Effects of iron oxidation state on the surface and structural properties of smectites*

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Abstract: The oxidation state of iron (Fe) in the crystal structure of smectite clay minerals profoundly alters their physical–chemical properties. Among the properties affected are layer charge, cation exchange and fixation capacity, swelling in water, particle size, specific surface area, layer stacking order, magnetic exchange interactions, octahedral site occupancy, surface acidity, and reduction potential. Also affected is the surface chemistry of the clay, which alters clay–water and clay–organic interaction mechanisms. Rates and extents of degradation of pesticides are increased in the presence of reduced smectites compared to oxidized and reduced–reoxidized counterparts. A hypothesis regarding the mechanism for Fe reduction in clay minerals was first developed in 1963, and subsequent modifications have been proposed periodically through the present time. Recent studies clearly reveal that the process of Fe reduction involves more than the mere transfer of an electron to octahedral Fe(III) in the clay crystal. Ancillary reactions occur that produce significant structural modifications, some of which are reversible and others of which are not. Such changes in the crystal–chemical environment of structural Fe are thought to play a dominant role in altering the clay surface chemistry.

INTRODUCTION

Studies over the past several decades have clearly demonstrated that the oxidation state of Fe in the crystal structure of smectite clay minerals greatly influences the physical, chemical, surface, and colloidal behavior of these finely divided layered structures [1]. These effects are of great importance to agriculture and the environment because clay minerals play a pivotal role in determining the physical–chemical properties and behavior of soils and sediments. The oxidation state may also exert significant influence on the efficiency of certain industrial processes and on the properties of numerous manufactured materials and products in which clay minerals are used. An understanding of the underlying mechanisms and relationships between Fe oxidation state and clay properties is, therefore, critical to many facets of Earth and its cultures.

The basic structure of smectite clay minerals has been defined and illustrated in many publications, one representation of which is given in Fig. 1. Iron normally occupies six-coordinate sites in the octahedral sheet of the clay layer, but may exist in small amounts in the four-coordinate tetrahedral sites where it replaces Si [2,3]. The isomorphous substitution of Fe for Al in the octahedral sheet affects many physical–chemical properties of the clay (Table 1), even without a change in oxidation state. Little is known about the role of tetrahedral Fe in determining physical and chemical properties.
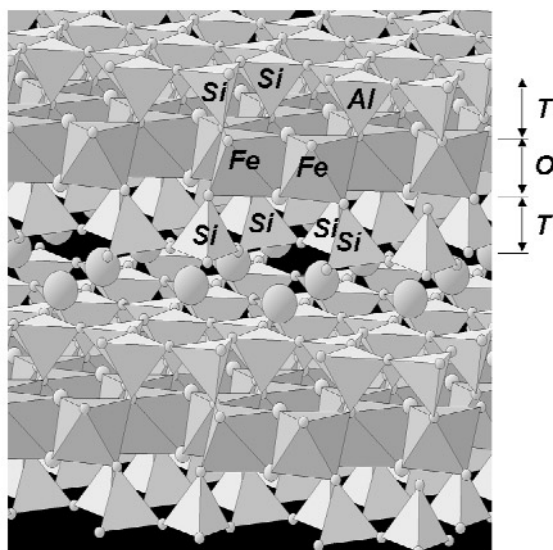

Fig. 1 Illustration of the layer structure of smectite.

Table 1 The effects of structural Fe on smectite properties (updated from Stucki [1]).

Property	Change in property due to		
	Fe(III)		Fe(II)
	Octahedral	Tetrahedral	Octahedral
Dioctahedral			
Layer charge	Nc	↑	↑
Cation exchange capacity	Nc	↑	↑
Cation fixation capacity	Nc	?	↑
Swelling in water	↓	?	↓↑
Crystallographic *b*-dimension	↑	↑	↑
Specific surface area	?	?	↓
Color	Greenish-yellow	?	Green, blue-green, blue-gray, gray
Chemical and thermal stability	↓	↓	↓
Trioctahedral			
Layer charge	Nc	↑	↑
Cation exchange capacity	Nc	↑	↑
Cation fixation capacity	?	?	?
Swelling in water	?	?	?
Crystallographic *b*-dimension		↑	↑
Specific surface area	?	?	?
Color	Yellow-brown	?	Green, blue
Chemical and thermal stability	↓	?	↑

Nc = no change

Studies of changes in the oxidation state of structural Fe in clays have focused primarily on the octahedral sheet [1]; although, Russell and coworkers [4–6] examined tetrahedral Fe in ferruginous smectites, finding that tetrahedral Fe is more common than previously known and that it can be liber-

ated at high pH. The precise effects of redox reactions on tetrahedral Fe are, however, still rather unclear.

