Clay—Microbe Interactions and Implications for Environmental Mitigation

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Clay minerals are ubiquitous in soils, sediments, and sedimentary rocks, and they play important roles in environmental processes. Microbes are also abundant in these geological media, and they interact with clays via a variety of mechanisms, such as reduction and oxidation of structural iron and mineral dissolution and precipitation through the production of siderophores and organic acids. These interactions greatly accelerate clay mineral reaction rates. While it is certain that microbes play important roles in clay mineral transformations, quantitative assessment of these roles is limited. This paper reviews some active areas of research on clay—microbe interactions and provides perspectives for future work.

KEYWORDS: clay minerals, microorganisms, oxidation, reduction, transformation

INTRODUCTION

Clay minerals are likely the minerals that we encounter most commonly in our daily lives. They form the soils in which plants grow, and they are the primary materials in a range of products and applications, including cat litter, animal feed, pottery, china, oil absorbents, pharmaceuticals, cosmetics, wastewater treatment, and even antibacterial agents. Clay minerals such as kaolinite and smectite have long been used to treat ailments of the digestive tract in certain countries (Ferrell 2008).

The diversity of clay mineral applications can be attributed to the chemistry and structure of these minerals. Clay minerals are hydrous aluminum layer silicates with structures similar to those of micas. Unlike the micas, however, interlayers of clay minerals contain a low cationic charge to "glue" adjacent silicate sheets, and water molecules can enter or exit the interlayer regions easily. Thus, these materials swell or shrink under wet or dry conditions. Clays are common products of the weathering and hydrothermal alteration of various rocks, but they can also precipitate directly from aqueous fluids. Because of their low-temperature genesis, clay minerals are very common in soils, sediments, and sedimentary rocks. Depending on their specific mode of formation, clay minerals can form extensive deposits of economic value (Fig. 1).

Because clay minerals are common in low-temperature environments where microorganisms thrive, the interactions between clays and microbes are important to a number of surficial properties. Microorganisms can dissolve, precipitate, and transform clay minerals and thus change their physical and chemical properties. Some of these changes are beneficial, whereas others are not desirable.

Some of these interactions generate distinct mineral assemblages in the ancient rock record, producing biosignatures.

Although clay mineralogy has been studied for more than half a century and various applications have been developed, the important role of microbes in clay mineral transformations has been recognized for only about 20 years. In the last decade, interest in this field has risen dramatically, as it has become clear that reduced clays can sequester toxic metals and radionuclides and that clays can degrade organic compounds (Stucki and Kostka 2006; Dong et al. 2009). In this article, I will start with a short review of clay mineralogy and then follow with a comprehensive overview of clay mineral—microbe interactions. I will end with a consideration of the environmental implications of clay mineral—microbe interactions and the outlook for future developments.

CLAY MINERALOGY

Clays are built of tetrahedral and octahedral sheets, typically in a 1:1 or 2:1 ratio. A 1:1 clay structure consists of one tetrahedral sheet and one octahedral sheet, and...
examples include kaolinite and serpentine. A 2:1 clay structure consists of an octahedral sheet sandwiched between two tetrahedral sheets (Fig. 2), and examples include smectite, illite, and vermiculite.

Of special importance are two 2:1 clay mineral families: smectite and illite (Fig. 3). Smectite minerals are 2:1 layer silicates with a total negative charge between 0.2 and 0.6 per half unit cell. The low charge accounts for the capacity of smectites to swell. A member of the smectite family called nontronite (iron-rich smectite) has the following ideal formula:

$$(K_{0.01} Na_{0.30} Ca_{0.12})Al_{0.69}Fe^{3+0.76}Fe^{2+0.06}Mg_{0.43}Ti_{0.06})_{(Si_{6.77}Al_{1.23})O_{20}(OH)_{4}}.$$  

The large cations (Na+, Ca2+, and K+) enter the interlayer space to balance the net negative charge created by the substitution of trivalent Al and Fe for tetravalent Si in the tetrahedral site and divalent Mg for trivalent Fe in the octahedral site.

Illite minerals have the same basic structure as smectite, but with a higher net negative layer charge of 0.6 to 0.9 per half unit cell, a result of the greater degree of tetrahedral and/or octahedral substitution. A typical illite from Silver Hill, Montana, USA, has the following formula:

$$(Mg_{0.09}Ca_{0.06}K_{1.37})Al_{0.69}Fe^{3+0.76}Fe^{2+0.06}Mg_{0.43}Ti_{0.06})_{(Si_{6.77}Al_{1.23})O_{20}(OH)_{4}}.$$  

Because of the higher charge of the interlayer cations, the electrostatic attraction between the basal surface and the interlayer cations is stronger in illite than in smectite. Consequently, illite does not expand when hydrated.

