

THE 10TH GEORGE BROWN LECTURE

# A review of microbial redox interactions with structural Fe in clay minerals

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**ABSTRACT:** Virtually all 2:1 clay minerals contain some Fe in their crystal structure, which may undergo redox reaction with surrounding redox-active species causing potentially significant changes in the chemical and physical properties of the clay mineral and its surrounding matrix. This phenomenon was originally of interest mostly as a laboratory experiment using strong inorganic reduction agents, but the discovery that the structural Fe could be reduced by microorganisms in natural soils and sediments opened the way for this to become a practical method for altering the chemical and physical properties of soils and sediments *in situ*. The purpose of this report was to review the body of literature that has been published since the inception of this field of inquiry and to complement, update, and complete three other reviews that have been published during the intervening years. Studies of microbial reduction of structural Fe in smectites have revealed the extent of reduction, effects on chemical and physical properties, reversibility (or lack thereof) of microbial reduction, stoichiometry, possible reaction mechanism, and types of organisms involved. Some organisms are also capable of oxidizing structural Fe, such as in biotite or reduced smectite, while one appears to be able to do both. Illitic layers resist reduction by microorganisms, but this can be partially overcome by the presence of an electron shuttle compound such as anthraquinone-2,6-disulfonate, which also enhances the extent of reduction in smectites. Microorganisms may be employed as an *in situ* reducing agent to drive redox cycles for structural Fe in constituent clay minerals of soils and sediments, which in turn can serve as an abiotic source for redox-mediated remediation of environmental contaminants.

**KEYWORDS:** redox reactions, iron, smectite, microorganisms, microbial reduction, environmental contaminants.

The first bacterial redox interaction with clay minerals was observed more than 25 years ago, and the first published report of microbial influence on the oxidation state of structural iron (Fe) in smectite was provided by Stucki & Getty (1986). A new and exciting phenomenon in clay science was born. Since that time the bio-redox interactions

between phyllosilicates and microorganisms have been the aim of study of many clay, geo and bio scientists (e.g. Stucki *et al.*, 1987, 1996; Kostka *et al.*, 1996, 1999a,b, 2002a,b; Stucki, 2006, 2009, 2013; Stucki & Kostka, 2006; Kim *et al.*, 2003, 2004; Shelobolina *et al.*, 2003, 2004, 2005, 2012a,b; Kukkadapu *et al.*, 2006; Jaisi *et al.*, 2007a,b,c, 2008a,b, 2009, 2011; Dong *et al.*, 2009a,b, 2010; Dong, 2012; Perdrial *et al.*, 2009; Zhang *et al.*, 2009, 2012; Bishop *et al.*, 2010, 2011; Bishop & Dong 2010; Dong, 2010; Liu *et al.*, 2010, 2011; 2012; Gorski *et al.*, 2012a,b; Wu *et al.*,

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2012), with the number of published papers increasing steadily (Fig. 1), including three reviews (Stucki & Kostka, 2006; Vodyanitskii, 2007; Dong *et al.*, 2009a).

The purpose of the present review was to describe the chronological history and the milestones of development in the study of redox reactions between microorganisms and structural Fe in clay minerals, from the beginning to the present, including bacterial identification, classification, and characterization and the potential industrial and environmental applications.

### EVOLUTION OF MICROBIAL REDUCTION OF FE

Early, the ability of bacteria to be a mediator of Fe reduction processes in (oxyhydr)oxide minerals (hereafter referred to as Fe oxides) was observed by Starkey & Halvorson (1927) who reported the growth of microorganisms during the reduction of Fe(III) oxides to Fe(II). Later, Bromfield (1954) noted that microbial reduction of Fe oxides may be enhanced by metabolic enzymes as mobilizers of the Fe(III) from the oxides. Further progress was accomplished with the extraction of Fe-reducing bacteria from Fe oxides in nature (Ottow, 1968,

1969; Ottow & Klopotek, 1969; Munch & Ottow, 1977, 1982; Munch *et al.*, 1978; Rinder, 1979; Sugio *et al.*, 1981; Onysko *et al.*, 1984; Soljanto *et al.*, 1985; Sand, 1989), but the ability of bacteria to modify structural Fe in phyllosilicate clay minerals was undocumented until Stucki & Getty (1986) observed that stimulation of microbial growth in the clay mineral converted structural Fe(III) to Fe(II). They measured the extent of Fe reduction in sterilized and unsterilized, nutrient-broth dispersions of ferruginous smectite inoculated with pure cultures of four different *Bacillus* bacteria common to soils and with the native organisms isolated from the clay mineral. Each culture produced significant levels of Fe(II) in the clay mineral structure, up to at least 0.6 mmol/g (20% of the total Fe). They concluded that factors controlling the extent of reduction included the organism and the incubation time. Komadel *et al.* (1987) continued with the investigation of microbial reduction of Fe in clay minerals, with the first publication of such in a peer-reviewed journal. They reduced structural Fe(III) in three different smectites (ferruginous smectite SWa-1 from Grant County, Washington; API 33a, Garfield nontronite; and API 25, Upton montmorillonite) by bacterial growth. Clay mineral dispersions were incubated at

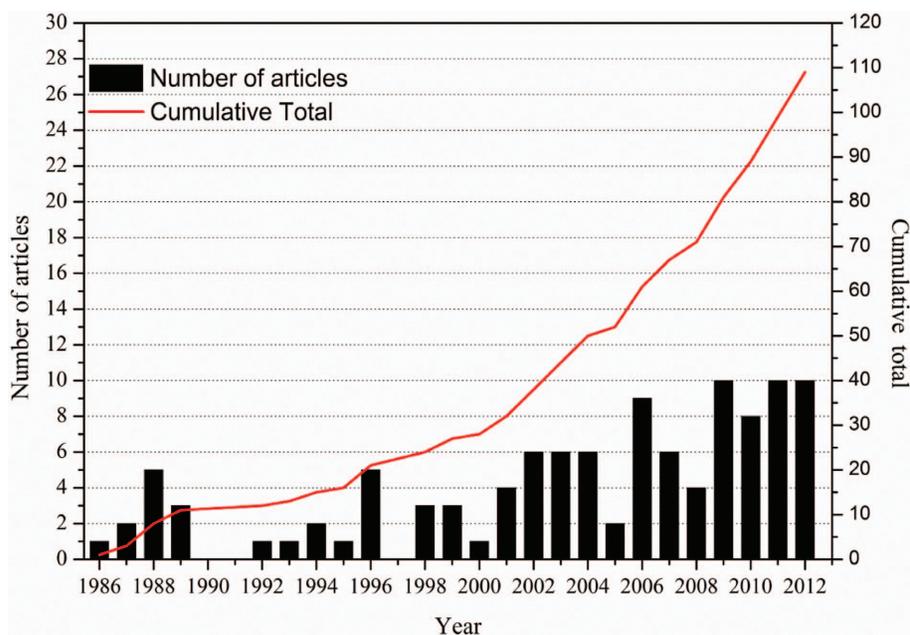


FIG. 1. Number of articles published per year related to microbial reduction or oxidation of structural Fe in clay minerals.

room temperature in a nutrient-broth solution consisting of peptone and beef extract. Some samples were first sterilized by autoclaving and then seeded with bacteria that had been isolated previously from the SWa-1 sample. They found that in all three clay minerals, approximately 0.30 mmol Fe(III)/g clay was reduced to Fe(II) by bacteria in a 28-day period. The specific organism responsible for Fe reduction was never classified, but it was more efficient in samples that had not been purged of O<sub>2</sub> and it was clearly indigenous to ferruginous smectite.

Wu *et al.* (1988) tested indigenous microorganisms in rice-paddy soils and found that they have great ability to reduce structural Fe. They mixed sucrose with an aqueous nontronite dispersion and then added an aqueous extract from a Chinese paddy soil and incubated it for 14 days at room temperature. Results revealed that the optical reflectance spectra of microbially reduced nontronite were comparable to dithionite-reduced smectite, thus the microorganisms from the soil extract were able to reduce the structural Fe(III) in this dioctahedral smectite.

Gates *et al.* (1993) studied the reduction of structural Fe in ferruginous smectites by a mixture of five *Pseudomonas* species of bacteria, which are generally indigenous to wheat roots, and found that a consortium of these bacteria was a more effective reductant than any of the individual species alone. Levels of reduction achieved in ferruginous smectite were in the range from 1.047 to 1.242 mmol Fe(II)/g clay (30–35% of total Fe). These levels, while less than achieved with dithionite, were sufficient to invoke a change in physical-chemical properties of the smectite. The water content vs. swelling pressure curves revealed less swelling compared with the unreduced smectites. This result is similar to, or at least in the same direction as, the effect of dithionite reduction on smectite swelling (Stucki *et al.*, 1984).

Two years later, Vempati *et al.* (1995) found that bacteria are not the only soil organisms capable of Fe reduction in clay minerals, but that this could also be accomplished by exudates from fungi attached to soybean roots as grown in an *in vitro* geponic system. They used hydroponic solutions containing Fe salts or chelates to reflect the quasi soil environment. In their experiment, Fe(III) in Upton montmorillonite, ferruginous smectite, or Si-containing amorphous Fe oxide served as the electron acceptor from the fungi. The amount of

Fe reduced in these samples was 0.012, 0.095 and 0.182 mmol/g, respectively. The reducing agent in this case was believed to be the phenolic groups in the exudates arising from the fungi attached to the soybean roots. The exudates were then oxidized to diquinones. This study revealed that a potentially large range of possibilities exist for reductive reactivity in soils, and it reinforced the importance of linking the scientific disciplines of microbiology, plant physiology, and clay mineral chemistry when studying redox phenomena in natural soils and sediments.

Bacteria which are specialized in Fe reduction were not investigated until 1996 when Kostka *et al.* (1996) used a pure culture of *Shewanella putrefaciens* (strain MR-1). This family of metal-reducing bacteria was discovered by Myers & Nealson (1988) in Lake Oneida, New York, and has been used extensively for Fe reduction in many different systems. It has a versatile respiratory metabolism involving electron shuttles, is a facultative anaerobe, and robustly reduces structural Fe(III) in smectite. Kostka *et al.* (1996) found that at pH 5–6 and at 25 to 37°C, the MR-1 strain of *Shewanella putrefaciens* rapidly reduces the structural Fe in ferruginous smectite (SWa-1) up to 15% in just 4 h. This is in contrast with several days that were required with the *Pseudomonas* species. Longer reaction time (6 to 12 days) with *Shewanella* led to the 25% to 41% range of Fe reduction in the SWa-1 culture. This study identified optimum conditions of pH (5–6), time (4 h), and temperature (37°C) for the most efficient reduction to occur, and concluded that the reaction is consistent with an enzymatic process and not with simple chemical reduction.

