceau [2000] presented a mechanistic model that is consistent with the structural changes observed by Manceau et al. [2000b] and the observed changes in layer charge [Stucki and Roth, 1977; Lear and Stucki, 1985]. It differs from the mechanism proposed by Stucki and Roth [1977] and Lear and Stucki [Lear and Stucki, 1985; Stucki and Lear, 1989] in the following ways (compare Equations 8.6 and 8.7): (1) iron retains six-fold coordination in the reduced structure, instead of converting to five-fold; and (2) dehydroxylation of the structure as a result of iron reduction is initiated by the adsorption of protons by structural OH groups to form H₂O, which then diffuses into solution; rather than following the sequence presented by Stucki and Roth [1977] where two adjacent OH groups coalesce to form one H₂O molecule, which then diffuses into solution, leaving behind one O²⁻ in the structure. The O²⁻ is subsequently protonated by the solvent. The Drits and Manceau model takes into account the elimination of a cis-dihydroxide octahedral site during iron reduction, as proposed by Manceau et al. [2000b], due to the loss of its two hydroxyl groups, and the migration of Fe²⁺ into the trans-dihydroxide site. This migration preserves the six-fold coordination of the iron, but, as noted above, creates trioctahedral domains mixed with the defects in the crystal where the cis sites existed previously (Figure 8.17).

These mechanisms are compared in equations 8.6 and 8.7. The mechanism proposed by Stucki and Roth [1977] is given by





where subscripts c and s represent species in the clay crystal and the surrounding solution, respectively, and m and n are stoichiometry coefficients related by $n = 0.32m$ [Lear and Stucki, 1985].

The mechanism of Drits and Manceau [2000] is given by



where n_i is the stoichiometry coefficient governing the protonation of structural OH groups from the solvent (and equivalently the amount of dehydroxylation). Notice that Equations 8.6a and 8.7a are identical, and the principal difference in these two mechanisms is the manner in which dehydroxylation occurs. Drits and Manceau [2000] found that n_i depends on m , but in a more complex manner than n [Lear and Stucki, 1985]. This dependence on the extent of iron reduction is given by

$$n_i = \frac{K_0(m^2 / m_{tot})}{1 + K_0(m / m_{tot})} \quad [8.8]$$

where m_{tot} is the total iron content of the clay and K_0 is a constant that depends on the clay. The corresponding increase in layer charge in both mechanisms is given by the increased amount of interlayer cation that is measured [Stucki et al., 1984a], which was represented by Drits and Manceau [2000] by the symbol p and related to the total layer charge before and after reduction by the expression

$$w = w_0 + p \quad [8.9]$$

where w and w_0 are the total layer charge of the reduced and unaltered (oxidized) smectites, respectively. They further expressed p as a function of the extent of reduction (m) by the expression

$$p = \frac{m}{1 + K_0(m / m_{tot})} \quad [8.10]$$

Combining Equations 8.9 and 8.10 gives

$$w = w_0 + \frac{m}{1 + K_0(m / m_{tot})} \quad [8.11]$$

They found that by empirically optimizing the value of K_0 they could accurately predict

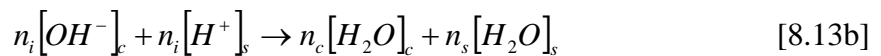
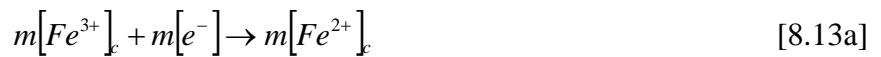
from this equation the total layer charge observed by Stucki et al. [1984a] in reduced smectites as a function of m . If no ancillary reactions or structural changes occurred during the reduction process, the layer charge would be expected to increase by the same amount as the level of reduction, i.e., p would be equal to m . If dehydroxylation occurs, however, the increased negative charge due to iron reduction will be partially compensated by the elimination of negatively charged structural OH groups, causing the value of p to decline by the amount of dehydroxylation, or n_i . This leads to the conclusion that .

$$m = p + n_i \quad [8.12]$$

The Drits and Manceau [2000] model is self-consistent with this relationship.

While Equations 8.7 to 8.12 provide a meaningful mathematical model for predicting layer charge from the extent of reduction and total iron content of the clay, efforts to give physical meaning to K_0 , especially in terms of the particular site occupancy of structural iron (cis vs. trans), appear to have been less successful. The model mineral system chosen by Drits and Manceau [2000], and the particular combinations of parameters used to glean further information from this term, yields the unintended consequence that the cation exchange capacity (CEC) of the smectite must decrease as the level of reduction increases. Since this is contrary to known measurements of CEC vs. low to mid reduction levels, any conclusions based on that model mineral system are questionable. This does not, however, invalidate their proposed reaction mechanism (Equations 8.7).

Further refinements of the reduction mechanism may be found by removing the assumption that n_i represents both the amount of H^+ adsorbed and the amount of OH⁻ lost. Some of the H₂O formed by H⁺ adsorption may, in fact, remain in the smectite structure at higher levels of iron reduction. Evidence for this is found in the infrared spectra of reduced smectites (Figure 8.9 [Huo, 1997; Fialips et al., 2002a,b]), which reveal a steady increase in an H-O-H stretching band at about 3400 cm⁻¹ with increasing m . All samples were submitted to the same dehydration treatment, so increased persistence of this band suggests that it derives from H₂O molecules that are held more strongly in the clay structure than those that are simply adsorbed to the outer surfaces, as appeared to be the case for the unreduced and lesser-reduced samples. One interpretation of this phenomenon is that the hydration energy of the reduced smectite surface is greater than the oxidized surface (see Section 8.5), but another equally valid interpretation is that the H₂O is actually part of the structure. Studies by Roth and Tullock [1973] and Lear and Stucki [1985] clearly showed that H⁺ in the solvent became incorporated into the smectite structure during reduction. This could well be in the form of H₂O instead of OH, as originally proposed by those authors. While the strict application of the Drits and Manceau mechanism would preclude this possibility, reverting to a process that involves protonation of structural OH groups without the subsequent dehydroxylation is a scenario that is consistent with the body of information currently available. In this case, the mechanism would be



where n_c and n_s are, respectively, the stoichiometry coefficients for the amount of H_2O that remains in the clay structure and the amount that diffuses into solution to cause structural dehydroxylation. Notice that Equation 8.13a is identical to Equations 8.6a and 8.7a, but Equation 8.13b allows the possibility for proton adsorption to evoke any degree of dehydroxylation up to n_i , where $n_i = n_c + n_s$. Since neutralization of the increased negative charge due to iron reduction occurs when H^+ is adsorbed, whether or not the resulting H_2O molecule diffuses out of the clay structure, the expressions relating n_i to total layer charge and extent of reduction (Equations 8.8 and 8.11) are also valid for this revised mechanism.

If n_c is non-zero, some of the cis-dihydroxide sites in the octahedral sheet will remain intact and the extent of iron migration from cis to trans sites will be lessened. Infrared spectra (Figure 8.9) indicate that n_c could, in fact, account for a large fraction of n_i . If this is true, then the model proposed by Manceau et al. [2000b], which involves the destruction of cis sites via dehydroxylation resulting in the creation of structural defects and trioctahedral domains, may be only one possible model to explain observations by polarized EXAFS, and/or the extent of such radical alterations of the structure may be rather small.

The extent to which the structure can be reduced may depend on the site occupancy of iron in the octahedral sheet. For example, Komadel et al. [2000] studied Griffithite, a mixed di-tri-octahedral smectite which has about 26% of the octahedra in trioctahedral domains. The extent of maximum reduction of octahedral Fe^{3+} in this clay is only 60%, compared to almost 100% in ferruginous smectite. The pre-existence of Fe^{3+} in trioctahedral domains may either resist reduction because protonation of a fully bonded OH group may be energetically difficult and/or dehydroxylation would require the breakage of three instead of two bonds. This is direct evidence that reduction is impossible or very difficult without concomitant changes in clay structure.

8.8. USE OF REDOX-MODIFIED SMECTITES IN CLAY-MODIFIED ELECTRODES (CME)

Cyclic voltammetry is a method that imposes oxidizing and reducing conditions on the elements of a set of electrodes, and enables the study of a variety of systems in which electron transfer processes are active. The modification of these electrodes by coating them with smectite clays has been employed for a variety of purposes. With respect to studying the clay itself, this method could become useful as a way to impose redox cycles on structural Fe^{3+} in the smectite or for characterizing the effects of redox state in the clay on surface and textural properties of the clay. Fitch et al. [1995] found that coating the electrode with reduced smectite rather than with oxidized smectite increased the rate of transport of an electroactive species, namely, $\text{Fe}(\text{CN})_6^{3-}$, through the clay film in response to the cyclic current applied through the electrode, which may be related to the change in CEC of the smectite upon reduction. The key factor appears to be the change in redox status of the structural iron, since total iron content appears to have little or no influence on the transport of electroactive species [Xiang and Villemure, 1994].