SOURCES OF REDUCTION

Iron in the octahedral sheet can be reduced from Fe(III) to Fe(II) using a number of different methods and reducing agents (Table 2). The level of Fe(II) achieved in the clay structure cannot be predicted, however, merely based on the standard reduction potential of the reducing agent. For example, hydrazine and dithionite have approximately the same electrode reduction potential, but dithionite is able to reduce virtually all of the structural Fe if the reaction is allowed to proceed in an open, but inert atmosphere, system [7]; whereas, the effectiveness of hydrazine as a reductant is much less. The difference appears to be related to the fact that dithionite disproportionates into sulfoxylate free radicals when added to aqueous clay suspension, which greatly enhances its electron activity and reducing capacity [8]. Dithionite is, in fact, the only inorganic agent tested thus far that can reduce virtually all structural Fe under ambient conditions. The exact mechanism for electron transfer into the clay, however, has yet to be identified.

Table 2 Methods used to reduce structural Fe in smectites.

Reducing agent	Smectite	References
Dithionite in citrate-bicarbonate	Nontronite, ferruginous smectite, montmorillonite, griffithite	23–25,52–55
Dithionite in water	Nontronite, montmorillonite	56,57
Hydrazine	Nontronite, montmorillonite	24,57–59
Sodium sulfide	Nontronite, montmorillonite	60
Sodium hydrosulfide	Soil clays, montmorillonite	61
Benzidine	Hectorite, montmorillonite	62,63
Hydrogen gas at high temperature (>300 ºC)	Nontronite	61,64,65
Electron irradiation	Vermiculite, talc	66
Bacteria	Nontronite, ferruginous smectite, montmorillonite	12,13,15,16,18–21,67,68

Bacteria have been known for many years to reduce Fe in various primary minerals such as Fe oxides [9–11], but discovery of their ability to reduce the less-accessible Fe in phyllosilicates was reported for the first time only more recently [12,13]. The level of Fe(II) produced by bacteria can be as high as 60 % in nontronite and ferruginous smectite [14,15]. Among other reducing agents, this level is exceeded only by dithionite. Bacteria in natural systems are thus expected to have a significant impact on the redox state of Fe in soil minerals, which has now been confirmed by Ernstsen et al. [16] and Favre et al. [17]. A very active research effort is currently in progress to learn more about the mechanisms and range of consequences for bacterial reduction of Fe in clay minerals [18–22].

EFFECTS OF REDOX ON CLAY STRUCTURE

Redox reactions have a large impact on the structure of smectites. Roth and Tullock [23] suggested that reduction of structural Fe in nontronite invoked concurrent dehydroxylation of the octahedral sheet. This was confirmed and quantified by Stucki and Roth [24] and Lear and Stucki [25]. Such changes in structure can be probed by various spectroscopic methods, which have revealed further refinements of our understanding of these changes. Using polarized extended X-ray absorption fine structure (EXAFS), Manceau et al. [3] demonstrated that, upon reduction, Fe migrates from *cis-* to *trans*-octa-

hedral sites, creating defects in the octahedral sheet (Fig. 2). The extent to which these defects permeate the sheet is still unclear, but Fialips et al. [26,27] found by infrared (FTIR) spectroscopy that, if the clay is fully reduced, it loses most of the structural OH stretching and bending bands (Fig. 3), except for some O–H stretching vibrations, which are associated with trioctahedral sites (M_3, small band at 3623 cm^{-1}) and strongly bound H_2O (broad band centered at 3400 cm^{-1}) environments. The strongly bound water is probably at least partially connected to the defects in the octahedral sheet rather than being entirely at the basal surface. By using the total area of the stretching vibrational mode for structural O–H, Fialips et al. [27] estimated the relation between the level of Fe reduction and dehydroxylation (Fig. 4) to be generally consistent with the findings of Lear and Stucki [25].
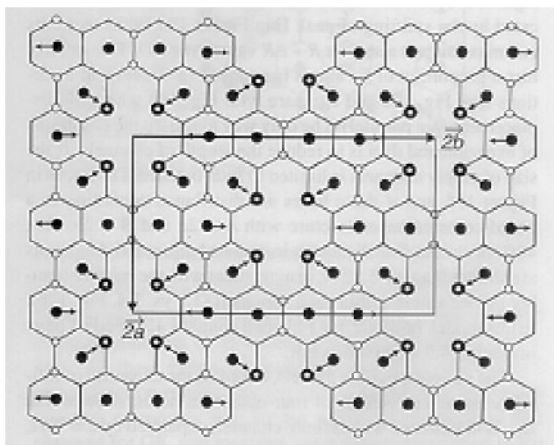