Other ongoing investigations focused on identification, classification, and characterization of microorganisms with their ability to grow in a clay mineral environment and reduce structural Fe in the clay minerals (Komadel *et al.*, 1987; Stucki *et al.*, 1987, 1992; Stucki, 1988; Wu *et al.*, 1988; Stucki & Lear, 1989; Gates *et al.*, 1993, 1994; Zhang *et al.*, 2006; Kashefi *et al.*, 2008). However, the reaction conditions (Lee *et al.*, 2006; Ribeiro *et al.*, 2009a,b), structural changes (Gates *et al.*, 1996; Stucki *et al.*, 2002; Kim *et al.*, 2003; Li *et al.*, 2003; Alimova *et al.*, 2006, 2009), and properties (Gates *et al.*, 1998) of modified clay products after bacterial treatment were studied as well.

Gates *et al.* (1996) studied the structural properties of reduced Upton montmorillonite. Their aim was to characterize the relationships between

reduction of octahedral Fe in the crystalline structure of smectites and surface-sensitive physical and chemical properties. The reducing agents were Na-dithionite and bacteria, and the resulting reduced smectites were analyzed by solid state multinuclear ( $^{29}\text{Si}$  and  $^{27}\text{Al}$ ) magic-angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy. The MAS NMR analyses indicated that reduction of structural Fe caused reversible changes in the smectite structure, at least as far as this method could discern. The relative level of Na-dithionite Fe(III) reduction and Fe(II) generation was 0.261 mmol/g Fe(II), while for microbial treatment it was 0.101 mmol/g. They observed in both bacterial and dithionite cases that reduction of structural Fe resulted in a positive (down field) chemical shift of the main Si Q(3) (Q(3)(0Al)) site, which was strongly correlated with Fe(II) content, and inferred that distortions in Si–*T* (*T* = Si, Al) bond angles and Si–O bond lengths occurred with increasing layer charge due to the Fe reduction. The line width (W) of the Si-29 Q(3) signal also increased with increasing levels of reduction. No change occurred in the position of the peak maximum for the octahedral Al(Al-27(VI)) signal; however, an increased W was observed for this peak with increasing Fe(II) content. These results are attributed to decreases in Si–O–*T* bond angles and Si–O bond distances, corresponding to a better fit between the tetrahedral and octahedral sheets brought about by the presence of Fe(II) in the clay mineral structure. The increased Al-27(VI) signal W may also be due to a lessening of the paramagnetic influence of Fe(III) nuclei and enhancement of Al-27(VI) signals with different quadrupole coupling constants (QCC). They further concluded that changes in the smectite structure brought about by microbial reduction were reversible, at least as far as this method could discern.

Further studies revealed other effects of microbial reduction on the physical-chemical properties of smectites, such as swelling pressure (Stucki *et al.*, 1984; Lear & Stucki, 1989; Gates *et al.*, 1993, 1998), layer charge (Gates *et al.*, 1996; Stucki *et al.*, 2002; Kashefi *et al.*, 2008), cation exchange capacity (Stucki, 1988; Kostka, *et al.*, 1999b; Favre *et al.*, 2002a,b, 2004; Stucki *et al.*, 2002), and specific surface area (Lear & Stucki, 1989; Stucki & Lear, 1989; Kostka, *et al.*, 1999b; Stucki *et al.*, 2002).

Another team of co-workers (Stucki *et al.*, 1996) surveyed the effects of a variety of different

reducing agents on structural Fe oxidation states and on the physicochemical properties of the smectite in order to have a comparison with microbially reduced smectite. They compared the reductive strengths of dithionite ( $\text{S}_2\text{O}_4^{2-}$ ), sulfide ( $\text{S}^{2-}$ ), thiosulfate ( $\text{S}_2\text{O}_3^{2-}$ ), hydrazine ( $\text{N}_2\text{H}_4$ ), ascorbic acid ( $\text{C}_6\text{H}_8\text{O}_6$ ), hydroquinone ( $\text{C}_6\text{H}_6\text{O}_2$ ), and sodium oxalate ( $\text{Na}_2\text{C}_2\text{H}_2\text{O}_4$ ) by measuring the resulting level of structural Fe(II) using both the photo-colorimetric method (Komadel & Stucki, 1988) and Mössbauer spectroscopy. The reducing capacity followed the order  $\text{S}_2\text{O}_4^{2-} > \text{S}^{2-} > \text{C}_6\text{H}_8\text{O}_6 > \text{S}_2\text{O}_3^{2-} > \text{C}_6\text{H}_6\text{O}_2 \sim \text{C}_2\text{H}_2\text{O}_4$ . The physical-chemical property measured was viscosity of the dispersion, which increased with increasing Fe(II) content. The reduction capacity of microorganisms is generally greater than all of these except dithionite, so one might expect an increase also in viscosity of the clay dispersion with microbial reduction.

#### RELEVANCE TO NATURAL SYSTEMS

A possible correlation between microbial reduction of smectite Fe and observed soil properties was suggested by Ernstsens *et al.* (1998). A previous study (Ernstsens, 1996) discovered that nitrate levels in a Danish soil profile dropped sharply at the oxic-anoxic boundary zone. They hypothesized that the cause for this drop was reaction with structural Fe(II) in the soil clay minerals, created by microbial activity. To test this hypothesis, samples from the Danish soils were incubated for up to 160 days with a consortium of *Pseudomonas* bacterial strains. They found that incubation times from 4 to 10 days after inoculation increased the structural Fe(II) content in the soil clays from approximately 10% to 20–34% of total clay Fe, thus demonstrating that bacteria could have, indeed, been responsible for creating the anoxic zone in the soil profile. They further hypothesized that, as reoxidation of Fe(II) in the soil clay occurred by reaction with nitrate or by weathering, the bacterial reduction could renew the anoxic state in an imperfectly drained soil or sediment by electron transfer back to the structural Fe(III) and, thereby, control geochemical redox processes.

Unfortunately, Ernstsens *et al.* (1998) were unable to demonstrate in the laboratory the link between structural Fe(II) in the soil clay minerals and nitrate reduction. This was a puzzle because nitrate reduction was clearly observed in the field and

correlated with Fe(II) oxidation. The puzzle was solved later by Su *et al.* (2012) who demonstrated that coulombic repulsion between the negatively charged, pure reduced smectite and the nitrate anion inhibits the reduction reaction in the laboratory. Reversing the charge on the smectite by exchange of a polymeric cation, however, overcame the coulombic repulsion and enabled the nitrate reduction by structural Fe(II). This same reaction may occur in natural soils if polymeric cations from humic materials become adsorbed to the smectite, and may explain the field observations of Ernstsén (1996).

The very important role of Fe in clay minerals on the carbon cycle in microorganisms was described by Kostka *et al.* (1999a). They were the first to report the stoichiometric coupling between microbially mediated Fe reduction in clay minerals and the oxidation of organic carbon to CO<sub>2</sub>, using the Fe(III)-reducing bacterium *Shewanella putrefaciens* strain MR-1 with formate or lactate as the carbon source. They also demonstrated that the extent of clay mineral reduction was enhanced by as much as double in the presence of other organic acids, in the order nitrilotriacetic acid (NTA) > oxalate > citrate > malate, which was accompanied by structural Fe dissolution in the same order. CO<sub>2</sub> production, consumption of organic acids, and structural Fe(III) reduction and dissolution in the smectite were directly measured, and revealed that bacteria can combine their Fe reducing capacity with the activity of organic acids to enhance the bioavailability of Fe(III) in clay minerals.

The soil appears to contain many indigenous microorganisms capable of reducing structural Fe in the clay minerals, which in turn are able to alter the chemical and physical properties of the soil. Kostka *et al.* (1999b) prepared enrichment cultures of bacteria from flooded rice-paddy soils in China as well as from upland, aerated soils in Indiana, then used these as the inocula for sterile smectite samples in a minimal medium and found that they all can catalyze the rapid reduction of structural Fe(III) in the smectite clay minerals. Similar results were found using bacteria from the saprolitic soils of southeastern Tennessee. A new organism, named *Geobacter daltonii*, was subsequently classified as one of the primary Fe reducers in these soils (Prakash *et al.*, 2010).

Not only were these bacteria capable of reducing the structural Fe in the smectites, but this process also altered the surface properties (swelling pressure,

hydration energy, and surface area) of the smectite (Lear & Stucki, 1989; Stucki & Lear, 1989; Stucki *et al.*, 2002), much like that observed in dithionite-reduced smectite (Stucki *et al.*, 2002) using the organic cation trimethylphenylammonium (TMPA). Specific surface area decreased by 26% to 46% in response to bacterial reduction, and the surface charge density as measured by the ratio of cation exchange capacity to specific surface area increased over the same scale. The fact that the surface charge density increased but the swelling decreased contradicts the classical theory of clay swelling, i.e., that swelling is osmotic, which predicts a direct rather than an inverse relationship between swelling pressure ( $\Pi$ ) and surface charge density ( $\sigma$ ) according to the Langmuir equation, *viz.*,

$$\Pi = 2n^0kT \left( \cosh \frac{2e\psi_d}{kT} - 1 \right) \quad (1)$$

where  $n^0$  is the outer solution concentration;  $k$ , Boltzmann's constant;  $T$ , the absolute temperature;  $e$ , the charge on the electron; and  $\psi_d$ , the electrostatic potential at the mid plane between the clay mineral layers, which is directly proportional to  $\sigma$ .

## INDUSTRIAL, ENVIRONMENTAL AND GEOLOGICAL APPLICATIONS

The ability of microorganisms to modify the Fe in clays and clay minerals has been employed in industrial, environmental, and geological applications. One industrial use has been bioreduction to remove Fe(III) impurities from clay minerals used in porcelain and pottery production (Lee *et al.*, 1999, 2002; Shelobolina *et al.*, 2005). Indigenous dissimilatory Fe(III)-reducing bacteria (DIRB) were stimulated by the addition of sugars such as glucose, maltose, and sucrose as carbon sources, which in turn enhanced the Fe(III) reduction reaction, resulting in increased whiteness. The red staining from the Fe(III) impurities was clearly decreased. This is an excellent example to prove that bacterial reduction has an important role in the clay products industry. It also decreases the environmental impact of previously used industrial processes by eliminating certain harmful chemicals (e.g. dithionite) from the process stream. Later, Guo *et al.* (2010a,b) studied the effects of different C and N sources on the removal of Fe impurities from kaolin by DIRB using glucose, sucrose, food-sugar,

maltose, and soluble starch as energy sources. They observed that the Fe was selectively leached from the kaolin without formation of a secondary mineral phase. XRD and SEM measurements revealed minimal structural changes but the crystallinity was improved. Sometimes the nutrient medium for the bacteria also contains agents, such as oxalic acid, which further enhance the ability of DIRB to remove Fe impurities from kaolin (He *et al.*, 2011).