Smectite is stable at low temperature and pressure, which are the typical conditions in soils and surficial sediments. As soils and sediments are buried, smectite becomes unstable and transforms into illite according to the following reaction:

$$\text{smectite} + \text{Al}^{3+} + K^+ \rightarrow \text{illite} + \text{silica}.$$  

Three important variables drive the smectite-to-illite (S-I) reaction: time, temperature, and potassium concentration. The S-I reaction is of special significance because the extent of the reaction, termed “smectite illitization,” is associated with a specific combination of temperature and time. These same conditions can trigger maturation, migration, and trapping of hydrocarbons (Pevear 1999). Thus, the S-I reaction is often used as an index for the generation of petroleum and natural gas. In terrigenous sediments, the S-I reaction typically takes place over the temperature range of about 90–120°C (Moore and Reynolds 1997). To better understand the kinetics and the controlling conditions for this reaction, laboratory simulation experiments are typically performed (Huang et al. 1993). These efforts reveal that, in the absence of any microbial activity, conditions of 250–350°C and 50–100 MPa are often needed to achieve realistic reaction rates (a few months) (Huang et al. 1993; Kim et al. 2004). However, in the presence of microbial activity, this reaction occurs via various mechanisms, at much lower temperatures and pressures over shorter time durations.

**MICROBE–CLAY MINERAL INTERACTIONS**

**Microbial Dissolution of Clay Minerals**

In soils and sediments, microorganisms play important roles in the dissolution of clay minerals, contributing to elemental cycling, soil fertility, and water quality. Microbes can accelerate clay mineral dissolution, either directly or through reactions of structural iron (see below) or through the release of metabolic by-products. In contrast to abiotic dissolution where pH is a primary driving force, biotic dissolution requires many organic compounds to destabilize the mineral structure. These compounds include siderophores (a group of element-scavenging compounds that contribute to the weathering of Fe oxides and silicate minerals), organic acids, iron chelators (small organic molecules that bind to Fe and help its transport), and extracellular polymeric substances (high-molecular-weight compounds composed of polysaccharides that are secreted by microorganisms into the environment). In microbially mediated clay mineral dissolution, the mineral surface reactivity seems to play a secondary role (Grybos et al. 2011).

Microbially mediated mineral dissolution is usually incongruent, meaning that certain elements are removed preferentially relative to others, producing nonstoichiometric minerals. Silica is a common dissolution product and has been observed in both laboratory experiments and natural mineral assemblages. This material is largely amorphous, with particle sizes in the nanometer range. Other biogenic minerals include pyrite, siderite, and vivianite. A mineral assemblage of quartz, pyrite, and calcite has been used to recognize the role of microbes in mediating mineral reactions in ancient marine sediments and in regulating global Si and Fe fluxes (Vorhies and Gaines 2009).

**Microbial Formation of Clay Minerals**

Clay minerals are common weathering products at low temperatures and neutral to acidic pH. Therefore, it is common to find that microbes are involved in the process of rock weathering and clay formation. In fact, microbially catalyzed rock and mineral weathering rates can be orders of magnitude higher than the chemical equivalent, especially when rocks and minerals contain nutrients such as phosphorus, a limiting nutrient in microbial metabolism (Rogers and Bennett 2004). Fisk et al. (2006) showed that microbial weathering of mafic silicates, basalts, and glasses produces many varieties of clay minerals, such as smectite, zeolite, and serpentine. Typically, microbes do not precipitate clay minerals directly, but the products of their weathering reactions reprecipitate to form clay minerals when conditions become favorable. Reactive sites on bacterial surfaces can promote nucleation. Indeed, poorly crystalline clay minerals are commonly observed as surface coatings on microbial cells (Konhauser 2006). Upon aging, the primary precipitates on bacterial filaments and cell walls...
are likely transformed into crystalline clay minerals. In this process, extracellular polymeric substances can serve as a template for clay mineral synthesis.