Fig. 2 Defects appearing in the octahedral sheet of reduced Garfield nontronite as a result of Fe migration from *cis-* to *trans*-octahedral sites (from Manceau et al. [3]).
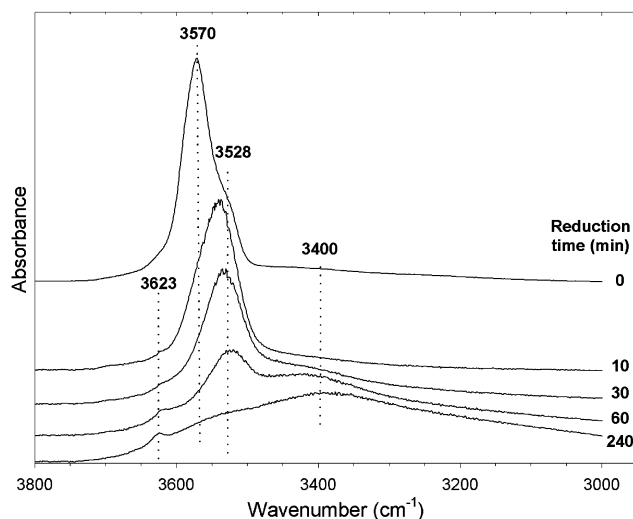

Fig. 3 Infrared spectra of redox-treated Garfield nontronite, showing structural O–H stretching region (from Fialips et al. [26]).
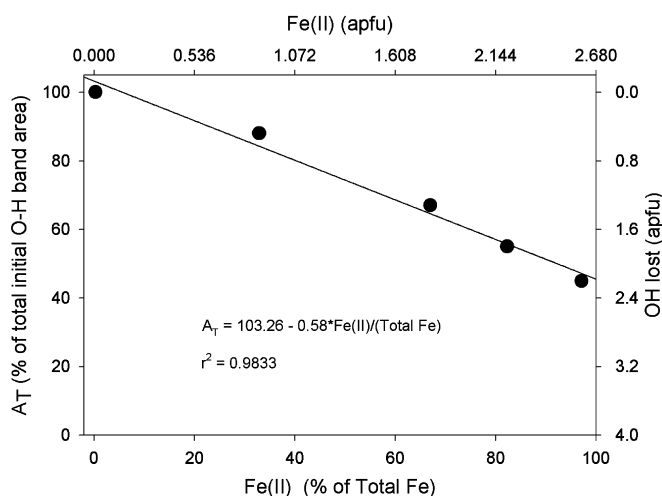
Fig. 4 Relation between structural O–H stretching band area and octahedral OH content in ferruginous smectite (from Fialips et al. [27]). Data are normalized to the Na^+, oxidized form.

These changes in structural composition occur progressively as the extent of Fe(II) increases in the octahedral sheet, and the ability to reverse the structural changes by reoxidation becomes increasingly more difficult as the initial level of reduction increases [26–28]. The amount and chemical environment of structural OH is very different in a reduced–reoxidized smectite that was initially reduced to a level of 100 % than in one in which only 20 % of structural Fe was initially reduced before reoxidation. This phenomenon is revealed in both the stretching and deformation modes involving structural OH. The structural Si–O bands of these respective reduced–reoxidized samples are also different, thus further supporting the hypothesis that the extent of reversibility depends in large part on the extent of initial reduction.

EFFECTS OF REDOX ON CLAY HYDRATION

When structural Fe(III) is reduced to Fe(II), whether by sodium dithionite or by bacteria, the surface properties of smectite clay minerals are significantly altered with respect to their interactions with H_2O and various organic compounds. In order to understand the surface chemistry of redox-treated smectites, one must first understand two fundamental properties of swelling clays. The first is that the surfaces of smectite clays are hydrophilic and readily become directly hydrated, regardless of the interlayer cation [29–33]. The second is that the difference in swellability between two smectites is due to a difference in the number of layers participating in free swelling, rather than being due to a difference in the separation distance between the individual clay layers. Viani et al. [34,35] convincingly demonstrated that the separation distance is the same at any given swelling pressure, even though water contents can vary widely. The dominant role of the interlayer cation appears to be control of the fraction of layers that participate in free swelling. Understanding these two properties of smectites is essential to understanding the clay–water interactions of redox-treated smectites.