Xiang and Villemure [1992, 1995] prepared CME using reduced-iron smectites, and found that the oxidation of structural iron in the smectite may account for an increased intensity in the anodic (oxidative) peak when an electron transport shuttle or mediator was present, such as

Fe²⁺ bipyridyl or Ru²⁺ hexamine. They also used CME to monitor the behaviour of synthetic smectites prepared with either iron or nickel as the transition metal cation in the octahedral sheet. They found that the addition of nickel in the synthesis of an iron-bearing smectite enhanced both the cathodic (reductive) and anodic (oxidative) waves. This hybrid synthetic sample performed better than either the pure iron or pure nickel analogues. Changes in intensity of the 246-nm UV absorption band (O → Fe³⁺ charge transfer, [Karickhoff and Bailey, 1973; Sherman and Vergo, 1988]) were correlated with the initial reduction of structural iron followed by its oxidation as the potential was swept in the presence of Fe²⁺ bipyridyl or Ru²⁺ hexamine.

8.9 SUMMARY AND CONCLUSIONS

The chemical and physical properties of clay minerals are of great importance to agriculture, industry, and the environment because of their great abundance, high specific surface area, layer charge, laminar morphology, and chemical reactivity with both neutral and charged species. The presence of iron in the crystal structures of the clay minerals infuses an exceptionally important additional facet into their importance because its oxidation state can be rather easily modified in situ and such changes evoke profound differences in the surface chemical and structural behaviour of the clay. Examples of clay properties that are greatly affected by changes in iron oxidation state are swelling in water, cation exchange capacity, cation fixation capacity, surface area, clay-organic interactions, surface pH, reduction potential, ability to transform chlorinated organic compounds, and ability to degrade pesticides and thereby alter their mammalian toxicity. Reduction of structural iron from Fe³⁺ to Fe²⁺ in smectites has been observed both in the laboratory and in situ in the field. Bacteria are the second most-effective reductant that has been found (second only to dithionite) and the most important agent responsible for this phenomenon in natural soils and sediments.

Because the manipulation of the iron oxidation state causes such large changes in chemical and physical behaviour and because such changes can be invoked under field conditions, a great opportunity exists to exploit this phenomenon for a myriad of purposes beneficial to mankind. Such exploitation has yet to occur to any large extent, except it has found application in the remediation of subsurface soils contaminated with radioactive and other harmful metals. Studies are also beginning to emerge that recognize this as an important factor in the fertility and sustainability of flooded soils. Clearly, other opportunities will arise for its use in creating designer minerals for industrial uses.

Challenges and many unanswered questions still face those who study redox processes of iron in clay minerals, especially with respect to the mechanisms governing the electron transfer and the linkages between Fe²⁺ and surface behaviour. How is the electron passed from the outer surfaces of the clay layers into the octahedral sheet? What are the precise energies associated with this process? The exact surface forces altered by the redox process appear to be both coulombic and non-coulombic, but the precise nature of the latter have not been well characterized. What is the mechanism for electron transfer from bacteria to the clay layers – is it done through a direct membrane contact or are electron shuttles or mediators utilized? Is the mechanism the same for all bacteria? Even though the phenomenon of iron redox in clays has been studied for several decades, the number of scientists who have participated in such studies is still rather small. Interest in this field of inquiry is beginning to grow, however, and answers to these and other questions are anticipated to be forthcoming.

On a personal note, this author has been the beneficiary of many intriguing twists and

turns along the path in the realm of iron redox chemistry, which has provided a most interesting, challenging, and rewarding perspective to his study of clay mineral science. He has been awed by the intricacies of Nature as seen at such a seemingly insignificant level in the grand overall scheme of things, but which reveal such majestic order and complexity at the same time. His feelings about this are well captured in the words of the poet Elizabeth Barrett Browning [1937], who declared, "*Earth's crammed with heaven, and every common bush afire with God; only he who sees takes off his shoes.*" My shoes are off!

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References

- Addison, W.E., Sharp, J.H., 1963. Redox behavior of iron in hydroxylated silicates. *Clays and Clay Minerals*, 11, 95–104.
- Amonette, J.E., 2003. Iron redox chemistry of clays and oxides: environmental applications. In: Fitch, A. (Ed.), *Electrochemical Properties of Clays*, CMS Workshop Lectures, Vol. 10, The Clay Minerals Society, Aurora, pp. 89-148.
- Amonette, J.E., Scott, A.D., 1988. Iron in Micas. In: Stucki, J.W., Goodman, B.A., Schwertmann, U. (Eds.), *Iron in Soils and Clay Minerals*. D. Reidel, Dordrecht, pp.576-624.
- Anderson, W.L., Stucki, J.W., 1979. Effect of structural Fe²⁺ on visible absorption spectra of nontronite suspensions. In: Mortland, M.M, Farmer, V.C. (Eds.), *Proceedings International Clay Conference, 1978*, Oxford. Elsevier, Amsterdam, pp. 75-83.
- Aoki, S., Kohyama, N., 1991. Vertical change in clay mineral composition and chemical characteristics of smectite in sediment cores from the southern part of the Central Pacific Basin. *Marine Geology*, 98, 41–49.
- Aronowitz, S., Coyne, L., Lawless, J., Rishpon, J., 1982. Quantum-chemical modeling of smectite clays. *Inorganic Chemistry*, 21, 3589–3593.
- Badaut, D., Decarreau, A., Besson, G., 1992. Ferripyrophyllite and related Fe³⁺-rich 2:1 clays in recent deposits of Atlantis II Deep, Red Sea. *Clay Minerals*, 27, 227–244.
- Badraoui, M., Bloom, P.R., 1990. Iron-rich high-charge beidellite in vertisols and mollisols of the High Chaouia region of Morocco. *Soil Science Society of America Journal*, 54, 267–274.
- Ballet, O., Coey, J.M.D., 1982. Magnetic properties of sheet silicates; 2:1 layer minerals. *Physics and Chemistry of Minerals*, 8, 218–29.
- Barbayiannis, N., Evangelou, V.P., Keramidis, V.C., 1996. Potassium-ammonium-calcium quantity/intensity studies in the binary and ternary modes in two soils of micaceous mineralogi of northern Greece. *Soil Science*, 161, 716–724.
- Bergaya, F., Barrault, J., 1990. Mixed Al-Fe pillared laponites: Preparation, characterization and their catalytic properties in syngas conversion. In: Mitchell, I.V. (Ed.), *Pillared Layered Structures. Current trends and applications*. Elsevier Applied Science. 167–184.
- Bergaya, F., Hassoun, N., Gatineau, L., Barrault, J., 1991. Mixed Al-Fe pillared laponites: Preparation, characterization and catalytic properties in syngas conversion. In: Poncelet, G., Jacobs, P.A., Grange, P., Delmon B.(Eds.), *Preparation of Catalysts V*, Elsevier Science. 329–336.
- Besson, G., Dainyak, L.G., De la Calle, C., Tsipursky, S.I., Rautureau, M., Bookin, A.S., Tchoubar, C., Drits, V.A., 1981. Cation distribution pattern, nature, and concentration of stacking faults in the structure of potassium-saturated nontronite. *Mineralogicheskii Zhurnal*. 36, 66–77.
- Besson, G., Bookin, A.S., Dainyak, L.G., Rautureau, M., Tsipursky, S.I., Tchoubar, C., Drits, V.A., 1983. Use of diffraction and Mössbauer methods for the structural and crystallochemical characterization of nontronites. *Journal of Applied Crystallography*, 16, 374–383.
- Bhattacharyya, J., Saha, S.K., 1990. Aqueous polymerization on clay surfaces. V. role of lattice substituted iron in montmorillonite in polymerizing methyl methacrylate in the presence of thiourea. *Journal of Polymer Science A: Polymer Chemistry*, 28, 2249–2254.