**Microbial Reduction of Fe(III) in Clay Minerals and Its Effects on Their Physical and Chemical Properties**

Iron is the fourth most abundant element in the Earth’s crust and occurs in all clay minerals (Moore and Reynolds 1997; Stucki 2006). Clay minerals often account for about half the iron in soils and sediments. Much of the structural iron in clay minerals is ferric iron, which can be reduced either chemically or biologically. In a typical bioreduction experiment, structural Fe(III) in clay minerals serves as an electron acceptor, and organic matter acts as an electron donor in either a nongrowth or growth medium (Fig. 2). After a few weeks, the color of the solution changes to deeper green in the experimental tubes (Fig. 4a) indicating reduction of Fe(III) to Fe(II). Iron-reducing bacteria typically attach themselves to clay mineral surfaces during bioreduction (Fig. 4b, c).

To date, a wide range of bacteria and archaea have been used to reduce structural Fe(III) in clays (Dong et al. 2009; Liu et al. 2011; Bishop et al. 2011). In general, methanogens are less efficient in reducing structural Fe(III) than iron-reducing and sulfate-reducing bacteria. Smectites have been shown to be more reducible than other clay minerals, likely due to their high layer expandability, low layer charge, and high surface area (Dong et al. 2009).

Multiple factors influence the rate and extent of Fe(III) bioreduction. The most important are the microbe/clay ratio, the clay mineral surface area, the chemistry of the aqueous medium, the presence or absence of electron-shuttling compounds, and temperature (Dong et al. 2009). Even under ideal conditions, not all structural Fe(III) in clay is biologically reducible, likely due to an inhibition effect of biogenic Fe(II) that may be released during reductive dissolution of clay and then sorbed onto clay and bacterial surfaces. The sorbed Fe(II) may block electron transfer and hinder further bioreduction. This inhibition effect may be alleviated by removing Fe(II) from clay and bacterial surfaces through dynamic flow of the aqueous solution. The incomplete reduction of structural Fe(III) by microorganisms may also be caused by inhibition due to the accumulation of solid products on reactive clay and cell surfaces or by change to the energetics of the system (Dong et al. 2009).

What happens to the clay mineral structure and chemistry during and after Fe(III) bioreduction is a matter of debate. Several studies have reported that bacterial reduction of structural Fe(III) causes small and fully reversible changes in the structure and chemistry of the clay mineral. Other studies have observed reductive dissolution (Dong et al. 2009; Stucki 2011). It is now clear that both mechanisms operate and that the relative importance of one versus the other depends on many factors, including the nature of the clay minerals (i.e. iron content, layer charge, and crystal chemistry), the extent of reduction, the chemistry of the aqueous medium, and the type and nature of the microorganisms. Among these, the extent of reduction appears to play an important role. When the extent of reduction is small (<30%), the smectite structure remains stable, but above this threshold, it becomes unstable and the clay mineral may dissolve, with the formation of secondary mineral phases such as amorphous silica, siderite, vivianite, and illite, depending on the specific experimental conditions (Dong et al. 2009 and references therein).

The reduction of structural Fe(III) to Fe(II) tends to decrease the surface area, interlayer spacing, water swellability, and hydraulic conductivity of clay minerals. In general, reduction increases the negative layer charge and cation exchange capacity (Stucki and Kostka 2006; Stucki 2011), while the interlayer cations become less exchangeable. These physical and chemical changes of clay minerals would have profound effects on soil fertility and contaminant mobility. For instance, a decrease in the reactive surface area and the associated collapse of smectite layers would decrease the adsorption capacity of nutrients and even trap some nutrients (such as K and ammonium) in the smectite interlayer that would otherwise be available to plants. To overcome this problem, farmers may need to apply fertilizer more frequently to maintain a constant crop yield. Similarly, reduced smectites can more efficiently degrade pesticides, thus making them less effective in killing pests (Stucki and Kostka 2006). An alternative approach that mitigates these adverse effects is for farmers to till their agricultural lands, thus reoxidizing the reduced soils. Tilling soils has probably been practiced for thousands of years, but farmers may not be fully aware of this redox effect! The purpose of tilling and plowing is essentially to reoxidize structural Fe(II) in reduced smectite. However, reoxidation does not restore all the physical and chemical properties, and some of the changes are permanent (Stucki and Kostka 2006). With multiple cycles of reduction and oxidation, soil properties may deteriorate to a point where soil fertilization is increasingly needed. Because of the predominance of clay minerals in soils and their recyclable nature, the deterioration of soil properties is primarily due to clay mineral redox cycling.
Iron reduction may also exert a beneficial effect. One example is decreased contaminant mobility if, after structural Fe(III) reduction, contaminants are trapped inside the interlayer and thus become less exchangeable. For the purpose of remediation, iron reduction can be accelerated by injecting certain microbes or nutrients into the soil to stimulate indigenous microbes (Stucki et al. 2007).