Further evidence that Fe-reducing bacteria may play a role in kaolinite dissolution was reported by Maurice *et al.* (2001a,b), who found that kaolinite dissolution was enhanced by an aerobic *Pseudomonas mendocina* bacterium. This occurred under aerobic environments where Fe was a limiting nutrient, so the bacteria pulled it from the Fe contaminants in the kaolinite, using it as a terminal electron acceptor for oxidative phosphorylation and, thereby, acting as a bleaching agent for the kaolinite. The presence of Fe in the kaolinite allowed the bacteria to grow above levels of non-kaolinite-containing controls under Fe-limited conditions. They further demonstrated that the bacteria that reduced the Fe also significantly enhanced Al- and Si-release from the kaolinite.

Anthropogenic activity, including soil fertilization and spraying of agricultural crops, over the years has led to contamination of soils, rivers, lakes, and groundwater by herbicides, pesticides, fungicides, and nitrate. Direct microbial (biotic) degradation of these compounds has been widely investigated. Abiotic degradation, on the other hand, in which the compound reacts directly with the inorganic fraction of the soil, has received less attention but indications are that microorganisms may play a role in the abiotic processes as well (Ernsten *et al.*, 1998; Tor *et al.*, 2000; Xu *et al.*, 2001; Cervini-Silva *et al.*, 2003; Stucki, 2006, 2013; Fialips *et al.*, 2010). Tor *et al.* (2000) reported the anaerobic degradation of the herbicide trifluralin in anoxic environments by reduced, Fe(II)-bearing clay minerals. They found that trifluralin degradation was suppressed by the presence of  $\text{NO}_3^-$  or  $\text{O}_2$ , which supposedly acted as electron acceptors to oxidize the Fe(II) in the system before it could react with the trifluralin. On the other hand, the rate of trifluralin degradation was enhanced under Fe-reducing conditions. Similar conclusions were reached by Xu *et al.* (2001) who studied the fate of the herbicides atrazine and alachlor in contact with chemically or bacterially pretreated ferruginous smectite (SWa-1) in its

oxidized, reduced, or reduced-reoxidized state. The greatest amount of herbicide degradation occurred in the case of reduced clay, with GC-MS analysis providing at least 14 degradation products from atrazine after either chemical or microbial treatment. The parent herbicide concentration was decreased in both cases. They hypothesized that the mechanism for atrazine and alachlor interaction with the clay mineral basal surfaces is a pH-mediated process, but uncertainty still remains with respect to the exact mechanism of degradation for these two herbicides.

Further investigation of the degradation of p,p'-DDT (organochlorinated pesticides) by bacterial reduction of Fe(III) in NAu-2, using the metal-reducing bacteria *Shewanella oneidensis* MR-1 (the renamed version of *Shewanella putrefaciens*), revealed a progressive decrease in p,p'-DDT and production of biodegradable p,p'-DDD. The reductive degradation of DDT in Fe-bearing clay minerals indicated that clay materials have remediation capabilities for the passive treatment of contaminated land (Fialips *et al.*, 2010).

Studies of geochemical mineral transformations by microbial treatments have also been of interest. The presence and growth of bacterial biomass in subsurface granitic environments in deep groundwater was studied by Hama *et al.* (2001). They reported a loss and mobilization of fine-grained crushed material (<5  $\mu\text{m}$ ), which had originally adhered to grain surfaces in the starting material, and the formation of a secondary clay mineral. It was revealed that microbial activity can influence rock-water interactions even in nutrient-poor conditions. These results gained more meaning with respect to Fe reduction when, under extreme conditions for bacterial growth, Tung *et al.* (2006) discovered Fe-reducing microbial cells attached to clay grains in the bottom 13 m of the GISP2 (Greenland Ice Sheet Project) ice core, which led to a redox alteration process of the minerals by electron hopping from the mineral edges (see below under Mechanisms for more discussion on this topic).

## REACTIONS WITH REDOX-ACTIVE METALS

The bioremediation of contaminated areas by heavy metals such as U(VI) (Zhang *et al.*, 2009, 2011) and Cr(VI) or Tc(VII) (Fredrickson *et al.*, 2004; Jaisi *et al.*, 2008b, 2009; Dong *et al.*, 2009a,b; Bishop & Dong 2010; Dong 2010; Stucki, 2011; Bishop *et al.*,

2011; Yang *et al.*, 2012) has been investigated. The high oxidation state of heavy metals is responsible for their mobility in nature. They can be immobilized if reduced by Fe(II) in smectite generated either chemically or microbiologically. Zhang *et al.* (2011) evaluated the stability of biogenic nanoparticulate U(IV) in the presence of CCa-2, an Fe-bearing chlorite from Flagstaff Hill (El Dorado County, California, USA). The reduction of structural Fe(III) in chlorite CCa-2 and of U(VI) was performed by *Shewanella oneidensis* MR-1, assisted by anthraquinone-2,6-disulfonate (AQDS), and then it was re-oxidized with O<sub>2</sub>. They found that structural Fe(III) in the chlorite inhibited U(VI) loss from solution, while chlorite-associated Fe(II) enhanced the oxidation rate of U(IV) by dissolved O<sub>2</sub>. This indicated that chlorite-associated Fe(II) could not protect nanoparticulate U(IV) from O<sub>2</sub> intrusion but instead increased the oxidation rate of U(IV).

Bishop & Dong (2010) and Bishop *et al.* (2011) investigated the reactivity of clay minerals toward Tc(VII) immobilization utilizing a range of clay minerals, including montmorillonite, nontronite, rectorite, mixed layered I-S (70:30), illite, Fe-rich chlorite, and palygorskite, which are present in Tc contaminated sites of the US Department of Energy. Structural Fe(III) in the clay minerals was first bioreduced to Fe(II) (termed “biogenic Fe(II)”), and was then used to reduce Tc(VII). They used lactate as the electron donor and AQDS as an electron shuttle in bicarbonate buffer (pH 7) with *Shewanella putrefaciens* CN32 cells. The levels of Fe(III) reduction observed were Fe-chlorite (~1.5 mmol/g) > nontronite (~1.1 mmol/g) > montmorillonite (~0.16 mmol/g) > illite/smectite (~0.015 mmol/g) > illite (~0.002 mmol/g). The reduced smectite, however, was most effective in reducing Tc(VII), and illite was the least effective. Even though a large amount of Fe(III) was bioreduced in chlorite, most of it was not available for Tc(VII) reduction. Biogenic Fe(II) in palygorskite was available for Tc(VII) reduction, but the rate was very low. For all the clay minerals, the ratio of oxidized Fe(II) to reduced Tc(VII) was 3, as expected based on the stoichiometric reaction between Fe(II) and Tc(VII). These kinetics results are important for understanding how various clay minerals may be used to immobilize heavy metals in the environment.

An investigation (Yang *et al.*, 2012) of *in situ* <sup>99</sup>Tc immobilization by Fe(II) associated with clay

minerals discovered a two-step mechanism in the reaction kinetics. Multiple redox cycles of Fe in nontronite NAU-2 affected its reactivity toward Tc(VII) reduction. The NAU-2 dispersion was first bioreduced by *Shewanella putrefaciens* CN32, then re-oxidized by air, then re-reduced, etc. Each redox cycle resulted in a small fraction of the NAU-2 being dissolved. These authors hypothesized that Fe(II) released into solution during the dissolution reaction was likely adsorbed or complexed onto edge surface sites of the remaining smectite and became highly reactive. The re-oxidation of edge-complexed Fe(II) was more rapid than structural Fe(II), which would explain the two steps in the reoxidation kinetics of the redox-cycled NAU-2. They found, further, that the reduction kinetics of Tc(VII) was also a two-step process. The first rapid reduction of Tc(VII) was, therefore, believed to be coupled with the highly reactive, edge-complexed Fe(II) reoxidation, whereas the slower step in the Tc(VII) reduction kinetics is coupled with reoxidation of structural Fe(II). This was the first extended study of redox cycling in Fe-rich clay minerals using bacterial reduction, and can be compared with other investigations of redox cycling and reversibility in clay minerals (Stucki, 2011).

One can conceive of a reactor system (Fig. 2) in which the redox activity of the microorganisms and the clay minerals can be coupled in a cyclic fashion in order to evoke a redox reaction in a target system, such as to remove undesired contaminants from groundwater effluents, aquifers, rivers, or lakes. The stability of the Fe in the clay mineral structure during redox cycling in such a reactor is key to its success and would provide the reversibility desired in a heterogeneous catalysis operation. A good understanding of the extent of dissolution in the microbially reduced smectite is, therefore, of fundamental importance to industrial applications of this phenomenon (see further discussion on this topic below).

## REACTION MECHANISMS

### *Electron shuttles*

The early results established the fact that the presence of bacteria in the clay mineral environment has an indisputable impact on the redox state of structural Fe, but the electron transfer mechanism to the Fe across the clay-water interface from the bacteria during microbial respiration was still not

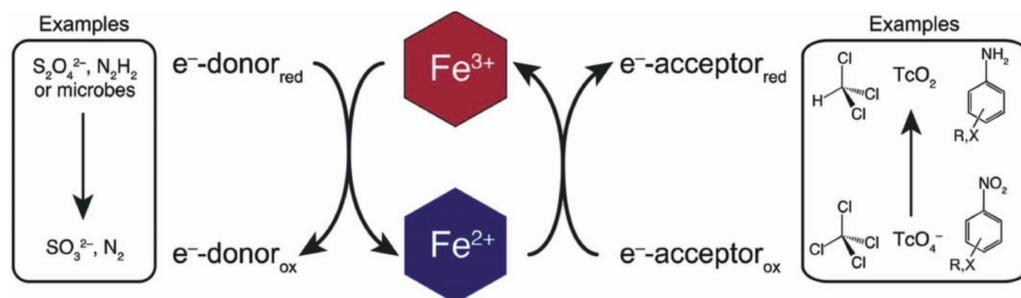


FIG. 2. Schematic representation of redox cycling of structural Fe in clay minerals. The coloured hexagons symbolize the octahedral binding environment of Fe(III) (top) and Fe(II) (bottom) in the clay mineral structure. Structural Fe(III) can be reduced by electron donors (e.g. dithionite, hydrazine, microorganisms, etc.). The resulting structural Fe(II), in turn, reduces oxidized organic contaminants (e.g. carbon tetrachloride or nitroaromatic compounds) or metals (e.g.  $Tc^{7+}$ ) (used with permission from Neumann *et al.*, 2011).

clear. A principal question was whether direct contact with the bacterial cell wall is necessary or if the organism uses water-soluble compounds to shuttle electrons between the cell wall and the mineral surface. As of this time, no study has clearly resolved this question, but indicators are suggesting that the electron shuttle option is more commonly reported than direct contact. The mechanism could also be different depending on the organism. Some bacteria, such as *Shewanella*, produce their own electron shuttles; others, such as *Geobacter metallireducens*, do not. Humic materials in natural environments are possible electron shuttles.