- Bishop, J., Murad, E., Dyar, M.D., 2002. Influence of octahedral and tetrahedral cation substitution on the structure of smectites and serpentines as observed through infrared spectroscopy. *Clay Minerals*, 37, 617–628.
- Bleam, W.F., 1993. Atomic theories of phyllosilicates: quantum chemistry, statistical mechanics, electrostatic theory, and crystal chemistry. *Reviews of Geophysics*, 31, 51–73.
- Bleam, W. F., Hoffmann, R., 1988a. Orbital interactions in phyllosilicates: perturbations of an idealized two-dimensional, infinite silicate frame. *Physics and Chemistry of Minerals*, 15, 398-408.
- Bleam, W.F., Hoffmann, R., 1988b. Isomorphous substitution in phyllosilicates as an electronegativity perturbation: its effect on bonding and charge distribution. *Inorganic Chemistry*, 27, 3180-3186.
- Boiavid, R., Badraoui, M., Bloom, P.R., 1991. Potassium fixation and charge characteristics of soil clays. *Soil Science Society of America Journal*, 55, 1493–1498.
- Boivin, P., Favre, F., Hammecker, C., Maeght, J.L., Delarivière, J., Poussin, J.C., Wopereis, M.C.S., 2002. Processes driving soil solution chemistry in a flooded rice-cropped vertisol: analysis of long-time monitoring data. *Geoderma*, 110, 87–107.
- Bookin, A.S., Dainyak, L.G., Drits, V.A., 1979. Interpretation of the Mössbauer spectra of iron(3+)-containing layered silicates based on structural modeling. *Kation Uporyadochenie V Strukturnakh Mineralov, Novosibirsk*, 23–41.
- Borggaard, O.K., 1988. Phase identification by selective dissolution techniques. In: Stucki, J.W., Goodman, B.A., Schwertmann, U. (Eds.) *Iron in Soils and Clay Minerals*. D. Reidel, Dordrecht, pp. 83–98.
- Brigatti, M.F., Lugli, C., Cibir, G., Marcelli, A.G.G., Paris, E., Mottana, A., Wu, Z., 2000. Reduction and sorption of chromium by Fe(II)-bearing phyllosilicates: Chemical treatments and x-ray absorption spectroscopy (XAS) studies. *Clays and Clay Minerals*, 48, 272–281.
- Browning, E.B., 1937. Quoted in Bartlett, J., *Familiar Quotations*. Little, Brown, and Company, Boston, p. 371.
- Cardile, C.M. 1989. Tetrahedral iron in smectite: a critical commentary. *Clays and Clay Minerals* 37, 185–188.
- Cardile, C.M., Slade, P.G., 1987. Structural study of a benzidine-vermiculite intercalate having a high tetrahedral-iron content by Fe57 Mössbauer spectroscopy. *Clays and Clay Minerals*, 35, 207–207.
- Cervini-Silva, J., Wu, J., Larson, R.A., Stucki, J.W., 2000a. Transformation of chloropicrin in the presence of iron-bearing clay minerals. *Environmental Science and Technology*, 34, 915–917.
- Cervini-Silva, J., Wu, J., Stucki, J.W., Larson, R.A., 2000b. Adsorption kinetics of pentachloroethane in iron-bearing smectites. *Clays and Clay Minerals*, 48, 132–138.
- Cervini-Silva, J., Larson, R.A., Wu, J., Stucki, J.W., 2001. Transformation of chlorinated aliphatic compounds by ferruginous smectite. *Environmental Science and Technology*, 35, 805–809.
- Cervini-Silva, J., Larson, R.A., Wu, J., Stucki, J.W., 2002. Dechlorination of pentachlorethane by commercial Fe and ferruginous smectite. *Chemosphere*, 47, 971–976.
- Cervini-Silva, J., Kostka, J.E., Larson, R.A., Stucki, J.W., Wu, J., 2003. Dehydrochlorination of 1,1,1 trichloroethane and pentachloroethane by microbially reduced ferruginous smectite. *Environmental Toxicology and Chemistry*, 22, 1046–1050.

- Chen, S.Z., Low, P.F., Roth, C.B., 1987. Relation between potassium fixation and the oxidation state of octahedral iron. *Soil Science Society of America Journal*, 51, 82–86.
- Chen, Y., Shaked, D., Banin, A., 1979. The role of structural iron(III) in the UV absorption by smectites. *Clay Minerals*, 14, 93–102.
- Chirchi, L., Ghorbel, A., 2002. Use of various Fe-modified montmorillonite samples for 4-nitrophenol degradation by H₂O₂. *Applied Clay Science*, 21, 271–276.
- Choudary, B.M., Ravichandra Sarma, M., Vijaya Kumar, K., 1994. Fe³⁺Montmorillonite catalyst for selective nitration of chlorobenzene. *Journal of Molecular Catalysis*, 87, 33–38.
- Cicel, B., Komadel, P., Hronsky, J., 1990. Dissolution of the fine fraction of Jelsovy Potok bentonite by hydrochloric and sulphuric acids. *Ceramics Silikaty*, 34, 41–48.
- Coey, J.M.D., 1988. Magnetic properties of iron in soil iron oxides and clay minerals. In: Stucki, J.W., Goodman, B.A., Schwertmann, U. (Eds.), *Iron in Soils and Clay Minerals*. D. Reidel, Dordrecht, pp. 397–466.
- Coey, J.M.D., Chukhrov, F.V., Zvyagin, B.B., 1983. Cation distribution, Mössbauer spectra, and magnetic properties of ferripyrophyllite. *Clays and Clay Minerals*, 32, 198–204.
- Coyne, L.M., Banin, A., 1986. Effect of adsorbed iron on thermoluminescence and electron spin resonance spectra of Ca-Fe- exchanged montmorillonite. *Clays and Clay Minerals*, 34, 645–650.
- Cuttler, A.H., Man, V., Cranshaw, T.E., Longworth, G., 1990. A Mössbauer study of green rust precipitates: I. Preparations from sulphate solutions. *Clay Minerals*, 25, 289–302.
- Dainyak, L.G., Dainyak, B.A., Bookin, A.S., Drits, V.A., 1984a. Interpretation of Mössbauer spectra of dioctahedral iron(3+)-containing layered silicates. I. Calculation of electric field gradients and relative intensities. *Kristallografiya*, 29, 94–100.
- Dainyak, L.G., Bookin, A.S., Drits, V.A., 1984b. Interpretation of Mössbauer spectra of dioctahedral iron(3+)-containing layered silicates. II. Nontronite. *Kristallografiya*, 29, 304–311.
- Dainyak, L.G., Drits, V.A., Heifits, L.M., 1992. Computer simulation of cation distribution in dioctahedral 2:1 layer silicates using IR data: Application to Mössbauer spectroscopy of a glauconite sample. *Clays and Clay Minerals*, 40, 470–479.
- Dainyak, L.G., Drits, V.A., 1987. Interpretation of Mössbauer spectra of nontronite, celadonite, and glauconite. *Clays and Clay Minerals*, 35, 363–372.
- Decarreau, A., Grauby, O., Petit, S., 1992. The actual distribution of octahedral cations in 2:1 clay minerals: results from clay synthesis. *Applied Clay Science*, 7, 147–167.
- Delville, A., 1991. Modeling the clay-water interface. *Langmuir*, 7, 547–555.
- Diamant, A., Pasternak, M., Banin, A., 1982. Characterization of adsorbed iron in montmorillonite by Mössbauer spectroscopy. *Clays and Clay Minerals*, 30, 63–66.
- Dong, H., Kostka, J.E., Kim, J., 2003a. Microscopic evidence for microbial dissolution of smectite. *Clays and Clay Minerals*, 51, 502–512.
- Dong, H.G., Kukkadapu, R.K., Frederickson, J.K., Zachara, J.M., Kennedy, D.W., Kostandarites, H.M., 2003b. Microbial reduction of structural Fe(III) in Illite and Goethite. *Environmental Science and Technology*, 37, 1268–1276.
- Drago, V., Saitovitch, E.B., Danon, J., 1977. Mössbauer spectroscopy of electron irradiated natural layered silicates. *Inorganic Nuclear Chemistry*, 39, 93–979.
- Drits, V.A., Manceau, A., 2000. A model for the mechanism of Fe³⁺ to Fe²⁺ reduction in dioctahedral smectites. *Clays and Clay Minerals*, 48, 185–195.