The strength of clay–water interactions can be measured by the water-holding capacity of the clay under a constant water potential or swelling pressure. Stucki et al. [36] compared the water-holding capacity of redox-treated smectites in the presence of an inorganic cation (Na^+) and an organic cation (trimethylphenylammonium, $TMPA^+$). In the oxidized state, the smectite exchanged with the inorganic cation held more water than the smectite exchanged with the more hydrophobic organic cation (Fig. 5). This observation is consistent with previous literature regarding the water uptake by organo-clays, and
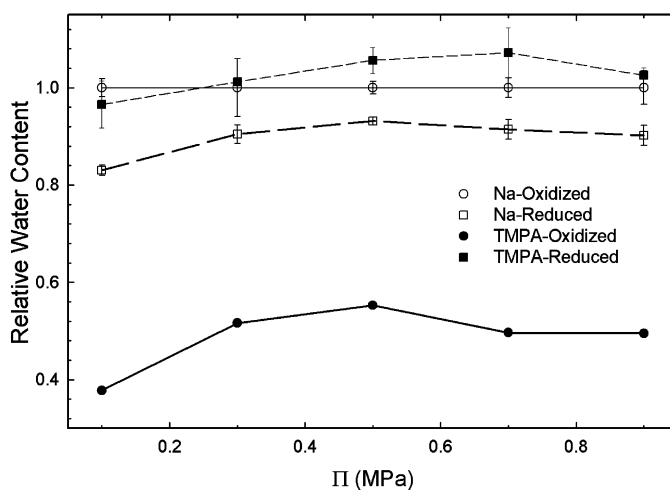
Fig. 5 Effect of redox treatment on equilibrium water content of Upton, Wyoming, montmorillonite exchanged with either Na^+ or $TMPA^+$ (from Stucki et al. [36]). Data are normalized to the Na^+, oxidized form.

may be due to the presence of hydrophobic groups on the organic cation, which obstruct or inhibit the adsorption of H_2O by the clay surfaces.

After reduction of structural Fe, the Na-exchanged smectite held less water than in the oxidized state; but, in contrast with the oxidized state, the organic-exchanged, reduced smectite held more water than the Na-exchanged, reduced smectite (Fig. 5). The difference in water content for the Na-smectite in the oxidized and reduced states is entirely consistent with previous studies [37,38], which found that reduction of structural Fe in Na-nontronite decreases the water-holding capacity of the clay and simultaneously causes some of the clay layers to collapse. The greater fraction of collapsed layers, which do not participate in free swelling, in the reduced Na-clay accounted for its lesser water-holding capacity at all applied swelling pressures (water potentials) studied. This is illustrated in Fig. 6.

The dramatic increase in water content in the TMPA-exchanged, reduced smectite over the Na-exchanged, reduced smectite is an extremely significant finding and opens our view to a clear understanding of the effect of Fe reduction on clay surface hydration properties. We conclude that reduced smectite surfaces at the clay–water interface are more strongly hydrated than oxidized surfaces. This conclusion is based on the following self-consistent arguments.

1. The water content of organo-exchanged smectites increases upon Fe reduction (Fig. 5), thus reversing the trend observed with Na-saturated smectites (Fig. 5). These differences cannot be explained by different hydration energies of the interlayer cations because the effect of the organic cation alone causes the system to retain less rather than more water than if Na is the cation (Fig. 5).
2. The reduced organo-smectite must contain more expanded interlayers than the reduced Na-saturated smectite. If reduction causes a change in the intrinsic nature of the clay surface that affects its affinity for water, the effect will apply regardless of which interlayer cation is present. Since the organic cation itself has less affinity for water than does Na, the organo-smectite must have more surface area exposed in order for the water content to be greater. The organic cations must, therefore, disrupt the mechanism that causes clay interlayers to collapse and become nonswelling, so they keep more interlayers accessible for swelling and hydration than inorganic cations, such as Na^+.
3. The increased H_2O content of the reduced organo-smectite cannot be explained only by an increase in the number of expandable interlayers, however, because this requires the organo-clay

to be more expanded than the unaltered Na form of Upton or SWa-1 (Fig. 5). The Na or Li forms of Upton are the most dispersed or expanded forms of smectite known, and both cations yield similar H_2O contents.

4.   In order for arguments 1, 2, and 3 to be correct and consistent with one another, the reduced smectite surface must be more strongly hydrated than the oxidized surface, enabling the reduced organo-smectite to contain more H_2O than the fully expanded Na-saturated smectite.

The net swellability of reduced smectites is, therefore, determined by the balance achieved between the opposing forces of increased hydration energy of reduced surfaces and the increased tendency for reduced layers to collapse. Under some conditions (e.g., where organic cations inhibit interlayer collapse) the hydration energy dominates, whereas for other conditions (e.g., Na-exchanged form) the tendency for interlayers to collapse is dominant. These results also provide further evidence that the clay surface hydrates directly and strongly, even in the presence of a hydrophobic organic cation (TMPA), which is also supported by the results of Yan and Stucki [39,40]. These observations strongly refute the popular belief that clay surfaces are inherently hydrophobic and hydrate only because of the presence of inorganic exchangeable cations [41,42].
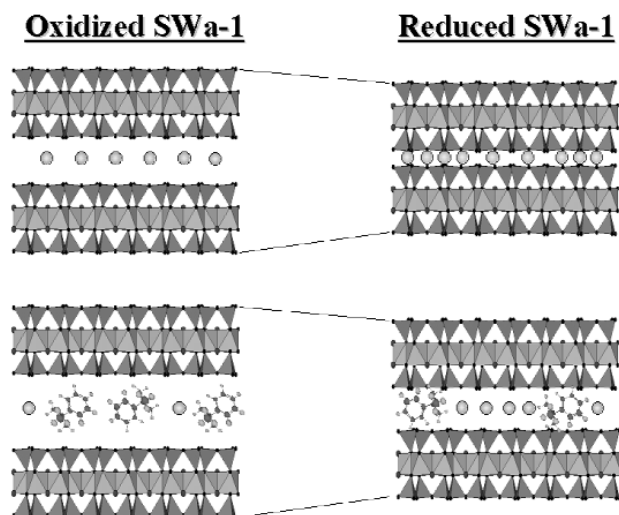