Lovley *et al.* (1998) studied electron shuttles, such as AQDS, lawsone and menadione. AQDS is commonly believed to be a good analog for humic substances in soils and sediments. They found that the extent of reduction of poorly crystalline Fe(III) oxide by *G. metallireducens* increased greatly when one of these shuttles was added. This indicates that reduction sites in poorly crystalline Fe oxides are not very accessible for direct contact with the *Geobacter* cells, but are accessible to the smaller electron-shuttle molecules. These data tend to support the electron shuttle mechanism.

Kostka *et al.* (1996) compared the levels of reduction achieved in ferruginous smectite by *Shewanella putrefaciens* strain MR-1 in the presence or absence of AQDS. They found that AQDS caused the level of reduction to increase by only about 10%, suggesting that most reaction sites in the smectite were available to the *Shewanella* cells either directly or through their natural electron shuttles. These data do not rule out either mechanism, however.

Part of understanding the reaction mechanism is locating the reaction sites in the clay mineral layers. Are they primarily at the basal surfaces, or are they primarily at the edges, and how does the organism gain access to them? Studies of *Shewanella* reduction of illite revealed results that were quite different from smectites (Dong *et al.*, 2003a,b; Seabaugh *et al.* 2006; Jaisi *et al.*, 2007a). In the case of smectite in these studies, 26% of Fe(III) was reduced. In one of the illite samples, which contained a minor component of goethite ( $\alpha$ -FeOOH) in addition to fibrous illite, only the goethite was reduced and no reduction of structural Fe in the illite was observed. With the addition of AQDS, however, reduction of Fe in the illite increased up to 25% of the total Fe. The collapsed nature of the illite layers obviously precluded access to reaction sites, either directly by the bacterial cells or indirectly by the electron shuttle molecules produced naturally by *Shewanella*.

Using several different bacterial strains, Kukkadapu *et al.* (2006), Bishop *et al.* (2011), Zhang *et al.* (2012) and Liu *et al.* (2012) also observed either no reduction or severely limited bacterial reduction of structural Fe in illite in the absence of AQDS. Addition of AQDS made reduction possible, although in one case (Muloorina illite) even AQDS failed to enable reduction of Fe in the illite. This clearly demonstrated that the extent of reduction is greater in a more expandable type of clay mineral layer, and proves that electron shuttles play an assertive role. This information does not, however, preclude the possibility that reduction could also occur by direct contact with the microbial cells.

Interestingly, the AQDS molecule has access to reaction sites in the clay mineral that are

unavailable to the electron shuttles produced naturally by *Shewanella*. Why this is true has yet to be answered. Further insight into understanding the effect of layer expandability on the extent of bacterial reduction, therefore, depends on finding the mechanism employed by AQDS to enhance bacterial reduction and uncovering how that compares with the naturally produced compounds.

In the study by Tung *et al.* (2006) of the GISP2 ice core referenced above, Fe-reducing microbes were immobilized on clay mineral surfaces, and then were activated to metabolize by “shuttle” molecules (humics and phenols) which transported electrons to grain edges. Formate and acetate ions trapped in water films on the clay mineral surfaces served as electron donors and structural Fe(III) ions in the clay grains were electron acceptors. At the grain edges, Fe(III) ions were reduced to Fe(II) while organic acids were oxidized to CO<sub>2</sub>. They proposed a mechanism in which polarons in the system may be generated by the hopping of extra electrons on Fe(II) to Fe(III) sites, thus freeing up Fe(III) at the edges for further reduction. The validity of this mechanism for electron shuttling and diffusion along basal planes was supported by the linear correlation of the number of attached cells with grain perimeter, along with the analogy of electron transport parallel with basal surfaces, to the direct-current electrical conductivity in Fe-rich phyllosilicates.

Ribeiro *et al.* (2009b), using variable-temperature Mössbauer spectroscopy, identified Fe(II) domains in microbially reduced Garfield nontronite, and proposed that reduction proceeds from the clay mineral edge inward toward the center, creating distinct Fe(II) domains and Fe(III) domains. These results have significant implications regarding the reversibility of the reduction reaction (see below for more details), but they also raise the question as to how the edge-reduction model fits with the observations above that the expandability of the clay mineral layer affects the extent of reduction. If the reduction occurs primarily at the layer edges, why would bacteria react differently with the edges of smectite layers compared with the edges of illite layers? One possible explanation is that the distribution of the Fe in the octahedral sheets of smectite is considerably different from that in illite. In nontronite, the Fe is close to the layer edges and is available for electron transfer from the bacteria. If in illite the Fe resides further away from the layer edges, the electron transfer would be more difficult.

The present authors, however, are unaware of any studies describing the edge-site Fe content in either illite or smectite. Such information would be useful in helping to resolve this question.

Recent studies of electron transfer mechanisms in smectites by abiotic reduction, using electrochemical (Shaefer *et al.*, 2011), cyclic voltammetry or chronocoulometry (Neumann *et al.* 2011; Gorski *et al.*, 2012a,b), and theoretical calculations (Alexandrov *et al.*, 2013), may also be helpful by providing tools and insight for gaining a better understanding of the electron transfer mechanisms at the clay-water interface. Future experiments of bacteria-mediated reduction using these methods would be of great interest.

### *Reversibility of microbial reduction*

A major unresolved issue in the literature pertains to the reversibility of the microbial reduction reaction. What are the structural changes that occur in the smectite when reduced by microorganisms, and is the original structure restored upon reoxidation by atmospheric oxygen? Lee *et al.* (2006) compared dithionite and microbially mediated reduction and its reversibility. Dithionite is capable of reducing the structural Fe to almost 100%, whereas the maximum observed by microorganisms is approximately 25–30% or about 1.0 mmol Fe(II)/g clay. They, therefore, limited the time of exposure of the smectite to dithionite in order to achieve a level similar to that attained in the reaction with microorganisms. Using infrared spectroscopy to monitor the structural O–H stretching bands of the octahedral sheet, they found that the shifts in the spectra were remarkably similar regardless of the reduction medium, as long as the extent of reduction was similar. Moreover, after reoxidation the spectral peak positions and shapes returned to virtually the same as in the unaltered or oxidized state. These results indicate that as far as the structural O–H stretching bands are able to reveal, structural changes are reversible under the condition of a modest level of reduction and that bacteria and dithionite affect the spectra in a similar manner.

In a companion study, Ribeiro *et al.* (2009b) compared the Mössbauer spectra of dithionite- and bacteria-reduced Garfield nontronite. The fully dithionite-reduced Garfield nontronite at liquid-nitrogen temperature (77 K) revealed a characteristic doublet for octahedral Fe(II) (Fig. 3a), with only a small component for octahedral Fe(III),

indicating the level of reduction to be more than 90%. At 4 K, however, the spectrum exhibited significant features that had never before been reported (Fig. 3b). No known theoretical model has been proposed for this spectrum, but it can be considered to be a reference spectrum for a completely reduced, Fe-rich, dioctahedral smectite. Upon reoxidation, the spectrum at any temperature bore little resemblance to the spectrum of the original nontronite, indicating that irreversible changes had occurred in the structure surrounding the Fe.

For samples reduced to a lesser extent (~1.0 mmol Fe(II)/g clay), Ribeiro *et al.* (2009b) found that the Mössbauer spectra at 77 K were virtually the same regardless of whether the sample was reduced by a limited dithionite treatment or by microorganisms (Fig. 4a,c), showing doublets assigned to both Fe(II) and Fe(III) in proportions consistent with the chemical analyses for Fe oxidation state. At 4 K, however, the spectra for partially dithionite-reduced Garfield nontronite were dramatically different from those of the microbially reduced samples (Fig. 4b,d). The 4 K spectrum from the partially dithionite-reduced Garfield (Fig. 4b) showed a central peak with a flaring baseline, suggesting a partially, but very poorly magnetically ordered system. They attributed this behaviour to an octahedral sheet in which Fe(II) was distributed mostly randomly in the *a-b* plane and was dominated by mixed-valent Fe(II)-Fe(III) pairs.

The microbially reduced sample, on the other hand, produced a spectrum at 4 K which had the appearance of an overlap of two distinct types of spectra (Fig. 4d). One type was reminiscent of the

completely reduced sample (Fig. 3b), whereas the other type exhibited more typical magnetic order with components of a six-line pattern. This second type was assigned to structural Fe(III) domains, whereas the first type was assigned to structural Fe(II) domains in the octahedral sheet (Ribeiro *et al.*, 2009b). These results provide evidence that the site for electron transfer in microbially reduced smectites is the edge of the mineral layer rather than the basal plane, which produces a reducing front of Fe(II)-Fe(III) pairs that moves from the outer edges toward the centre of the layer (Fig. 5a), leaving behind it a domain of all Fe(II) and, in front of it, a domain of all Fe(III). A similar “front of Fe(II)-Fe(III) pairs” phenomenon was observed in the oxidation of Fe-rich mica (Fig. 5b), characterized by a golden colour for the all Fe(III) domain behind the front and a black colour for the all Fe(II) domain ahead of the Fe(II)-Fe(III) boundary (Scott & Amonette, 1988). This assertion that microbial reduction occurs at the clay mineral edges rather than at the basal surfaces provides a practical reason for the limited extent of structural Fe reduction by bacteria compared to dithionite. If reduction occurs at the edges, complete reduction would depend on electron hopping through the octahedral sheet, which could easily be disrupted by discontinuities in the Fe-Fe linkages across the layer, thus limiting the extent of reduction.