- Drits, V.A., Dainyak, L.G., Slonimskaya, M.V., 1981. Procedure for the calculation of crystal-chemical formulas of iron-containing sheet silicates. *Izvestiia Akademii Nauk SSSR, Seriya Geologicheskaya*, 12, 87–98.
- Dyar, M.D., Delaney, J.S., Sutton, S.R., 2001. Fe XANES spectra of iron-rich micas. *European Journal of Mineralogy*, 13, 1079–1098.
- Dyar, M.D., Gunter, M., Delaney, J.S., Lanzarotti, A., Sutton, S.R., 2002. Systematics in the structure and XANES spectra of pyroxenes, amphiboles, and micas as derived from oriented single crystals. *Canadian Mineralogist*, 40, 1375–1393.
- Ebitani, K., Ide, M., Mitsudome, T., Mizugaki, T., Kaneda, K., 2002. Creation of a chain-like cationic iron species in montmorillonite as a highly active heterogeneous catalyst for alkane oxygenations using hydrogen peroxide. *Chemical Communication*, 2002, 690–691.
- Egashira, K., Ohtsubo, M., 1983. Swelling and mineralogy of smectites in paddy soils derived from marine alluvium, Japan. *Geoderma*, 29, 119–127.
- Erbs, M., Hansen, H.C.B., Olsen, C.E., 1999. Reductive dechlorination of carbon tetrachloride using iron(II)-iron(III) hydroxide sulfate (green rust). *Environmental Science and Technology*, 33, 307–311.
- Ericsson, T., Linares, J., Lotse, E., 1984. A Mössbauer study of the effect of dithionite/citrate/bicarbonate treatment on a vermiculite, smectite and a soil. *Clay Minerals*, 19, 85–91.
- Ernstsen, V., 1996. Reduction of nitrate by Fe²⁺ in clay minerals. *Clays and Clay Minerals*, 44, 599–608.
- Ernstsen, V., Gates, W.P., Stucki, J.W., 1998. Microbial reduction of structural iron in clays -- A renewable source of reduction capacity. *Journal of Environmental Quality*, 27, 761–766.
- Eslinger, E., Highsmith, P., Albers, D., deMayo, B., 1979. Role of iron reduction in the conversion of smectite to illite in bentonites in the Disturbed Belt, Montana. *Clays and Clay Minerals*, 27, 327–338.
- Evangelou, V.P., Wang, J., Phillips, R.E., 1994. New developments and perspectives on soil potassium quantity/intensity relationships. *Advances in Agronomy*, 52, 173–227.
- Farmer, V.C., Russell, J.D., 1964. The infra-red spectra of layer silicates. *Spectrochimica Acta*, 20, 1149–1173.
- Farmer, V.C., Russell, J.D., 1966. Effects of particle size and structure on the vibrational frequencies of layer silicates. *Spectrochimica Acta*, 22, 389–398.
- Farmer, V.C., Russell, J.D., 1967. Infrared absorption spectrometry in clay studies. *Clays and Clay Minerals*, 15, 121–142.
- Favre, F., Ernstsen, V., Tessier, D., Boivin, P., 2002a. Short scale changes in soil properties due to structural iron reduction. *Geochimica et Cosmochimica Acta, Goldschmidt Conference Abstracts*, A226.
- Favre, F., Tessier, D., Abdelmoula, M., Genin, J.M., Gates, W.P., Boivin, P., 2002b. Iron reduction and changes in cation exchange capacity in intermittently waterlogged soil. *European Journal of Soil Science*, 53, 175–183.
- Favre, F., Jaunet, A.M., Pernes, M., Badraoui, M., Boivin, P., Tessier, D., 2004. Changes in clay organization due to structural iron reduction in a flooded vertisol. *Clay Minerals*, 39, 123–134.
- Fialips, C.-I., Huo, D., Yan, L., Wu, J., Stucki, J.W., 2002a. Infrared study of reduced and reduced-reoxidized ferruginous smectite. *Clays and Clay Minerals*, 50, 455–469.

- Fialips, C.-I., Huo, D., Yan, L., Wu, J., Stucki, J.W., 2002b. Effect of iron oxidation state on the IR spectra of Garfield nontronite. *American Mineralogist*, 87, 630–641.
- Fitch, A., Du, J., Gan, H., Stucki, J.W., 1995. Effect of clay charge on swelling: A clay-modified electrode study. *Clays and Clay Minerals*, 43, 607–614.
- Foster, M.D. 1953. Geochemical studies of clay minerals: II. relation between ionic substitution and swelling in montmorillonites. *American Mineralogist*, 38, 994–1006.
- Foster, M.D. 1955. The relationship between composition and swelling in clays. *Clays and Clay Minerals*, 3, 205–220.
- Frost, R.L., Klopogge, J.T., Ding, Z., 2002a. Garfield and Uley nontronites – an infrared spectroscopic comparison. *Spectrochimica Acta*, A 58, 1881–1894.
- Frost, R.L., Klopogge, J.T., Ding, Z., 2002b. Near-infrared spectroscopic study of nontronites and ferruginous smectite. *Spectrochimica Acta*, A 58, 1657–1668.
- Gan, H., Stucki, J.W., Bailey, G.W., 1992. Reduction of structural iron in ferruginous smectite by free radicals. *Clays and Clay Minerals*, 40, 659–665.
- Gan, H., Bailey, G.W., Yu, Y.S., 1996. Morphology of Lead(II) and Chromium(III) reaction products on phyllosilicate surfaces as determined by Atomic Force Microscopy. *Clays and Clay Minerals*, 44, 734–743.
- Gates, W.P., Wilkinson, H.T., Stucki, J.W., 1993. Swelling properties of microbially reduced ferruginous smectite. *Clays and Clay Minerals*, 41, 360–364.
- Gates, W.P., Stucki, J.W., Kirkpatrick, R.J., 1996. Structural properties of reduced Upton montmorillonite. *Physics and Chemistry of Minerals*, 23, 535–541.
- Gates, W.P., Jaunet, A.-M., Tessier, D., Cole, M.A., Wilkinson, H.T., Stucki, J.W., 1998. Swelling and texture of iron-bearing smectites reduced by bacteria. *Clays and Clay Minerals*, 46, 487–497.
- Gates, W.P., Komadel, P., Madejova, J., Bujdak, J., Stucki, J.W., and Kirkpatrick, R.J., 2000. Electronic and structural properties of reduced-charge montmorillonites. *Applied Clay Science*, 16, 257–271.
- Gates, W.P., Slade, P.G., Manceau, A., Lanson, B., 2002. Site occupancies by iron in nontronites. *Clays and Clay Minerals*, 50, 223–239.
- Genin, J.M.R., Bourrie, G., Trolard, F., Abdelmoula, M., Jaffrezic, A., Refait, P., Maitre, V., Humbert, B., Herbillon, A., 1998. Thermodynamic equilibria in aqueous suspensions of synthetic and natural Fe(II)-Fe(III) green rusts: occurrences of the mineral in hydromorphic soils. *Environmental Science and Technology*, 32, 1058–1068.
- Giresse, P. and Wiewiora, A., 2001. Stratigraphic condensed deposition and diagenetic evolution of green clay minerals in deep water sediments on the Ivory Coast-Ghana Ridge. *Marine Geology*, 179, 51–70.
- Goodman, B.A. 1978. The Mössbauer spectra of nontronites: consideration of an alternative assignment. *Clays and Clay Minerals*, 26, 176–177.
- Goodman, B.A., Russell, J.D., Fraser, A.R., Woodhams, F.D., 1976. A Mössbauer and I.R. spectroscopic study of the structure of nontronite. *Clays and Clay Minerals*, 24, 53–59.
- Gorby, Y.A., Amonette, J.E., and Fruchter, J.S., 1994. Remediation of contaminated subsurface materials by a metal-reducing bacterium. In: Gee, G.W., Wing, N.R. (Eds.), *Thirty-third Hanford Symposium on Health and the Environment*, Battelle Pacific Northwest National Laboratory, pp. 233–247.
- Grauby, O. 1993. Nature et étendue des solutions solides octaédriques argileuses. Approche par synthèse minérale. Thesis. University of Poitiers.

- Grauby, O., Petit, S., Decarreau, A., Baronnet, A., 1993. The beidellite-saponite series: an experimental approach. *European Journal of Mineralogy*, 5, 623–635.
- Grauby, O., Petit, S., Decarreau, A., Baronnet, A., 1994. Nontronite-saponite series: an experimental approach. *European Journal of Mineralogy*, 4, 99–112.
- Hansen, H.C.B. 1989. Composition, stabilization and light absorption of Fe(II)Fe(III) hydroxy carbonate ("Green Rust"). *Clay Minerals*, 24, 663–670.
- Hansen, H.C.B., Koch, C.B., 1998. Reduction of nitrate to ammonium by sulphate green rust: activation energy and reaction mechanism. *Clay Minerals*, 33, 87–101.
- Hansen, H.C.B., Poulsen, I.F., 1999. Interaction of synthetic sulphate "Green Rust" with phosphate and the crystallization of vivianite. *Clays and Clay Minerals*, 47, 312–318.
- Heller-Kallai, L., Rozenson, I., 1981. The use of Mössbauer spectroscopy of iron in clay mineralogy. *Physics and Chemistry of Minerals*, 7, 223–238.
- Heller-Kallai, L. 1997. Reduction and reoxidation of nontronite: The data reassessed. *Clays and Clay Minerals*, 45, 476–479.
- Helsen, J.A., Goodman, B.A., 1983. Characterization of iron(II)- and iron(III)-exchanged montmorillonite and hectorite using the Mössbauer effect. *Clay Minerals*, 13, 117–125.
- Hirt, A.M., Banin, A., Gehring, A.U., 1993. Thermal generation of ferromagnetic minerals from iron-enriched smectites. *Geophysical Journal International*, 115, 1161–1168.
- Hofstetter, T.B., Schwarzenbach, R.P., Haderlein, S.B., 2003. Reactivity of Fe(II) species associated with clay minerals. *Environmental Science and Technology*, 37, 519–528.
- Hunter, D.B., Bertsch, P.M., 1994. In situ measurements of tetraphenylboron degradation kinetics on clay mineral surfaces by IR. *Environmental Science and Technology*, 28, 686–691.
- Hunter, D.B., Gates, W.P., Bertsch, P.M., Kemner, K.M., 1998. Degradation of tetraphenylboron at hydrated smectite surfaces studied by time resolved IR and X-ray absorption spectroscopies. In: Sparks, D.L., Grundl, T.J. (Eds.), *Mineral-water interfacial reactions*, American Chemical Society, Washington, D.C., pp. 282–299.
- Huo, D. 1997. Infrared Study of Oxidized and Reduced Nontronite and Ca-K Competition in the Interlayer. Ph.D. Dissertation, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801.
- Istok, J.D., Amonette, J.E., Cole, C.R., Fruchter, J.S., Humphrey, M.D., Szecsody, J.E., Teel, S.S., Vermeul, V.R., Williams, M.D., Yabusaki, S.B., 1999. In situ redox manipulation by dithionite injection: intermediate-scale laboratory experiments. *Ground Water*, 37, 884–889.
- Johnston, J.H., Cardile, C.M., 1985. Iron sites in nontronite and the effect of interlayer cations from Mössbauer spectra. *Clays and Clay Minerals*, 33, 21–30.
- Johnston, J.H., Cardile, C.M., 1987. Iron substitution in montmorillonite, illite, and glauconite by Fe57 Mössbauer spectroscopy. *Clays and Clay Minerals*, 35, 170–176.
- Karickhoff, S.W., Bailey, G.W., 1973. Optical absorption spectra of clay minerals. *Clays and Clay Minerals*, 21, 59–70.
- Kawasaki, H. 1974. Change of ferric iron to ferrous iron in 2:1 type layer silicates by reduction. *Nippon Dojo Hiriyogaku Zasshi*, 45, 318–320.
- Keeling John, Raven, M., Gates, W.P., 2000. Geology and preliminary characterisation of two nontronites from Uley graphite mine, South Australia. *Clays and Clay Minerals*, 48, 537–548.
- Khaled, E.M., Stucki, J.W., 1991. Fe oxidation state effects on cation fixation in smectites. *Soil*