Fig. 6 Illustration of the effect of structural Fe reduction on interlayer expansion/collapse of smectite with either Na$^+$ or TMPA$^+$ as the exchanged cation.

EFFECTS OF REDOX ON CLAY–ORGANIC INTERACTIONS

The reaction of smectite clay minerals with organic compounds has almost infinite possibilities for modifying the fate, properties, and behavior of both the clay and the organic. The association of certain organic molecules with clay surfaces can drastically change clay surface chemistry, such as from hydrophilic to organophilic by exchange with an organic cation [43,44]. These organo-clay surfaces have numerous applications for industrial, environmental, and agricultural uses of clay minerals [45]. The clay mineral surface can also serve as a reaction site where interacting organic molecules experience various chemical alterations. The product depends heavily on the nature of the organic molecule and on the clay surface site that is accessible to it. Prior activation of the clay surface plays a key role in determining the nature of the clay surface and how it will react with organics [36]. The focus of the present discussion will be on the reaction of pesticides and chlorinated and nitro aliphatics at clay surfaces that have been modified through chemical or biological oxidation–reduction reactions.

The effect of structural Fe oxidation state on chlorinated hydrocarbons at the clay–water interface was examined using pentachloroethane (5CA) as the model compound [46,47]. It was reacted with oxidized, reduced, and reoxidized forms of three different smectites: montmorillonite, ferruginous smectite (SWa-1), and nontronite (NG-1) in aqueous suspension under controlled atmosphere conditions. Pentachloroethane was found to adsorb at different rates for the three smectites, and the 5CA-adsorption rate constants in the presence of these clays showed a strong correlation with the Fe(II) content of the clay ($r^2 = 0.98$) (Fig. 7). The reaction product with the reduced smectite is tetrachloroethene, which is the result of a dehydrochlorination reaction occurring at the basal surface of the clay (Fig. 8). In this case, the clay surface behaves as a Brønsted base. This finding is consistent with observations of Yan and Stucki [39,40] that Fe reduction increases the interaction between the smectite basal oxygens and the protons from adsorbed H_2O. A precursor complex may be formed at the clay–water interface prior to 5CA dehydrochlorination.
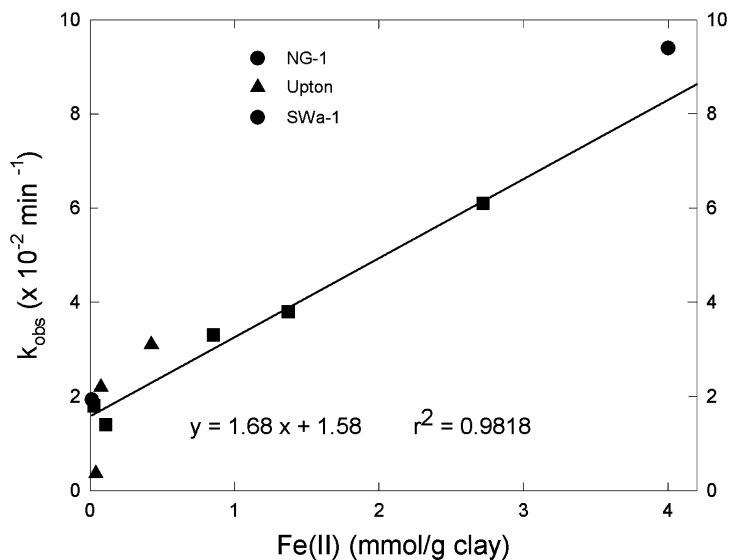