Reoxidation of the partially dithionite-reduced and the microbially reduced nontronites restored both structures to their original state. Mössbauer spectra at 4 K of these reoxidized samples were virtually indistinguishable from one another (Fig. 6) and similar to the original sample, except for the

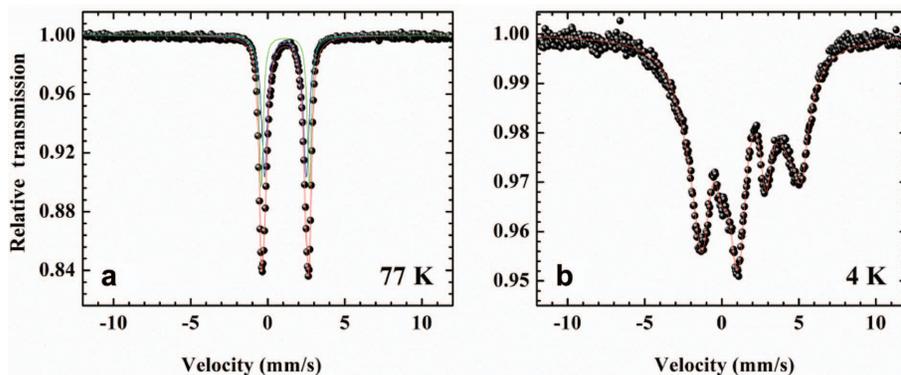


FIG. 3. Mössbauer spectra of Garfield nontronite fully dithionite-reduced: (a) at 77 K, (b) at 4 K (data from Ribeiro *et al.*, 2009b).

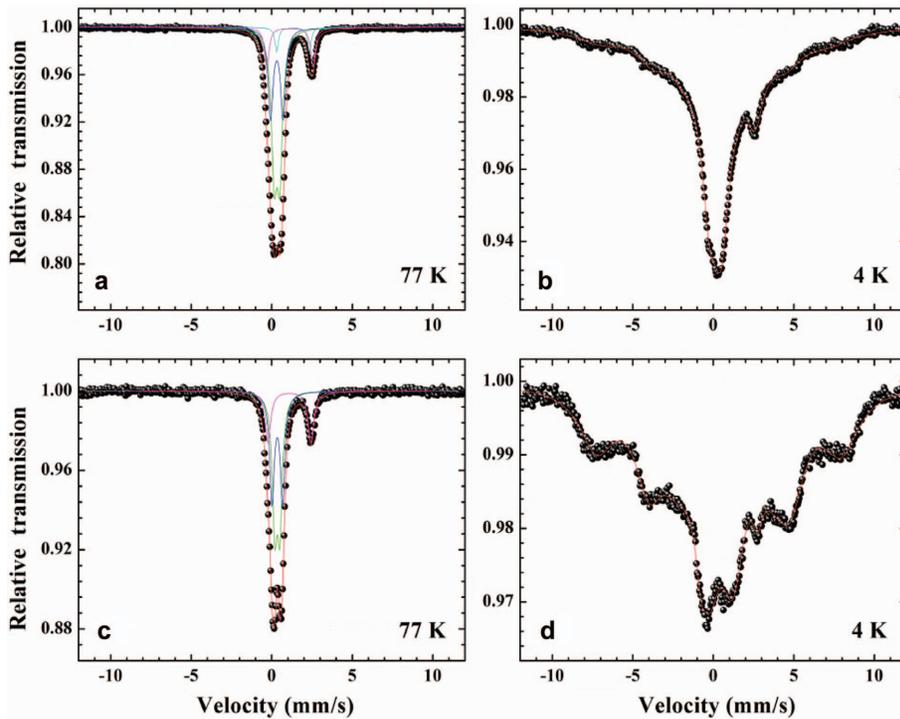


FIG. 4. Mössbauer spectra of Garfield nontronite partially dithionite-reduced: (a) at 77 K, (b) at 4 K; and microbially reduced: (c) at 77 K, (D) at 4 K (data from Ribeiro *et al.*, 2009b).

small amount of goethite impurity in the original sample.

Still unresolved, however, is whether clay mineral dissolution occurs during bacteria-mediated

Fe reduction or not. Several workers have reported various extents of clay mineral dissolution (Dong *et al.*, 2003a; Li *et al.*, 2004; O'Reilly *et al.*, 2004, 2005, 2006; Grybos *et al.*, 2011) and the

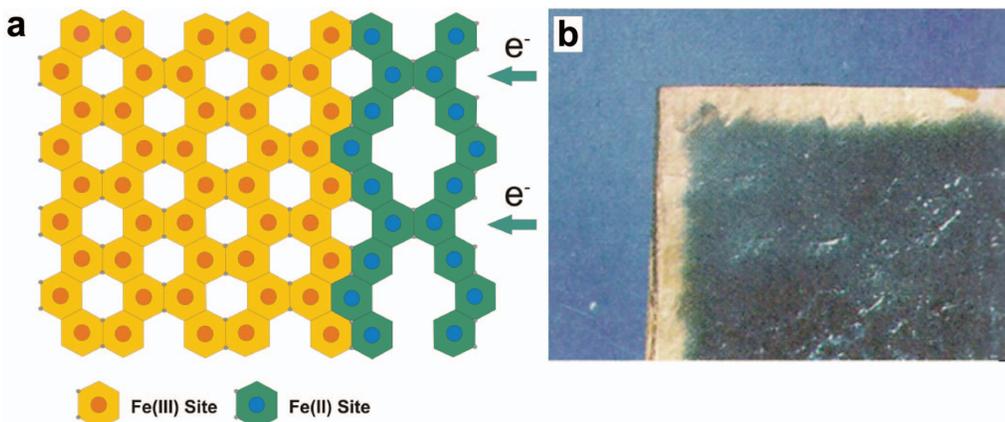


FIG. 5. (a) Schematic illustration of a reducing boundary or front of Fe(II)-Fe(III) moving through a clay mineral layer during microbial reduction; (b) photograph of an analogue oxidizing boundary or front of Fe(III)-Fe(II) that moved through a mica flake (lepidomelane flake, 1 × 2 cm) after treatment with an oxidizing solution of Br<sub>2</sub>-saturated 1 M KCl solution at 90°C for 80 weeks (modified from Scott & Amonette, 1988).

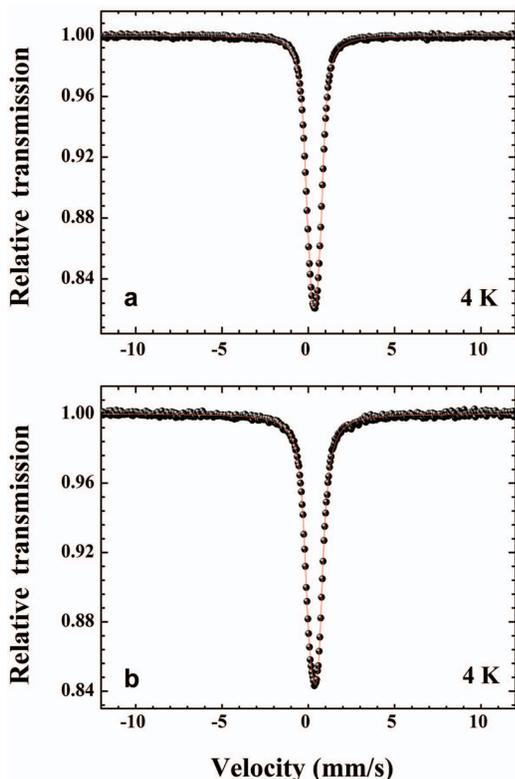


FIG. 6. Mössbauer spectra at 4 K of reoxidized Garfield nontronite after (a) partial dithionite-reduction and (b) microbial reduction (data from Ribeiro *et al.*, 2009b).

neof ormation of illite (Dong *et al.*, 2003b; Seabaugh *et al.*, 2006; Jaisi *et al.*, 2007a), mixed-layered illite-smectite (Eslinger *et al.*, 1979; Kim *et al.*, 2004; Kukkadapu *et al.*, 2006; Dong *et al.*, 2009a; Dong, 2010; Liu *et al.*, 2012; Shelobolina *et al.*, 2012a,b) and vivianite (Zhang *et al.*, 2012) during microbial reduction of Fe-bearing clay minerals. In contrast, studies by Stucki and co-workers, however, have not observed a dissolution-precipitation process. Formation of an illitic structure as a consequence of Fe reduction-reoxidation cycles in smectite is not particularly new or controversial, however, as it was hypothesized and demonstrated by Shen & Stucki (1994). Such a reduction of Fe during illitization of smectite was also hypothesized earlier by Eslinger *et al.* (1979). Those studies did not, however, contemplate this transformation occurring as a dissolution-precipitation process, with changes in chemical composition as well as mineral structure as observed in the more recent studies

(Vodyanitskii, 2007; Zhang *et al.*, 2007a,b; Stanjek & Marchel, 2008; Vorhies & Gaines, 2009; Jaisi *et al.*, 2011). The reader is referred to these works, and especially to the review by Dong *et al.* (2009a), for a more expanded discussion about the reductive dissolution and illitization of smectites by microorganisms.

The reduced clay mineral structure was found to be more susceptible to dissolution than the oxidized structure as evidenced by more rapid dissolution in acid (Kostka, Stucki, and co-workers). Opposite to the work by Dong and others mentioned before, these studies observed little or no dissolution within the bacterial incubations, and certainly no extensive transformation or alteration of the mineral structures was reported (e.g. Lee *et al.*, 2006; Ribeiro *et al.*, 2009b), except in the presence of organic acids (Kostka *et al.*, 1999). These different observations have yet to be reconciled, and the reasons for the differences still need to be explained by further investigation.

At the moment, one can only speculate as to why such disparate evidence exists regarding the dissolution of smectite upon microbial reduction. One possible explanation could be that different experimental conditions have been used in the microbial incubations in the different laboratories; no effort has yet been made to standardize these methods across laboratories, including the nutrient-solution compositions, initial growth phase and population of the microorganisms, and even the selected microbial strain. Another possibility is that interpretations are based on different types of observations. For example, studies showing dissolution base some of their conclusions on TEM observation, whereas comparative TEM results are not available for those studies in which no dissolution was observed. On the other hand, Mössbauer spectra at 4 K were not obtained in studies showing dissolution, rendering comparison difficult. In the current authors' opinion, this is the most critical place to begin if this conflict is to be resolved, because the 4-K Mössbauer spectra reveal more about the environment of the Fe than any other single method.

#### EXPANSION OF NUMBER AND TYPES OF MICROORGANISMS USED

The number and types of bacteria capable of reducing structural Fe in smectites were well reviewed previously (Stucki & Kostka, 2006;

Dong *et al.*, 2009a), but since then a few more have appeared. Liu *et al.* (2012) measured the rate and extent of reduction of structural Fe(III) in dioctahedral clay minerals by the mesophilic sulfate-reducing bacterium *Desulfovibrio vulgaris*. They also investigated its potential role in catalyzing smectite illitization. Bioreduction experiments were performed in batch systems, where four different clay minerals (nontronite NAu-2, mixed-layer illite-smectites RAr-1 and ISCz-1, and illite IMt-1) were exposed to *D. vulgaris* in a non-growth medium with and without AQDS and sulfate. Their results demonstrated that it was able to reduce structural Fe(III) in these clay minerals, and AQDS enhanced the reduction rate and extent. In the presence of AQDS, sulfate had little effect on Fe(III) bioreduction. These data collectively showed that *D. vulgaris* could promote smectite illitization through reduction of structural Fe(III) in clay minerals. Similar results were obtained by Zhang *et al.* (2012) using the mesophilic methanogen *Methanosarcina mazei*.