- Science Society of America Journal, 55, 550–554.
- Kim, J., Furukawa, Y., Daulton, T.E., Lavoie, D., Newell, S.W., 2003. Characterization of microbially Fe(III) reduced nontronite: environmental cell-transmission electron microscopy study. *Clays and Clay Minerals*, 51, 382–389.
- Kim, J., Dong, H., Seabaugh, J., Newell, S.W., Eberl, D.D., 2004. Role of microbes in the smectite-to-illite reaction. *Science*, 303, 830–832.
- Koch, C.B., Morup, S., 1991. Identification of green rust in an ochre sludge. *Clay Minerals*, 26, 577–582.
- Kocherginsky, N.M., Stucki, J.W., 2000. Sorption, diffusion, and desorption ofalachlor in oxidized and reduced smectite membranes. *Environmental Science and Technology*, 34, 3574–3578.
- Komadel, P., 1999. Structure and chemical characteristics of modified clays. In: Misaelides, P., Macasek, F., Pinnavaia, T.J., Colella, C. (Eds.), *Natural Microporous Materials in Environmental Technology*. Kluwer Academic Publishers, Dordrecht, pp. 3-18.
- Komadel, P., Stucki, J.W., Wilkinson, H.T., 1987. Reduction of structural iron in smectites by microorganisms. In: Galan, E. (Ed.), *The Sixth Meeting of the European Clay Groups*. Madrid, p. 322–324.
- Komadel, P., Lear, P.R., Stucki, J.W., 1990. Reduction and reoxidation of nontronite: Extent of reduction and reaction rates. *Clays and Clay Minerals*, 38, 203–208.
- Komadel, P., Stucki, J.W., Cícel, B., 1993. Readily HCl-soluble iron in the fine fractions of some Czech bentonites. *Geologica Carpathica, Series Clays*, 44, 11–16.
- Komadel, P., Doff, D.H., Stucki, J.W., 1994. Chemical stability of aluminium-iron- and iron-pillared montmorillonite: Extraction and reduction of iron. *Journal of the Chemical Society, Chemical Communications*, 1994, 1243–1244.
- Komadel, P., Madejova, J., Janek, M., Gates, W.P., Kirkpatrick, R.J., Stucki, J.W., 1996. Dissolution of hectorite in inorganic acids. *Clays and Clay Minerals*, 44, 228–236.
- Komadel, P., Grygar, T., Mehner, H., 1998. Reductive dissolution and Mössbauer spectroscopic study of Fe forms in the fine fractions of Slovak Fe-rich bentonites. *Clay Minerals*, 33, 593–599.
- Komadel, P., Madejová, J., Laird, D.A., Xia, Y., Stucki, J.W., 2000. Reduction of Fe(III) in griffithite. *Clay Minerals*, 35, 625–634.
- Koster, H. M., Ehrlicher, U., Gilg, H.A., Jordan, R., Murad, E., Onnich, K., 1999. Mineralogical and chemical characteristics of five nontronites and Fe-rich smectites. *Clay Minerals*, 34, 579–600.
- Kostka, J.E., Stucki, J.W., Nealson, K.H., Wu, J., 1996. Reduction of structural Fe(III) in smectite by a pure culture of the Fe-reducing bacterium *Shewanella putrefaciens* strain MR-1. *Clays and Clay Minerals*, 44, 522–529.
- Kostka, J.E., Wu, J., Nealson, K.H., Stucki, J.W., 1999a. Effects of microbial reduction on physical and chemical properties of clay minerals. *Geochimica et Cosmochimica Acta*, 63, 3705–3713.
- Kostka, J.E., Haeferle, E., Viehweger, R., Stucki, J.W., 1999b. Respiration and dissolution of Fe(III)-containing clay minerals by bacteria. *Environmental Science and Technology*, 33, 3127–3133.
- Kostka, J.E., Dalton, D.D., Skelton, H., Dollhopf, S., Stucki, J.W., 2002. Growth of iron(III)-reducing bacteria on clay minerals as the sole electron acceptor and comparison of growth yields on a variety of oxidized iron forms. *Applied and Environmental*

- Microbiology, 68, 6256–6262.
- Kriegman-King, M.R., Reinhard, M., 1994. Transformation of carbon tetrachloride by pyrite in aqueous solution. *Environmental Science and Technology*, 28, 692–700.
- Lear, P.R., Stucki, J.W., 1985. The role of structural hydrogen in the reduction and reoxidation of iron in nontronite. *Clays and Clay Minerals*, 33, 539–545.
- Lear, P.R., Stucki, J.W., 1987. Intervalence electron transfer and magnetic exchange in reduced nontronite. *Clays and Clay Minerals*, 35, 373–378.
- Lear, P.R., Stucki, J.W., 1990. Magnetic properties and site occupancy of iron in nontronite. *Clay Minerals*, 25, 3–13.
- Lee, W., Batchelor, B., 2002. Abiotic reductive dechlorination of chlorinated ethylenes by iron-bearing soil minerals. 2. Green Rust. *Environmental Science and Technology*, 36, 5348–5354.
- Lee, K., Kostka, J.E., Stucki, J.W., 2005. Infrared spectra of bacteria-reduced smectite. *Clays and Clay Minerals* (submitted).
- Leite, S.Q.M., Colodete, C.H.A., Dieguez, L.C., 2000. Extração de ferro de esmectita brasileira com emprego do método ditionito-citrato-bicarbonato. *Quimica Nova*, 23, 297–302.
- Lerf, A., Wagner, L.F., Poyato, J., 2001. Mössbauer spectroscopic investigation of redox reactions in vermiculites from Santa Olalla (Huelva, Spain). *Solid State Ionics*, 141–142, 479–486.
- Letaief, S., Casal, B., Kbir-Arighuib, N., Trabelsi-Ayadi, M., Ruiz-Hitzky, E., 2002. Fe-rich smectites from Gafsa (Tunisia): characterization and pillaring behavior. *Clay Minerals*, 37, 517–529.
- Li, O., Bleam, W.F., Kostka, J.E., Stucki, J.W., Lee, K., 2003. Polarized EXAFS studies of nontronite reduced by anaerobic bacteria. *Abstracts of Papers of the American Chemical Society*, Abstracts, 226, U492, 152-ENVR Part 1, Sep 2003.
- Li, O., Lee, K., Kostka, J.E., Stucki, J.W., Bleam, W.F., 2003. Polarized EXAFS studies of nontronite: Effect of repeated reduction-oxidation cycles and iron-reducing bacteria on structure. *American Mineralogist* (submitted)
- Loeppert, R.H., 1988. Chemistry of iron in calcareous systems. In: Stucki, J.W., Goodman, B.A., Schwertmann, U. (Eds.), *Iron in Soils and Clay Minerals*. D. Reidel, Dordrecht, pp. 689–713.
- Lovley, D.R., Fraga, J.L., Blunt-Harris, E.L., Hayes, L.A., Phillips, E.J.P., Coates, J.D., 1998. Humic substances as a mediator for microbially catalyzed metal reduction. *Acta Hydrochimica et Hydrobiologica*, 26, 152–157.
- Low, P.F., 1951. Force fields and chemical equilibrium in heterogeneous systems with special reference to soils. *Soil Science*, 71, 409–418.
- Low, P.F., 1961. Physical chemistry of clay-water interaction. *Advances in Agronomy*, 13, 269–327.
- Low, P.F., 1979. Nature and properties of water in montmorillonite-water systems. *Soil Science Society of America Journal*, 43, 651–658.
- Low, P.F., 1980. The swelling of clay. II. Montmorillonites. *Soil Science Society of America Journal*, 44, 667–676.
- Low, P.F., 1987. Structural component of the swelling pressure of clays. *Langmuir*, 3, 18–25.
- Luca, V., 1991a. Detection of tetrahedral Fe³⁺ site in nontronite and vermiculite by Mössbauer spectroscopy. *Clays and Clay Minerals*, 39, 467–477.
- Luca, V., 1991b. ⁵⁷Fe Mössbauer spectroscopic study of structural changes during dehydration