Fig. 7 Relation between structural Fe(II) content in ferruginous smectite and the rate of transformation of pentachloroethane to tetrachloroethene (from Cervini-Siliva et al. [47]).
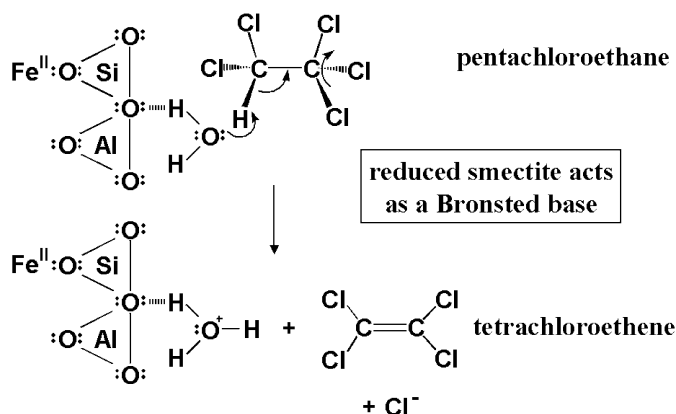

Fig. 8 Possible Brønsted base-catalyzed reaction mechanism between reduced smectite surface and pentachloroethane (from Cervini-Silva et al. [47]).

Studies have also shown that the oxidation state of structural Fe in clay minerals affects the adsorption and degradation of pesticides in the environment. Atrazine, alachlor, trifluralin, and oxamyl have specifically been investigated. Compared to oxidized clays, reduction by either chemical or microbial treatments [22,48] decreased the concentrations of all of these pesticides in the surrounding solution, by increased sorption and degradation. Reoxidized clay exhibited similar behavior toward the pesticide as did the oxidized clay. Atrazine underwent base-catalyzed hydrolysis-dechlorination to form hydroxyatrazine in the presence of chemically reduced SWa-1 (Fig. 9), and at least 14 degradation products from alachlor were observed after treatment with reduced clay, whereas only two were found with the oxidized clay (Fig. 10), indicating that adsorption is accompanied by a degree of degradation in
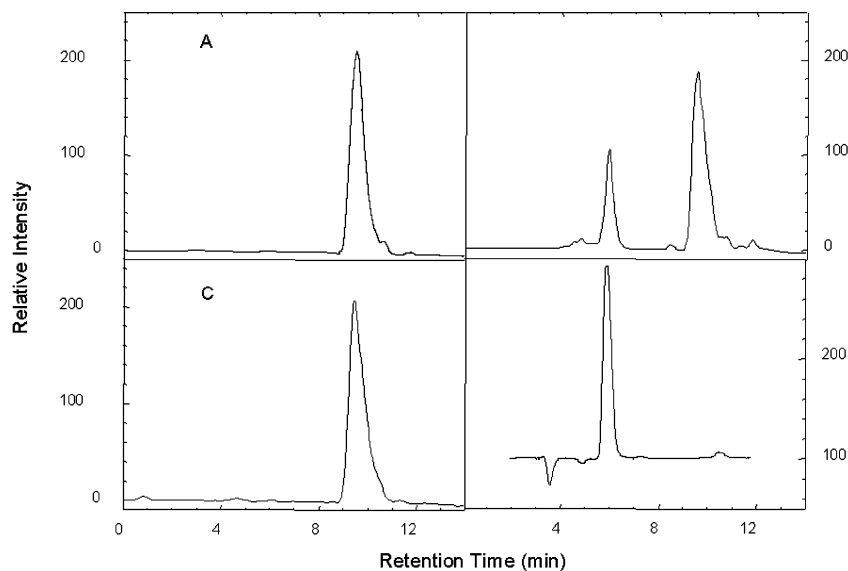

Fig. 9 High-performance liquid chromatography (HPLC) patterns of atrazine solution reacted with oxidized and reduced ferruginous smectite (from Xu et al. [22]).
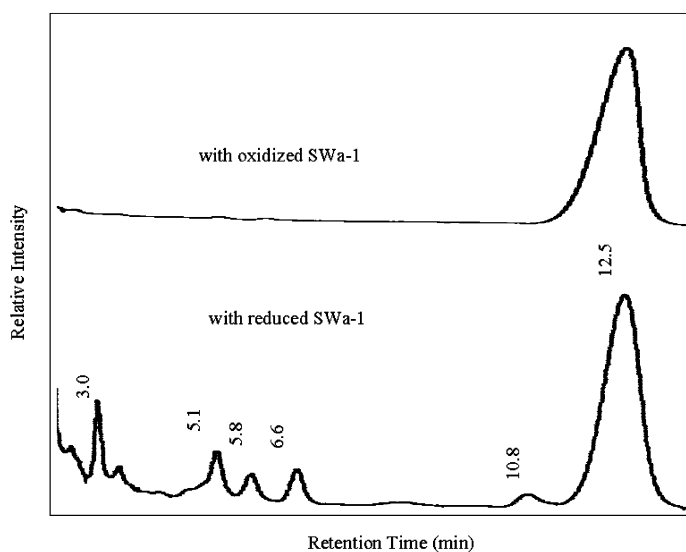

Fig. 10 HPLC patterns of alachlor solution reacted with oxidized and reduced ferruginous smectite (from Kocherginsky and Stucki [48]).