Some microorganisms are able to both reduce and oxidize structural Fe in clay minerals. Shelobolina *et al.* (2003) observed that *Desulfitobacterium frappieri* strain G2 readily uses poorly crystalline Fe(III) oxides, soluble forms of Fe(III), and Fe(III) in the structure of phyllosilicate minerals as electron acceptors, thus bringing about Fe reduction. They reported further, however, that beside its ability to reduce Fe(III), *D. frappieri* strain G2 also has the potential to oxidize Fe(II) if nitrate is present to serve as the electron acceptor. This organism may, therefore, play an important role in iron cycling in sedimentary environments.

Redox cycling of Fe in soils may also occur by the simultaneous presence of both Fe-reducing and Fe-oxidizing microorganisms. Shelobolina *et al.* (2012a,b) isolated Fe-oxidizing bacteria from a hydromorphic soil in Wisconsin (Shovelers Sink, a small glacial depression) which were identified as *Bradyrhizobium* spp. and strains of *Cupriavidus necator* and *Ralstonia solanacearum*. These organisms were cultured using the method of Straub *et al.* (1996), in the presence of either soluble Fe<sup>2+</sup> in solution or Fe(II) in the structure of Bancroft, Ontario, biotite, which served as the electron donor, and with O<sub>2</sub> or nitrate as the electron acceptor. This microbial oxidation of structural Fe(II) resulted in biotite alteration and weathering, including Fe and K release. Their hypothesis was that structural Fe(II) oxidation by these organisms involves either

direct enzymatic oxidation, followed by solid-state mineral transformation, or indirect oxidation as a result of the formation of aqueous Fe, followed by electron transfer from Fe(II) in the mineral to Fe<sup>3+</sup> in solution. In addition to promoting the oxidation of biotite and soluble Fe<sup>3+</sup>, each of the isolates above was able to oxidize Fe(II) in reduced NAu-2 nontronite with NO<sub>3</sub><sup>-</sup> as the electron acceptor. These organisms may, therefore, play an important role in the weathering of soils.

Also discovered in the Shovelers Sink soil (Shelobolina *et al.*, 2012a,b) was an organism related to *Geobacter toluenoxydans* which reduced the oxidized form of Fe in NAu-2 nontronite and in amorphous Fe(III) oxide. This means that this soil contains both Fe-oxidizing and Fe-reducing microorganisms, suggesting that, depending on which organisms are being stimulated by environmental conditions, the phyllosilicate clay minerals will be subjected to either oxidizing or reducing reactions with the indigenous microorganisms, which, when acting in concert, have the ability to cycle Fe by redox transformations.

## SUMMARY

Microbial reduction of structural Fe in clay minerals has been investigated extensively since its inception in 1986. Studies have revealed that organisms capable of reducing this form of Fe are ubiquitous in nature and are not limited to submerged or hydromorphic soils. They are present in a wide range of soils and sediments, and only require stimulation by the presence of an electron donor or C source to react metabolically with the clay minerals serving as the electron acceptors. The Fe in the more expandable clay minerals is more susceptible to microbial reduction than the Fe in illitic or collapsed-layer structures, even though significant evidence is presented that the site of electron transfer from the bacterial cells to the clay mineral layer may be at the layer edge. The extent of reduction is limited to ~1.0 mmole Fe(II)/g clay, and the percentage reduction varies widely among the clay minerals, depending on their total Fe content and its distribution within the octahedral sheet. Whether this limit is due to thermodynamic potentials or simply due to steric constraints is unknown.

An extremely important consequence of the now documented phenomenon of microbial reduction of Fe in clay minerals is the clear understanding that it

occurs in nature. This gives much relevance to laboratory studies which have shown and continue to demonstrate that the redox state of the structural Fe affects important physical and chemical properties of the clay mineral, and in turn of the surrounding soil or sediment. Such a relationship inspires and gives insight into the creation of systems and practices for the *in situ* management of remediation strategies for environmental contaminants, of soil properties, of agronomic productivity, and of a variety of industrial processes.

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#### REFERENCES

- Alexandrov V., Neumann A., Scherer M.M. & Rosso K. (2013) Electron exchange and conduction in nontronite from first principles. *Journal of Physical Chemistry C*, **117**, 2032–2040.
- Alimova A., Block K., Rudolph E., Katz A., Steiner J.C., Gottlieb P. & Alfano R.R. (2006) Bacteria-clay interactions investigated by light scattering and phase contrast microscopy. Pp. 76–79 in: *Optical Diagnostics and Sensing VI* (G.L. Coté & A.V. Priezhev, editors). SPIE Proc., 6094.
- Alimova A., Katz A., Steiner N., Rudolph E., Wei H., Steiner J.C. & Gottlieb P. (2009) Bacteria-clay interaction: Structural changes in smectite induced during biofilm formation. *Clays and Clay Minerals*, **57**, 205–212.
- Bishop M.E. & Dong H.L. (2010) Reactivity of clay minerals towards technetium immobilization. *Geochimica et Cosmochimica Acta*, **74**, A93, Supplement 1.
- Bishop M.E., Jaisi D.P., Dong H.L., Kukkadapu R.K. & Ji J. (2010) Bioavailability of Fe(III) in loess sediments: An important source of electron acceptors. *Clays and Clay Minerals*, **58**, 542–557.
- Bishop M.E., Dong H.L., Kukkadapu R.K. & Edelmann R.E. (2011) Microbial reduction of Fe(III) in multiple clay minerals by *Shewanella putrefaciens* and reactivity of bioreduced clay minerals toward Tc(VII) immobilization. *Geochimica et Cosmochimica Acta*, **75**, 5229–5246.
- Bromfield S.M. (1954) Reduction of ferric compounds by soil bacteria. *Journal of General Microbiology*, **11**, 1–6.
- 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.
- Dong H.L. (2010) Mineral-microbe interactions: a review. *Frontiers of Earth Science in China*, **4**, 127–147.
- Dong H.L. (2012) Clay-microbe interactions and implications for environmental mitigation. *Elements*, **8**, 113–118.
- Dong H.L., Kostka J.E. & Kim J. (2003a) Microscopic evidence for microbial dissolution of smectite. *Clays and Clay Minerals*, **51**, 502–512.
- Dong H.L., Kukkadapu R.K., Fredrickson J.K., Zachara J.M., Kennedy D.W., & Kostandarithes H.M. (2003b) Microbial reduction of structural Fe(III) in illite and goethite. *Environmental Science & Technology*, **37**, 1268–1276.
- Dong H.L., Jaisi D.P., Kim J.W. & Zhang G.X. (2009a) Microbe-clay mineral interactions. *American Mineralogist*, **94**, 1505–1519.
- Dong H.L., Jaisi D.P., Zhang G.X. & Kim J.W. (2009b) Microbe-clay mineral interactions and implications for environmental remediation. *The 237<sup>th</sup> Annual Meeting of American Chemical Society, Salt Lake City, Abstracts*, 68.
- Ernstsen V. (1996) Reduction of nitrate by Fe<sup>2+</sup> 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.
- Favre F., Tessier D., Abdelmoula M., Génin J.M., Gates W.P. & Boivin P. (2002a) Iron reduction and CEC changes in intermittently reduced soil. *European Journal of Soil Science*, **53**, 1–9.
- Favre F., Tessier D., Abdelmoula M., Génin 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., Cooper N.G.A., Jones D.M., White M.L. & Gray N.D. (2010) Reductive degradation of p,p'-DDT by Fe(II) in nontronite NAu-2. *Clays and Clay Minerals*, **58**, 821–836.
- Fredrickson J.K., Zachara J.M., Kennedy D.W., Kukkadapu R.K., McKinley J.P., Heald S.M., Liu C. & Plymale A.E. (2004) Reduction of TcO<sub>4</sub><sup>-</sup> by sediment-associated biogenic Fe(II). *Geochimica et*