- of nontronite: Effect of different exchangeable cations. *Clays and Clay Minerals*, 39, 478–489.
- Luca, V., Cardile, C.M., 1989. Improved detection of tetrahedral Fe³⁺ in nontronite SWa-1 by Mössbauer spectroscopy. *Clay Minerals*, 24, 555–560.
- Luca, V., Maclachlan, D.J., 1992. Site occupancy in nontronite studied by acid dissolution and Mössbauer spectroscopy. *Clays and Clay Minerals*, 40, 1–7.
- Lumbanraja, J., Evangelou, V.P., 1990. Binary and ternary exchange behavior of potassium and ammonium on Kentucky subsoils. *Soil Science Society of America Journal*, 54, 698–705.
- Lumbanraja, J., Evangelou, V.P., 1992. Potassium quantity-intensity relationships in the presence and absence of NH₄ for three Kentucky soils. *Soil Science*, 154, 366–376.
- Lumbanraja, J., Evangelou, V.P., 1994. Adsorption-desorption of potassium and ammonium at low cation concentrations in three Kentucky subsoils. *Soil Science*, 157, 269–278.
- MacKenzie, K.J.D., Rogers, D.E., 1977. Thermal and Mössbauer studies of iron-containing hydrous silicates. I. Nontronite. *Thermochimica Acta*, 18, 177–196.
- Madejova, J., Komadel, P., Cícel, B., 1992. Infrared spectra of some Czech and Slovak smectites and their correlation with structural formulas. *Geologica Carpathica, Series Clays*, 1, 9–12.
- Madejova, J., Bednarikova, E., Komadel, P., Cícel, B., 1993. Structural study of acid-treated smectites by IR spectroscopy. *Eleventh Conference on Clay Mineralogy and Petrology*, C, Budejovice, pp. 267–271.
- Madejova, J., Komadel, P., Cícel, B., 1994. Infrared study of octahedral site populations in smectites. *Clay Minerals*, 29, 319–326.
- Madejova, J., Kraus, I., Komadel, P., 1995. Fourier transform infrared spectroscopic characterization of dioctahedral smectites and illites from the main Slovak deposits. *Geologica Carpathica, Series Clays*, 4, 23–32.
- Madejova, J., Bujdak, J., Janek, M., Komadel, P., 1998. Comparative FTIR study of structural modifications during acid treatment of dioctahedral smectites and hectorite. *Spectrochimica Acta, Part A*, 54, 1397–1406.
- Malysheva, T.V., 1994. Mössbauer study of redox processes in the evolution of chondrites. *Mineralogical Magazine*, 58, 151–158.
- Manceau A, Lanson, B., Drits, V.A., Chateigner, D., Gates, W.P., Wu, J., Huo, D., Stucki, J.W., 2000a. Oxidation-reduction mechanism of iron in dioctahedral smectites. 1. Crystal chemistry of oxidized reference nontronites. *American Mineralogist*, 85, 133–152.
- Manceau A, Lanson, B., Drits, V.A., Chateigner, D., Wu, J., Huo, D., Gates, W.P., Stucki, J.W., 2000b. Oxidation-reduction mechanism of iron in dioctahedral smectites. 2. Structural chemistry of reduced Garfield nontronite. *American Mineralogist*, 85, 153–172.
- Martin, F., Petit, M., Decarreau, A., Grauby, O., Hazemann, J.L., Noack, Y., 1992. Experimental study of Si-Ge tetrahedral solid solution in Ni-Co-Mg talcs. *Thin Solid Films*, 222, 189–195.
- Martin, F., Petit, S., Decarreau, A., Ildefonse, P., Grauby, O., Beziat, D., Parseval, P.D., Noack, Y., 1998. Ga/Al substitutions in synthetic kaolinites and smectites. *Clay Minerals*, 33, 231–241.
- McBride, M.B., 1979. Reactivity of adsorbed and structural iron in hectorite as indicated by oxidation of benzidine. *Clays and Clay Minerals*, 27, 224–230.
- Mehra, O.P., Jackson, M.L., 1960. Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. In: Swineford, A. (Ed.), *Seventh National*

- Conference on Clays and Clay Minerals, National Research Council, Washington, D.C., pp. 317–327.
- Mishra, T., Parida, K., 1998. Transition metal oxide pillared clay: 5. Synthesis, characterisation and catalytic activity of iron-chromium mixed oxide pillared montmorillonite. *Applied Catalysis A: General*, 174, 91–98.
- Mody, H.M., Oza, P.M., Pandya, V.P., 1993. Thermally stable and acidic iron oxide pillared clay. *Journal of Indian Chemical Society*, 70, 11–13.
- Muller, F., Besson, G., Manceau, A., Drits, V.A., 1997. Distribution of isomorphous cations within octahedral sheets in montmorillonite from Camp-Bertaux. *Physics and Chemistry of Minerals*, 24, 159–166.
- Murad, E., 1987. Mössbauer spectra of nontronites: structural implications and characterization of associated iron oxides. *Zeitschrift für Pflanzenernährung und Bodenkunde*, 150, 279–285.
- Murad, E., 1988. Properties and behavior of iron oxides as determined by Mössbauer spectroscopy. In: Stucki, J.W., Goodman, B.A., Schwertmann, U. (Eds.), *Iron in Soils and Clay Minerals*. D. Reidel, Dordrecht, pp. 309–350.
- Murad, E., 1998. Clays and clay minerals: What can Mössbauer spectroscopy do to help understand them? *Hyperfine Interactions*, 117, 39–70.
- Murad, E., Fischer, W.R., 1988. Geobiochemical cycle of iron. In: Stucki, J.W., Goodman, B.A., Schwertmann, U. (Eds.), *Iron in Soils and Clay Minerals*. D. Reidel, Dordrecht, pp. 1–18.
- Murad, E., Taylor, R.M., 1984. The Mössbauer spectra of hydroxycarbonate green rusts. *Clay Minerals*, 19, 77–83.
- Murad, E., Cashion, J.D., Brown, L.J., 1990. Magnetic ordering in Garfield nontronite under applied magnetic fields. *Clay Minerals*, 25, 261–265.
- Myers, C.R., Nealson, K.H., 1988. Bacterial manganese reduction and growth with manganese oxide as the sole electron acceptor. *Science*, 240, 1319–1321.
- Nembrini, G.P., Capobianco, J.A., View, M., Williams, A.F., 1983. A Mössbauer and chemical study of the formation of vivianite in sediments of Lago Maggiore (Italy). *Geochimica et Cosmochimica Acta*, 47, 1459–1464.
- Nzengung, V.A., Castillo, R.M., Gates, W.P., Mills, G.L., 2001. Abiotic transformation of perchloroethylene in homogeneous dithionite solution and in suspension of dithionite-treated clay minerals. *Environmental Science and Technology*, 35, 2244–2251.
- Osthaus, B.B., 1953. Chemical determination of tetrahedral ions in nontronite and montmorillonite. *Clays and Clay Minerals*, 2, 404–417.
- Osthaus, B.B., 1956. Kinetic studies on montmorillonites and nontronites by the acid dissolution technique. *Clays and Clay Minerals*, 4, 301–321.
- Peterson, R.C., Hill, R.J., Gibbs, G.V., 1979. A molecular-orbital study of distortions in the layer structures of brucite, gibbsite and serpentine. *Canadian Mineralogist*, 17, 703–711.
- Petit, S., Robert, J.L., Decarreau, A., Besson, G., Grauby, O., Martin, F., 1995. Contribution of spectroscopic methods to 2/1 clay characterization. *Bulletin des Centres de Recherches Exploration-Production Elf Aquitaine*, 19, 119–147.
- Petit, S., Madejova, J., Decarreau, A., Martin, F., 1999. Characterization of octahedral substitutions in kaolinites using near infrared spectroscopy. *Clays and Clay Minerals*, 47, 103–108.
- Rancourt, D.G., 1989. Accurate site populations from Mössbauer spectroscopy. *Nuclear Instruments and Methods in Physics Research*, 44, 199–210.