reduced clays. Adsorption of atrazine and alachlor to the clay may be through a H-bond with the waters of hydration surrounding the interlayer cations, the extent of which should increase with increasing acidity; but, in light of the findings with 5CA, the validity of this model under reduced conditions is unclear. Reduction of structural Fe may affect pH-dependent phenomena in two ways: (1) the increased surface charge density increases the number of hydrated interlayer cations, thereby enhancing surface acidity; and (2) increased electron density at basal surface oxygens increases their Brønsted basicity. Atrazine could, therefore, adsorb and/or degrade through either acid or alkaline hydrolysis pathways. Increased reduction potential of the reduced clay surfaces may also promote degradation through redox interactions, especially with alachlor. The same trends were observed for atrazine and alachlor in studies with smectite reduced by microorganisms, although to a lesser extent than with chemically reduced smectite. Desorption studies with microbially treated clays recovered a large fraction of the original herbicide adsorbed to the clay (including both unaltered and degraded forms), indicating that adsorption is largely reversible.

Trifluralin ranks among the most commonly used herbicides in the United States. The compound persists under most environmental conditions, yet it is rapidly transformed under certain anaerobic conditions. In a study by Tor et al. [49], the fate of trifluralin in anoxic environments and the contribution of Fe(II) to its anaerobic degradation were investigated. Degradation rate increased under Fe reducing conditions, which apparently involved the solid mineral phase and was not limited by bioavailability. In a soil-free aqueous system, no reaction of trifluralin with dissolved Fe^{2+} was detected in the presence or absence of kaolinite clay under anoxic conditions. Reduced, but not oxidized or reoxidized, forms of purified SWa-1 catalyzed the rapid transformation (72 % of applied in 30 h) of trifluralin to polar products (Fig. 11) with a concomitant reoxidation of structural Fe in the clay [from 70 % Fe(II) to 40 %].

Oxamyl is a carbamate pesticide that is widely used to control insects, mites, ticks, and roundworms in agricultural fields. Smectite has a significant effect on the stability of this pesticide, in both the oxidized and reduced state, except the latter has a greater effect than the former [21]. In the presence of chemically reduced and microbially reduced SWa-1, about 65–70 % of the pesticide was degraded, whereas only about 35–40 % was degraded in the presence of oxidized or reoxidized SWa-1
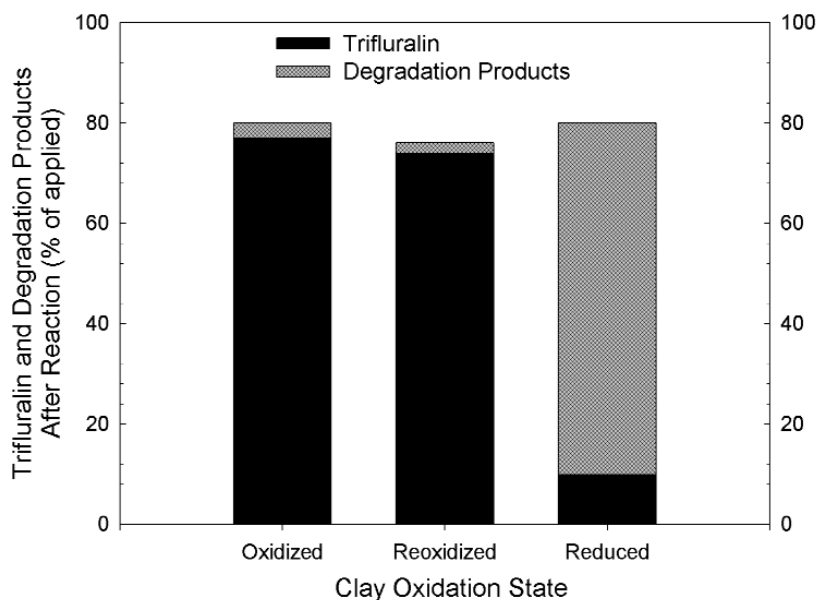

Fig. 11 Degradation of trifluralin by redox-treated ferruginous smectite (from Tor et al. [49]).

(Fig. 12). But the rate of degradation was about an order of magnitude faster in the reduced systems than in the oxidized forms. Two products were observed, namely, the elimination product oxamyl oxime (DMTO), and the reduction product *N,N*-dimethyl-1-cyanoformamide (DMCF), with DMTO comprising over 90 % of the product. In the presence of reoxidized and oxidized SWa-1, DMTO was the only product found. The rate of oxamyl degradation in a buffered solution at pH 8, with no clay present, was much slower than even in the presence of the oxidized forms of the clay, indicating that the clay surface, regardless of oxidation state, plays a vital role in the degradation of this compound. The surface pH and the redox state of the smectite are the two principal properties governing the interaction mechanism, where the surface pH operates primarily in the elimination reaction and the redox state controls in the reduction reaction. Since the elimination reaction is driven by higher pH, the effective or apparent pH of the clay surface must be greater than that of the surrounding outer solution.