- Cosmochimica Acta*, **68**, 3171–3187.
- 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. & Wilkinson H.T. (1994) Microbial reduction of smectite structural Fe. *The American Chemical Society, Abstracts*, **207**, 79.
- 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.
- Gorski C.A., Aeschbacher M., Soltermann D., Voegelin A., Baeyens B., Marques Fernandes M., Hofstetter T.B. & Sander M. (2012a) Redox properties of structural Fe in clay minerals. 1. Electrochemical quantification of electron-donating and -accepting capacities of smectites. *Environmental Science & Technology*, **46**, 9360–9368.
- Gorski C.A., Klüpfel L., Voegelin A., Sander M. & Hofstetter T.B. (2012b) Redox properties of structural Fe in clay minerals. 2. Electrochemical and spectroscopic characterization of electron transfer irreversibility in ferruginous smectite, SWa-1. *Environmental Science & Technology*, **46**, 9369–9377.
- Grybos M., Billard P., Desobry-Banon S., Michot L.J., Lenain J.F. & Mustin C. (2011) Bio-dissolution of colloidal-size clay minerals entrapped in microporous silica gels. *Journal of Colloid and Interface Science*, **362**, 317–324.
- Guo M.R., Lin Y.M., Xu X.P. & Chen Z.L. (2010a) Bioleaching of iron from kaolin using Fe(III)-reducing bacteria with various carbon nitrogen sources. *Applied Clay Science*, **48**, 379–383.
- Guo M.R., He Q.X., Li Y.M., Lu X.Q. & Chen Z.L. (2010b) Removal of Fe from kaolin using dissimilatory Fe(III)-reducing bacteria. *Clays and Clay Minerals*, **58**, 515–521.
- Hama K., Bateman K., Coombs P., Hards V.L., Milodowski A.E., West J.M., Wetton P.D., Yoshida H., & Aoki K. (2001) Influence of bacteria on rock-water interaction and clay mineral formation in subsurface granitic environments. *Clay Minerals*, **36**, 599–613.
- He Q.X., Huang X.C. & Chen Z.L. (2011) Influence of organic acids, complexing agents and heavy metals on the bioleaching of iron from kaolin using Fe(III)-reducing bacteria. *Applied Clay Science*, **51**, 478–483.
- Jaisi D.P., Dong H.L. & Liu C.X. (2007a) Influence of biogenic Fe(II) on the extent of microbial reduction of Fe(III) in clay minerals nontronite, illite, and chlorite. *Geochimica et Cosmochimica Acta*, **71**, 1145–1158.
- Jaisi D.P., Dong H.L., Kim J.W., He Z., & Morton J.P. (2007b) Particle aggregation kinetics during microbial reduction of Fe(III) in nontronite. *Clays and Clay Minerals*, **55**, 96–107.
- Jaisi D.P., Dong H. & Liu C.X. (2007c) Kinetic analysis of microbial reduction of Fe(III) in nontronite. *Environmental Science & Technology*, **41**, 2437–2444.
- Jaisi D.P., Ji S.S., Dong H.L., Blake R.E., Eberl D.D. & Kim J.W. (2008a) Role of microbial Fe(III) reduction and solution chemistry in aggregation and settling of suspended particles in the Mississippi River delta plain, Louisiana, USA. *Clays and Clay Minerals*, **56**, 416–428.
- Jaisi D.P., Dong H.L. & Morton J.P. (2008b) Partitioning of Fe(II) in reduced nontronite (NAu-2) to reactive sites: Reactivity in terms of Tc(VII) reduction. *Clays and Clay Minerals*, **56**, 175–189.
- Jaisi D.P., Dong H.L., Plymale A.E., Fredrickson J.K., Zachara J.M., Heald S.M. & Liu C.X. (2009) Reduction and long-term immobilization of technetium by Fe(II) associated with clay mineral nontronite. *Chemical Geology*, **264**, 127–138.
- Jaisi D.P., Eberl D.D., Dong H.L. & Kim J. (2011) The formation of illite from nontronite by mesophilic and thermophilic bacterial reaction. *Clays and Clay Minerals*, **59**, 21–33.
- Kashefi K., Shelobolina E.S., Elliott W.C. & Lovley D.R. (2008) Growth of thermophilic and hyperthermophilic Fe (III)-reducing microorganisms on a ferruginous smectite as the sole electron acceptor. *Applied and Environmental Microbiology*, **74**, 251–258.
- Kim J.W., Furukawa Y., Daulton T.L., 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.W., Dong H.L., Seabaugh J.L., Newell S.W. & Eberl D.D. (2004) Role of microbes in the smectite-to-illite reaction. *Science*, **303**, 830–832.
- Komadel P., Stucki J.W. & Wilkinson H.T. (1987) Reduction of structural iron in smectites by microorganisms. *The Sixth Meeting of the European Clay Groups Sevilla*, 322–324.
- Komadel P. & Stucki J.W. (1988) Quantitative assay of minerals for Fe<sup>2+</sup> and Fe<sup>3+</sup> using 1,10-phenanthroline: III. A rapid photochemical method. *Clays and Clay Minerals*, **36**, 379–381.
- Kostka J.E., Stucki J.W., Neelson K.H. & Wu J. (1996) Reduction of structural Fe(III) in smectite by a pure culture of *Shewanella putrefaciens* strain MR-1. *Clays and Clay Minerals*, **44**, 522–529.
- Kostka J.E., Haefele E., Viehweger R. & Stucki J.W. (1999a) Respiration and dissolution of iron(III)-

- containing clay minerals by bacteria. *Environmental Science & Technology*, **33**, 3127–3133.
- Kostka J.E., Wu J., Nealon K.H. & Stucki J.W. (1999b) The impact of structural Fe(III) reduction by bacteria on the surface chemistry of smectite clay minerals. *Geochimica et Cosmochimica Acta*, **63**, 3705–3713.
- Kostka J.E., Stucki J.W. & Dong H.L. (2002a) Microbial reduction of Fe(III) bound in clay minerals: Laboratory investigations of growth and mineral transformation. *The American Chemical Society, Abstracts*, **223**, 598.
- Kostka J.E., Dalton D.D., Skelton H., Dollhopf S. & Stucki J.W. (2002b) 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.
- Kukkadapu R.K., Zachara J.M., Fredrickson J.K., McKinley J.P., Kennedy D.W., Smith S.C. & Dong H.L. (2006) Reductive biotransformation of Fe in shale-limestone saprolite containing Fe(III) oxides and Fe(II)/Fe(III) phyllosilicates. *Geochimica et Cosmochimica Acta*, **70**, 3662–3676.
- Lear P.R. & Stucki J.W. (1989) Effects of iron oxidation state on the specific surface area of nontronite. *Clays and Clay Minerals*, **37**, 547–552.
- Lee E.Y., Cho K.S., Ryu H.W. & Chang Y.K. (1999) Microbial removal of Fe(III) impurities from clay using dissimilatory iron reducers. *Journal of Bioscience and Bioengineering*, **87**, 397–399.
- Lee E.Y., Cho K.S. & Ryu H.W. (2002) Microbial refinement of kaolin by iron-reducing bacteria. *Applied Clay Science*, **22**, 47–53.
- Lee K., Kostka J.E. & Stucki J.W. (2006) Comparisons of structural Fe reduction in smectites by bacteria and dithionite: an infrared spectroscopic study. *Clays and Clay Minerals*, **54**, 195–208.
- Li O., Bleam W.F., Kostka J.E., Stucki J.W. & Lee K. (2003) Polarized EXAFS studies of nontronite by anaerobic bacteria. *The American Chemical Society, Abstracts*, **226**, 492.
- Li Y.L., Vali H., Sears S.K., Yang J., Deng B. & Zhang C. (2004) Iron reduction and alteration of nontronite NAu-2 by a sulfate-reducing bacterium. *Geochimica et Cosmochimica Acta*, **68**, 3251–3260.
- Liu D., Wang H.M., Qiu X.A., & Dong H.L. (2010) Comparison of reduction extent of Fe(III) in nontronite by *Shewanella putrefaciens* and *Desulfovibrio vulgaris*. *Journal of Earth Science*, **21**, 297–299.
- Liu D., Dong H.L., Bishop M.E., Wang H.M., Agrawal A., Tritschler S., Eberl D.D. & Xie S. (2011) Reduction of structural Fe(III) in nontronite by methanogen *Methanosarcina barkeri*. *Geochimica et Cosmochimica Acta*, **75**, 1057–1071.
- Liu D., Dong H.L., Bishop M.E., Zhang J., Wang H., Xie S., Wang S., Huang L. & Eberl D.D. (2012) Microbial reduction of structural iron in interstratified illite-smectite minerals by a sulfate-reducing bacterium. *Geobiology*, **10**, 150–162.
- Lovley D.R., Fraga J.L., Blunt-Harris E.L., Hayes L.A., Philips E.J.P. & Coates J.D. (1998) Humic substances as a mediator for microbially catalyzed metal reduction. *Acta Hydrochimica et Hydrobiologica*, **26**, 152–157.
- Maurice P.A., Vierkorn M.A., Hersman L.E., Fulghum J.E. & Ferryman A. (2001a) Enhancement of kaolinite dissolution by an aerobic *Pseudomonas mendocina* bacterium. *Geomicrobiology Journal*, **18**, 21–35.
- Maurice P.A., Vierkorn M.A., Hersman L.E. & Fulghum J.E. (2001b) Dissolution of well and poorly ordered kaolinites by an aerobic bacterium. *Chemical Geology*, **180**, 81–97.
- Munch J.C. & Ottow J.C.G. (1977) Model experiments on the mechanism of bacterial iron-reduction in water-logged soils. *Zeitschrift für Pflanzenernährung und Bodenkunde*, **140**, 549–562.
- Munch J.C. & Ottow J.C.G. (1982) Effect of cell contact and iron(III)-oxide form on bacterial iron reduction. *Zeitschrift für Pflanzenernährung und Bodenkunde*, **145**, 66–77.
- Munch J.C., Hillebrand T. & Ottow J.C.G. (1978) Transformation in the Feo/Fed ratio of pedogenic iron oxides affected by iron-reducing bacteria. *Journal of Canadian Soil Science*, **58**, 475–486.
- Myers C.R. & Nealon K.H. (1988) Bacterial manganese reduction and growth with manganese oxide as the sole electron acceptor. *Science*, **240**, 1319–1321.
- Neumann A., Sander M. & Hofstetter T.B. (2011) Redox properties of structural Fe in smectite clay minerals. Chapter 17 in: *Aquatic Redox Chemistry* (P. Tratnyek et al., editors). *ACS Symposium Series*, American Chemical Society, Washington DC.
- Onysko S.J., Kleinmann R.L.P. & Erickson P.M. (1984) Ferrous iron oxidation by thiobacillus ferrooxidans: Inhibition with benzoic acid, sorbic acid, and sodium lauryl sulfate. *Applied and Environmental Microbiology*, **48**, 229–231.
- O'Reilly S.E., Bickmore B.R. & Furukawa Y. (2004) Dissolution of microbial reduced nontronite in a flow-through system. P. 86 in: *41<sup>st</sup> Annual Meeting of the Clay Minerals Society, Program and Abstracts*.
- O'Reilly S.E., Watkins J., & Furukawa Y. (2005) Secondary mineral formation associated with respiration of nontronite, NAU-1 by iron-reducing bacteria. *Geochemical Transactions*, **6**, 67–76.
- O'Reilly S.E., Furukawa Y. & Newell S. (2006) Dissolution and microbial Fe(III) reduction of nontronite (NAU-1). *Chemical Geology*, **235**, 1–11.
- Ottow J.C.G. (1968) Evaluation of iron-reducing bacteria in soil and the physiological mechanism of iron-reduction in aerobacter aerogenes. *Zeitschrift*