- Rancourt, D.G., 1994a. Mössbauer spectroscopy of minerals. I. Inadequacy of Lorentzian-line doublets in fitting spectra arising from quadrupole splitting distributions. *Physics and Chemistry of Minerals*, 21, 244–249.
- Rancourt, D.G., 1994b. Mössbauer spectroscopy of minerals. II. Problem of resolving cis and trans octahedral Fe²⁺ sites. *Physics and Chemistry of Minerals*, 21, 250–257.
- Rancourt, D.G., 1998. Mössbauer spectroscopy in clay science. *Hyperfine Interactions*, 117, 3–38.
- Rancourt, D.G., McDonald, A.M., Lalonde, A.E., Ping, J.Y., 1993. Mössbauer absorber thicknesses for accurate site populations in Fe-bearing minerals. *American Mineralogist*, 78, 1–7.
- Rancourt, D.G., Ping, J.Y., Berman, R.G., 1994a. Mössbauer spectroscopy of minerals. III. Octahedral-site Fe²⁺ quadrupole splitting distributions in the phlogopite-annite series. *Physics and Chemistry of Minerals*, 21, 258–267.
- Rancourt, D.G., Christie, I.A.D., Royer, M., Kodama, H., Robert, J.L., Lalonde, A.E., Murad, E., 1994b. Determination of accurate ⁴Fe³⁺, ⁶Fe³⁺, and ⁶Fe²⁺ site populations in synthetic annite by Mössbauer spectroscopy. *American Mineralogist*, 79, 51–62.
- Rightor, E.G., Tzou, M.S., Pinnavaia, T.J., 1991. Iron oxide pillared clay with large gallery height: synthesis and properties as a Fischer-Tropsch catalyst. *Journal of Catalysis*, 130, 29–40.
- Rinker, R.G., Gordon, T.P., Corcoran, W.H., 1964. Electron spin resonance studies of sodium dithionite and sodium formaldehyde sulfoxylate. *Inorganic Chemistry*, 3, 1467–1469.
- Robert, J.L., Kodama, H., 1988. Generalization of the correlations between hydroxyl-stretching wavenumbers and composition of micas in the system K₂O-MgO-Al₂O₃-SiO₂-H₂O: a single model for trioctahedral and dioctahedral micas. *American Journal of Science*, 288-A, 196–212.
- Rodriguez, E.A., Amonette, J.E., Divanfar, H.R., Marquez, J.F., 1999. Use of Fe(II) associated with layer silicates for remediation of groundwater contaminated by CCl₄, TCE, and TNT. Abstracts and Program, Environmental Molecular Sciences Symposia and First Users' Meeting, Pacific Northwest National Laboratory, Richland, pp. 41-42.
- Roth, C.B., Tullock, R.J., 1973. Deprotonation of nontronite resulting from chemical reduction of structural ferric iron. In: Serratos, J.M. (Ed.), *Proceedings of the International Clay Conference, 1972, Madrid*. Division Ciencias C.S.I.C., Madrid, pp. 107–114.
- Roth, C.B., Jackson, M.L., Lotse, E.G., Syers, J.K., 1968. Ferrous-ferric ratio and C. E. C. changes on deferration of weathered micaceous vermiculites. *Israel Journal of Chemistry*, 6, 261–273.
- Roth, C.B., Jackson, M.L., Syers, J.K., 1969. Deferration effect on structural ferrous-ferric iron ratio and CEC of vermiculites and soils. *Clays and Clay Minerals*, 17, 253–264.
- Rozenson, I., Heller-Kallai, L., 1976a. Reduction and oxidation of Fe³⁺ in dioctahedral smectite--1: Reduction with hydrazine and dithionite. *Clays and Clay Minerals*, 24, 271–282.
- Rozenson, I., Heller-Kallai, L., 1976b. Reduction and oxidation of Fe³⁺ in dioctahedral smectite--2: Reduction with sodium sulphide solution. *Clays and Clay Minerals*, 24, 283–288.
- Rozenson, I., Heller-Kallai, L., 1977. Mössbauer spectra of dioctahedral smectites. *Clays and Clay Minerals*, 25, 94–101.
- Russell, J.D., Goodman, B.A., Fraser, A.R., 1979. Infrared and Mössbauer studies of reduced nontronites. *Clays and Clay Minerals*, 27, 63–71.
- Scherer, H., Zhang, Y., 2002. Mechanisms of fixation and release of ammonium in paddy soils

- after flooding. III. Effect of the oxidation state of octahedral Fe on ammonium fixation. *Journal of Plant Nutrition and Soil Science*, 165, 185–189.
- Schuette, R., Goodman, B.A., Stucki, J.W., 2000. Magnetic properties of oxidized and reduced smectites. *Physics and Chemistry of Minerals*, 27, 251–257.
- Schwertmann, U., 1988a. Occurrence and formation of iron oxides in various pedoenvironments. In: Stucki, J.W., Goodman, B.A., Schwertmann, U. (Eds.), *Iron in Soils and Clay Minerals*. D. Reidel, Dordrecht, pp. 267–308.
- Schwertmann, U., 1988b. Some properties of soil and synthetic iron oxides. In: Stucki, J.W., Goodman, B.A., Schwertmann, U. (Eds.), *Iron in Soils and Clay Minerals*. D. Reidel, Dordrecht, pp. 203–250.
- Schwertmann, U., Fechter, H., 1994. The formation of green rust and its transformation to lepidocrocite. *Clay Minerals*, 29, 87–92.
- Shen, S., Stucki, J.W., 1994. Effects of iron oxidation state on the fate and behavior of potassium in soils. In: Havlin, J.L., Jacobsen, J.S. (Eds.), *Soil testing: prospects for improving nutrient recommendations*, SSSA Special Publication 40. Soil Science Society of America, Madison, pp. 173–185.
- Shen, S., Stucki, J.W., Boast, C.W., 1992. Effects of structural iron reduction on the hydraulic conductivity of Na-smectite. *Clays and Clay Minerals*, 40, 381–386.
- Sherman, D.M., Vergo, N., 1988. Optical (diffuse reflectance) and Mössbauer spectroscopic study of nontronite and related Fe-bearing smectites. *American Mineralogist*, 73, 1346–1354.
- Singh, B., Hefferman, S., 2002. Layer charge characteristics of smectites from Vertosols (Vertisols) of New South Wales. *Australian Journal of Soil Research*, 40, 1159–1170.
- Sorensen, K.C., Stucki, J.W., Plewa, M.J., 2003. Comparative quantitative analysis of agricultural chemicals using a microplate mammalian cell cytotoxicity assay. *Bulletin of Environmental Contamination and Toxicology*, 70, 1083–1088.
- Sorensen, K.C., Stucki, J.W., Warner, R.E., Plewa, M.J., 2004. Alteration of mammalian-cell toxicity of pesticides by structural iron(II) in ferruginous smectite. *Environmental Science and Technology*, 38, 4383–4389.
- Sorensen, K.C., Stucki, J.W., Warner, R.E., Wagner, E.D., Plewa, M.J. 2005. Modulation of the genotoxicity of pesticides reacted with redox-modified smectite clay. *Environmental and Molecular Mutagenesis* (submitted).
- Stubican, V., Roy, R., 1961a. Infrared spectra of layer-structure silicates. *Journal of the American Ceramic Society*, 44, 625–627.
- Stubican, V., Roy, R., 1961b. Isomorphous substitution and infrared spectra of the layer silicates. *American Mineralogist*, 46, 32–51.
- Stubican, V., Roy, R. 1961c. A new approach to assignment of infrared absorption bands in layer-structure silicates. *Zeitschrift für Kristallografie*, 115, 200–214.
- Stucki, J.W., 1988. Iron in smectites. In: Stucki, J.W., Goodman, B.A., Schwertmann, U. (Eds.), *Iron in Soils and Clay Minerals*. D. Reidel, Dordrecht, pp. 625–67
- Stucki, J.W., Getty, P.J. 1986. Microbial reduction of iron in nontronite. *Agronomy Abstracts*, 1986, 279.
- Stucki, J.W., Lear, P.R., 1989. Variable oxidation states of Fe in the crystal structure of smectite clay minerals. In: Coyne, L.M., McKeever, S.W.S., Blake, D.E. (Eds.), *Spectroscopic Characterization of Minerals and their Surfaces*. American Chemical Society, Washington, D.C., pp. 330–358.