Chloropicrin (trichloronitromethane, CP) was reacted with reduced SWa-1 in aqueous suspension [50], which promoted CP dechlorination to produce dichloro- (DCNM) and chloronitromethane (CNM) with yields of up to ~80 % within 30 min (Fig. 13). The simultaneous formation of DCNM and CNM
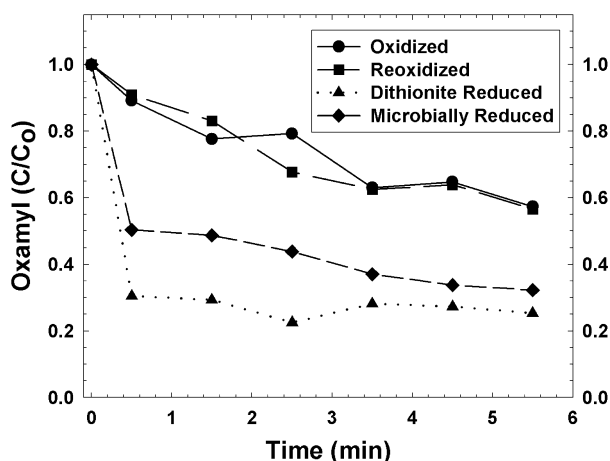

Fig. 12 Degradation of oxamyl by redox-treated ferruginous smectite (from Zhang et al. [21]).
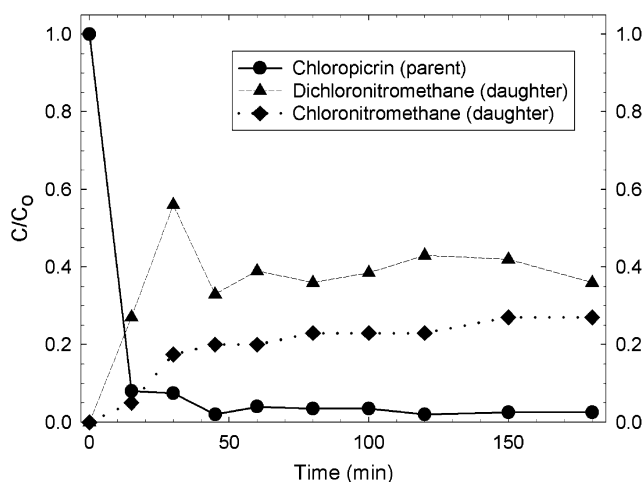

Fig. 13 Reduction of chloropicrin by redox-treated ferruginous smectite (from Cervini-Silva et al. [50]).

suggests that CP and the SWa-1 surfaces participate in two-electron transfer pathways. The CP adsorption and dechlorination rate constants in the presence of SWa-1 revealed a strong correlation with the Fe(II) content of SWa-1 (r^2 = 0.96 and 0.98, respectively). This study indicated that the oxidation state of structural Fe greatly alters surface chemistry and has a large impact on electron transfer during clay–organic interactions.

A recent study by Yan and Bailey [69] further expands the evidence for the greater surface reactivity of reduced smectite surfaces relative to their oxidized counterparts with respect to organic compounds. They found that reduced ferruginous smectite rapidly reduced nitrobenzene to aniline, whereas oxidized or unaltered smectite failed to make this conversion.

It is generally believed [51] that clay–organic interaction may occur by or at one or more of the following mechanisms or sites: (1) neutral siloxane surfaces where van der Waal's forces dominate; (2) coulombic attraction to isomorphic substitution sites at the clay surface; (3) coordination to metal cations occupying cation exchange sites; (4) hydrogen bonding interaction with acidic protons from waters of hydration around metal cations at exchange sites; (5) hydrophobic sites where van der Waal's attraction takes place; and (6) coordination at broken edges, kinks, and steps of clay mineral layers. We would add two more, namely, (7) basal oxygens behaving as a Brønsted base, and (8) electron transfer from the clay to the organic at the basal surfaces. These last two mechanisms may account for most of the organic degradation occurring as a result of clay redox chemistry.

SUMMARY

In summary, the oxidation state of structural Fe in smectite clay minerals greatly alters clay structure and surface chemistry. Structural changes include a decrease in structural OH content; migration of Fe from *cis*- to *trans*-octahedral sites, creating trioctahedral domains; and creation of defect sites within the octahedral sheet. The reversibility of these effects is more difficult as the initial level of reduction increases. These changes in structure are manifested at the surface as an increase in hydration energy, Brønsted basicity, and redox reactivity with organic pesticides, chloro- and nitro-aliphatics, and carbamates.

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