- für *Allgemeine Mikrobiologie*, **85**, 441–443.
- Ottow J.C.G. (1969) Influence of nitrate, chlorate, sulfate, form of iron oxide, and growth conditions on the extent of bacteriological reduction of iron. *Zeitschrift für Pflanzenernährung und Bodenkunde*, **124**, 238–253.
- Ottow J.C.G. & von Klopotek A. (1969) Enzymatic reduction of iron oxide by fungi. *Applied Microbiology*, **18**, 41–43.
- Perdrial J.N., Warr L.N., Perdrial N., Lett M.C. & Elsass F. (2009) Interaction between smectite and bacteria: Implications for bentonite as backfill material in the disposal of nuclear waste. *Chemical Geology*, **264**, 281–294.
- Prakash O., Gihring T.M., Dalton D.D., Chin K.-J., Green S.J., Akob D.M., Wanger G. & Kostka J.E. (2010) *Geobacter daltonii* sp. nov., an iron(III)- and uranium(VI)-reducing bacterium isolated from the shallow subsurface exposed to mixed heavy metal and hydrocarbon contamination. *International Journal of Systematic and Evolutionary Microbiology*, **60**, 546–553.
- Ribeiro F.R., Kostka J.E. & Stucki J.W. (2009a) Comparisons of structural iron reduction in phyllosilicates by bacteria and dithionite. P. 67 in: *The 237<sup>th</sup> Annual Meeting of American Chemical Society, Salt Lake City, Abstracts*.
- Ribeiro F.R., Fabris J.D., Kostka J.E., Komadel P. & Stucki J.W. (2009b) Comparisons of structural iron reduction in smectites by bacteria and dithionite: II. A variable-temperature Mössbauer spectroscopic study of Garfield nontronite. *Pure and Applied Chemistry*, **81**, 1499–1509.
- Rinder G. (1979) Effect of clay minerals on the behavior of acidophilic *Thiobacillus* species in suspensions. *Zeitschrift für Allgemeine Mikrobiologie*, **19**, 643–665.
- Sand W. (1989) Ferric iron reduction by *thiobacillus ferrooxidans* at extremely low pH-values. *Biogeochemistry*, **7**, 195–201.
- Schaefer M.V., Gorski C.A. & Scherer M.M. (2011) Spectroscopic evidence for interfacial Fe(II)-Fe(III) electron transfer in a clay mineral. *Environmental Science & Technology*, **45**, 540–545.
- Scott A.D. & Amonette J.E. (1988) Role of iron in mica weathering. Pp. 537–623 in: *Iron in Soils and Clay Minerals* (J.W. Stucki, B.A. Goodman & U. Schwermann, editors). Dordrecht, D. Reidel, The Netherlands.
- Seabaugh J.L., Dong H.L., Kukkadapu R.K., Eberl D., Morton J.P. & Kim J.W. (2006) Microbial reduction of Fe(III) in the Fithian and Muloorina illites: Contrasting extents and rates of bioreduction. *Clays and Clay Minerals*, **54**, 67–79.
- Shelobolina E.S., Vanpraagh C.G. & Lovley D.R. (2003) Use of ferric and ferrous iron containing minerals for respiration by *Desulfitobacterium frap-pieri*. *Geomicrobiology Journal*, **20**, 143–156.
- Shelobolina E.S., Anderson R.T., Vodyanitskii Y.N., Sivtsov A.M., Yuretich R. & Lovley D.R. (2004) Importance of clay size minerals for Fe(III) respiration in a petroleum-contaminated aquifer. *Geobiology*, **2**, 67–76.
- Shelobolina E.S., Pickering S.M. & Lovley D.R. (2005) Fe-cycle bacteria from industrial clays mined in Georgia, USA. *Clays and Clay Minerals*, **53**, 580–586.
- Shelobolina E.S., Konishi H., Xu H., Benzine J., Xiong M.Y., Wu T., Blöthe M., & Roden E. (2012a) Isolation of phyllosilicate-iron redox cycling microorganisms from an illite-smectite rich hydromorphic soil. *Frontiers in Microbiology*, **3**, 1–10.
- Shelobolina E.S., Xu H., Konishi H., Kukkadapu R., Wu T., Blöthe M., & Roden E. (2012b) Microbial lithotrophic oxidation of structural Fe(II) in biotite. *Applied and Environmental Microbiology*, **78**, 5746–5752.
- Shen S. & Stucki J.W. (1994) Effects of iron oxidation state on the fate and behavior of potassium in soils. Pp. 173–185 in: *Soil Testing: Prospects for Improving Nutrient Recommendations* (J.L. Havlin & J. Jacobsen, editors) Soil Science Society of America, Madison, Wisconsin.
- Soljanto P., Rehtijarvi P. & Tuovinen O.H. (1985) Ferrous iron oxidation by *Thiobacillus ferrooxidans*: Inhibition of finely ground particles. *Geomicrobiology Journal*, **2**, 1–12.
- Stanjek H. & Marchel C. (2008) Linking the redox cycles of Fe oxides and Fe-rich clay minerals: an example from a palaeosol of the Upper Freshwater Molasse. *Clay Minerals*, **43**, 69–82.
- Starkey R.L. & Halvorson H.O. (1927) Studies on the transformations of iron in nature. II Concerning the importance of microorganisms in the solution and precipitation of iron. *Soil Science*, **24**, 381–402.
- Straub K.L., Benz M., Schink B. & Widdel F. (1996) Anaerobic, nitrate-dependent microbial oxidation of ferrous iron. *Applied and Environmental Microbiology*, **62**, 1458–1460.
- Stucki J.W. (1988) Structural iron in smectites. Pp. 625–675 in: *Iron in Soils and Clay Minerals* (J.W. Stucki, B.A. Goodman & U. Schwermann, editors). D.Reidel, Dordrecht, The Netherlands.
- Stucki J.W. (2006) Properties and behaviour of iron in clay minerals. Pp. 429–482 in: *Handbook of Clay Science* (F. Bergaya, B.G.K. Theng, & G. Lagaly, editors). Elsevier, Amsterdam.
- Stucki J.W. (2009) Overview of redox biogeochemistry of iron in phyllosilicates. In: *The 237<sup>th</sup> Annual Meeting of American Chemical Society, Salt Lake City, Abstract 64*.
- Stucki J.W. (2011) A review of the effects of iron redox cycles on smectite properties. *Comptes Rendus - Geoscience*, **343**, 199–209.

- Stucki J.W. (2013). Properties and behaviour of iron in clay minerals. In: *Handbook of Clay Science, 2<sup>nd</sup> edition* (F. Bergaya & G. Lagaly, editors). Elsevier, Amsterdam (in press).
- Stucki J.W. & Getty P.J. (1986) Microbial reduction of iron in nontronite. P. 279 in: *Agronomy Abstracts, 1986 annual meetings of the Soil Science Society of America*.
- Stucki J.W. & Kostka J.E. (2006) Microbial reduction of iron in smectite. *Comptes Rendus - Geoscience*, **338**, 468–475.
- Stucki J.W. & Lear P.R. (1989) Variable oxidation states of iron in the crystal structure of smectite clay minerals. *ACS Symposium Series*, **415**, 330–358.
- Stucki J.W., Low P.F., Roth C.B. & Golden D.C. (1984) Effect of iron oxidation state 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., Gan H. & Wilkinson H.T. (1992) Effects of microorganisms on phyllosilicate properties and behavior. Pp. 227–254 in: *Advances in Soil Science* (R.J. Wagenet, P. Baveye & B.A. Stewart, editors). Lewis Publishers, Boca Raton, Florida.
- Stucki J.W., Bailey G.W. & Gan H. (1996) Oxidation-reduction mechanisms in iron-bearing phyllosilicates. *Applied Clay Science*, **10**, 417–430.
- Stucki J.W., Lee K., Zhang L.Z. & Larson R.A. (2002) Effects of iron oxidation state on the surface and structural properties of smectites. *Pure and Applied Chemistry*, **74**, 2145–2158.
- Su K., Radian A., Mishael Y., Yang L. & Stucki J.W. (2012) Nitrate reduction by redox-activated, polydiallyldimethylammonium-exchanged ferruginous smectite. *Clays and Clay Minerals*, **60**, 464–472.
- Sugio T., Tano T. & Imai K. (1981) Isolation and some properties of silver ion-resistant iron-oxidizing bacterium *Thiobacillus ferrooxidans*. *Agricultural and Biological Chemistry*, **459**, 2037–2051.
- Tor J.M., Xu J.C., Stucki J.W., Wander M.M. & Sims G.K. (2000) Trifluralin degradation under microbially induced nitrate and Fe(III) reducing conditions. *Environmental Science & Technology*, **34**, 3148–3152.
- Tung H.C., Price P.B., Bramall N.E. & Vrdoljak G. (2006) Microorganisms metabolizing on clay grains in 3-km-deep Greenland basal ice. *Astrobiology*, **6**, 69–86.
- Vempati R.K., Kollipara K.P., Stucki J.W. & Wilkinson H.T. (1995) Reduction of structural iron in selected iron-bearing minerals by soybean root exudates grown in an in vitro geponic system. *Journal of Plant Nutrition*, **18**, 343–353.
- Vodyanitskii Y.N. (2007) Reductive biogenic transformation of Fe(III)-containing phyllosilicates (review of publications). *Eurasian Soil Science*, **40**, 1355–1363.
- Vorhies J.S. & Gaines R.R. (2009) Microbial dissolution of clay minerals as a source of iron and silica in marine sediments. *Nature Geoscience*, **2**, 221–225.
- Wu J., Roth C.B. & Low P.F. (1988) Biological reduction of structural iron in sodium-nontronite. *Soil Science Society of America Journal*, **52**, 295–296.
- Wu T., Shelobolina E.S., Xu H., Konishi H., Kukkadapu R.K. & Roden E.E. (2012) Isolation and microbial reduction of Fe(III) phyllosilicates from subsurface sediments. *Environmental Science & Technology*, **46**, 11618–11626.
- Xu J.C., Stucki J.W., Wu J., Kostka J.E. & Sims G.K. (2001) Fate of atrazine and alachlor in redox-treated ferruginous smectite. *Environmental Toxicology and Chemistry*, **20**, 2717–2724.
- Yang J., Kukkadapu R.K., Dong H.L., Shelobolina E.S., Zhang J. & Kim J. (2012) Effects of redox cycling of iron in nontronite on reduction of technetium. *Chemical Geology*, **291**, 206–216.
- Zhang G.X., Dong H.L., Jiang H.C., Xu Z. & Eberl D.D. (2006) Unique microbial community in drilling fluids from Chinese continental scientific drilling. *Geomicrobiology Journal*, **23**, 499–514.
- Zhang G.X., Dong H.L., Kim J., & Eberl D.D. (2007a) Microbial reduction of structural Fe<sup>3+</sup> in nontronite by a thermophilic bacterium and its role in promoting the smectite to illite reaction. *American Mineralogist*, **92**, 1411–1419.
- Zhang G.X., Kim J.W., Dong H.L. & Andre J.S. (2007b) Microbial effects in promoting the smectite to illite reaction: Role of organic matter intercalated in the interlayer. *American Mineralogist*, **92**, 1401–1410.
- Zhang G.X., Senko J.M., Kelly S.D., Tan H., Kemner K.M. & Burgos W.D. (2009) Microbial reduction of iron(III)-rich nontronite and uranium(VI). *Geochimica et Cosmochimica Acta*, **73**, 3523–3538.
- Zhang G.X., Burgos W.D., Senko J.M., Bishop M.E., Dong H.L., Boyanov M.I. & Kemner K.M. (2011) Microbial reduction of chlorite and uranium followed by air oxidation. *Chemical Geology*, **283**, 242–250.
- Zhang J., Dong H.L., Liu D., Fischer T.B., Wang S. & Huang L. (2012) Microbial reduction of Fe(III) in illite-smectite minerals by methanogen *Methanosarcina mazei*. *Chemical Geology*, **292–293**, 35–44.