- Stucki, J.W., Roth, C.B., 1976. Interpretation of infrared spectra of oxidized and reduced nontronite. *Clays and Clay Minerals*, 24, 293–296.
- Stucki, J.W., Roth, C.B., 1977. Oxidation-reduction mechanism for structural iron in nontronite. *Soil Science Society of America Journal*, 41, 808–814.
- Stucki, J.W., Tessier, D., 1991. Effects of iron oxidation state on the texture and structural order of Na-nontronite gels. *Clays and Clay Minerals*, 39, 137–143.
- Stucki, J.W., Roth, C.B., Baitinger, W.E., 1976. Analysis of iron-bearing clay minerals by electron spectroscopy for chemical analysis (ESCA). *Clays and Clay Minerals*, 24, 289–292.
- Stucki, J.W., Golden, D.C., Roth, C.B., 1984a. Effects of reduction and reoxidation of structural Fe on the surface charge and dissolution of dioctahedral smectites. *Clays and Clay Minerals*, 32, 350–356.
- Stucki, J.W., Golden, D.C., Roth, C.B., 1984b. Preparation and handling of dithionite-reduced smectite suspensions. *Clays and Clay Minerals*, 32, 191–197.
- Stucki, J.W., Low, P.F., Roth, C.B., Golden, D.C., 1984c. Effects of oxidation state of octahedral iron on clay swelling. *Clays and Clay Minerals*, 32, 357–362.
- Stucki, J.W., Komadel, P., Wilkinson, H.T., 1987. Microbial reduction of structural iron(III) in smectites. *Soil Science Society of America Journal*, 51, 1663–1665.
- Stucki, J.W., Goodman, B.A., Schwertmann, U. (Eds.), 1988. *Iron in Soils and Clay Minerals*. D. Reidel, Dordrecht, 893 p.
- Stucki, J.W., Wu, J., Gan, H., Komadel, P., Banin, A., 2000. Effects of Fe oxidation state and organic cations on smectite hydration. *Clays and Clay Minerals*, 48, 290–298.
- Stucki, J.W., Lee, K., Zhang, L., Larson, R.A., 2002. The effects of iron oxidation state on the surface and structural properties of smectites. *Pure and Applied Chemistry*, 74, 2079–2092.
- Taylor, R.W., Shen, S., Blean, W.F., Tu, S.I., 2000. Chromate removal by dithionite-reduced clays: evidence from direct x-ray absorption near edge spectroscopy (XANES) of chromate reduction at clay surfaces. *Clays and Clay Minerals*, 48, 648–654.
- Tennakoon, D.T.B., Thomas, J.M., Tricker, M.J., 1974. Surface and intercalate chemistry of layered silicates. Part II. An iron-57 Mössbauer study of the role of lattice-substituted iron in the benzidine blue reaction of montmorillonite. *Journal of the Chemical Society, Dalton Transactions*, 1974, 2207–2211.
- Thompson, D.W., Tahir, N.M., 1991. Influence of a smectite clay on the hydrolysis of iron(III). *Colloids and Surfaces*, 60, 369–398.
- Tkac, I., Komadel, P., Muller, D., 1993. ^{29}Si and ^{27}Al MAS-NMR study of acid leaching of montmorillonite. *Eleventh Conference on Clay Mineralogy and Petrology*, C, Budejovice, pp. 273–279.
- Tkac, I., Komadel, P., Muller, D., 1994. Acid-treated montmorillonites – a study by ^{29}Si and ^{27}Al MAS NMR. *Clay Minerals*, 29, 11–19.
- Tor, J.M., Xu, C., Stucki, J.W., Wander, M.M., Sims, G.K., 2000. Trifluralin degradation under microbiologically induced nitrate and Fe(III) reduced conditions. *Environmental Science and Technology*, 34, 3148–3152.
- Tsipursky, S.I., Drits, V.A., 1984. The distribution of octahedral cations in the 2:1 layers of dioctahedral smectites studied by oblique-texture electron diffraction. *Clay Minerals*, 19, 177–193.
- Tsipursky, S.I., Drits, V.A., Checkin, S.S., 1978. Study of structural ordering of nontronite by

- oblique texture electron diffraction. *Investiya Akademii Nauk, SSSR, Seriya Geologicheskaya* 10, 105–113.
- van Breemen, N., 1988a. Effects of seasonal redox processes involving iron on the chemistry of periodically reduced soils. In: Stucki, J.W., Goodman, B.A., Schwertmann, U. (Eds.), *Iron in Soils and Clay Minerals*. D. Reidel, Dordrecht, pp. 797–809.
- van Breemen, N., 1988b. Long-term chemical, mineralogical, and morphological effects of iron-redox processes in periodically flooded soils. In: Stucki, J.W., Goodman, B.A., Schwertmann, U. (Eds.), *Iron in Soils and Clay Minerals*. D. Reidel, Dordrecht, pp. 811–823.
- van Breemen, N., 1988c. Redox processes of iron and sulfur involved in the formation of acid sulfate soils. In: Stucki, J.W., Goodman, B.A., Schwertmann, U. (Eds.), *Iron in Soils and Clay Minerals*. D. Reidel, Dordrecht, pp. 825–841.
- Viani, B.E., Low, P.F., Roth, C.B., 1983. Direct measurement of the relation between interlayer force and interlayer distance in the swelling of montmorillonites. *Journal of Colloid and Interface Science*, 96, 229–244.
- Viani, B.E., Roth, C.B., Low, P.F., 1985. Direct measurement of the relation between swelling pressure and interlayer distance in Li-vermiculite. *Clays and Clay Minerals*, 33, 244–250.
- Vieira Coelho, A.C., Ladriere, J., Poncelet, G., 2000. Nickel, iron-containing clay minerals from Niquelândia deposit, Brazil. 2. Behavior under reducing conditions. *Applied Clay Science*, 17, 183–204.
- Wasserman, S.R., Soderholm, L., 1998. Effect of surface modification on the interlayer chemistry of iron in a smectite clay. *Chemistry of Materials*, 10, 559–566.
- Wu, J., Roth, C.B., Low, P.F., 1988. Biological reduction of structural Fe in sodium-nontronite. *Soil Science Society of America Journal*, 52, 295–296.
- Wu, J., Low, P.F., Roth, C.B., 1989. Effects of octahedral iron reduction and swelling pressure on interlayer distances in Na-nontronite. *Clays and Clay Minerals*, 37, 211–218.
- Xiang, Y., Villemure, G., 1992. Electron transport in clay-modified electrodes: study of electron transfer between electrochemically oxidized tris(2,2'-bipyridyl) iron cations and clay structural iron(II) sites. *Canadian Journal of Chemistry*, 70, 1833–1837.
- Xiang, Y., Villemure, G., 1994. Influence of dissociation of tris(2,2'-bipyridyl) iron(II) cations on the time dependence of currents in clay-modified electrodes. *Journal of Electroanalytical Chemistry*, 370, 53–58.
- Xiang, Y., Villemure, G., 1995. Electrodes modified with synthetic clay minerals: evidence of direct electron transfer from structural iron sites in the clay lattice. *Journal of Electroanalytical Chemistry*, 381, 21–27.
- Xu, C., Kocherginsky, N.M., Stucki, J.W., Sims, G.K., 1996. Effect of soil oxidation state on the fate and behavior of agricultural chemicals. In: *Research on Agricultural Chemicals in Illinois Groundwater: Status and Future Directions*. VI. Proceedings of the Sixth Annual Conference. Illinois Groundwater Consortium, Carbondale, pp. 251–260.
- Xu, J.C., Sims, G.K., Kostka, J.E., Wu, J., Stucki, J.W., 2001. Fate of atrazine and alachlor in redox treated ferruginous smectite. *Environmental Toxicology and Chemistry*, 20, 2717–2724.
- Yamagishi, A., 1982. Racemic adsorption of iron(II)tris(1,10-phenanthroline) chelate on a colloidal clay. *Journal of Physical Chemistry*, 86, 2472–2479.
- Yan, L., Bailey, G.W., 2001. Sorption and abiotic redox transformation of nitrobenzene at the smectite-water interface. *Journal of Colloid and Interface Science*, 241, 142–153.

- Yan, L., Low, P.F., Roth, C.B., 1996a. Enthalpy changes accompanying the collapse of montmorillonite layers and the penetration of electrolyte into interlayer space. *Journal of Colloid and Interface Science*, 182, 417–424.
- Yan, L., Low, P.F., Roth, C.B., 1996b. Swelling pressure of montmorillonite layers versus H-O-H bending frequency of the interlayer water. *Clays and Clay Minerals*, 44, 749–765.
- Yan, L., Roth, C.B., Low, P.F., 1996c. Changes in the Si-O vibrations of smectite layers accompanying the sorption of interlayer water. *Langmuir*, 12, 4421–4429.
- Yan, L., Roth, C.B., Low, P.F., 1996d. Effects of monovalent, exchangeable cations and electrolytes on the infrared vibrations of smectite layers and interlayer water. *Journal of Colloid and Interface Science*, 184, 663–670.
- Yan, L., Stucki, J.W., 1999. Effects of structural Fe oxidation state and hydration on layer Si-O stretching vibrations of montmorillonite. *Langmuir*, 15, 4648–4657.
- Yan, L., Stucki, J.W., 2000. Structural perturbations in the solid-water interface of redox transformed nontronite. *Journal of Colloid and Interface Science*, 225, 429–439.
- Zhang, L., 2002. Impact of iron and iron-containing smectites on the fate of organic contaminants. M.S. Thesis, University of Illinois, Urbana, Illinois.
- Zhang, L., Larson, R.A., Stucki, J.W., Kostka, J.E., 2005. Transformation of oxamyl in redox-treated, iron-bearing smectites. *Clays and Clay Minerals* (submitted).