**Microbial Oxidation of Fe(II) in Clay Minerals**

Microorganisms can also oxidize structural Fe(II) in clay minerals, but the mechanisms and controlling factors are poorly understood. Shelobolina et al. (2003) have shown that the oxidation of structural Fe(II) in smectite by Desulfobacterium frappieri is coupled with the reduction of nitrate, which has implications for removing nitrate contamination from the environment using reduced clay minerals. Limited data indicate that, compared with chemical oxidation of structural Fe(II) by nitrate alone or by air, the rate of microbially mediated, nitrate-dependent Fe(II) oxidation appears faster (Yang 2010).

**The Microbially Mediated Smectite-to-Illite Reaction**

Although the importance of the S-I reaction has long been recognized, the role of microbes in promoting this reaction was only recently demonstrated (Kim et al. 2004). Under favorable conditions, the iron-reducing bacterium *Shewanella oneidensis* MR-1 can reduce structural Fe(III) in nontronite to Fe(II) and partially dissolve the nontronite. Upon recombination of the dissolved constituents, illite precipitates from the aqueous solution (Fig. 5). Because of compositional differences between nontronite and illite, the dissolution of one unit of nontronite does not make one unit of illite. More likely, the dissolution of multiple units of nontronite precipitates one unit of illite, with excess Si and Fe precipitated as silica and siderite or vivianite, depending on the chemistry of the solution. This microbially catalyzed S-I reaction took place in the laboratory at room temperature and pressure in 2 weeks, in contrast to the slow abiotic reaction rates in either a laboratory simulation system (250–350 °C, 50–100 MPa, for 4–5 months) (Huang et al. 1993) or in the natural environment (Pevear 1999).

Subsequent experiments under geologically more realistic conditions have expanded these initial results. The presence of organic matter favors microbial mediation of the S-I reaction (Dong et al. 2009). Anaerobic, thermophilic (65–68 °C), metal-reducing bacteria isolated from the deep subsurface were found to have the same ability as mesophilic bacteria in promoting the reaction under favorable conditions (alkaline pH, external supplies of Al and K) (Dong et al. 2009). Even sulfate-reducing bacteria and methanogens are capable of promoting the reaction. These results show that several types of microbes are capable of promoting this important mineral reaction under diagenetic conditions.

All these previous experiments used nontronite to study the role of microbes in the S-I reaction. Nontronite, an iron-rich smectite, is not a typical clay mineral in soils or recent sediments; instead, beidellite and montmorillonite, both iron-poor smectites, are more typical. Nonetheless, these compositions all contain structural Fe, and structural Fe in smectites in general is assumed to behave like Fe in nontronite. Under this assumption, recognition of the microbial role in promoting the S-I reaction is important for multiple reasons. First, this microbially mediated S-I reaction provides an example of the catalytic effect of microbes in mediating certain geological processes; this recognition is in some sense comparable to the discovery of the microbial role in promoting dolomite precipitation (Vascocelos et al. 1995). Second, the microbially catalyzed S-I reaction provides a physical basis and mechanism for refining the smectite illitization model, with possible implications for petroleum exploration (Huang et al. 1993). Third, when coupled with microbial measurements, this newly recognized model offers an explanation of why the S-I reaction occurs in certain modern sediments under low temperature and pressure (Kim et al. 2004). The microbially catalyzed S-I reaction has even been proposed to have occurred in ancient marine sediments, in which the reduction of structural Fe(III) dissolved smectite and formed biogenic minerals such as quartz, pyrite, and carbonates (Vorhies and Gaines 2009). Fourth, dramatic changes associated with the S-I reaction would significantly affect the physical and chemical properties of soils and sediments; thus, it is important to understand the rate and extent of this reaction when designing strategies for maximizing nutrient retention and minimizing contaminant mobility. Fifth, the illitization of smectite, a major component of bentonite used in radioactive waste disposal, releases water and leads to changes in hydraulic conductivity (Mulligan et al. 2009). This change would have a major effect on the stability of bentonites used for high-level radioactive waste disposal and could potentially result in the failure of waste canisters (Perdrial et al. 2009).

**ENVIRONMENTAL APPLICATIONS**

Redox-manipulated clay minerals have a wide range of applications. Below, I highlight a few examples for environmental remediation.

**Heavy Metal Remediation Using Redox-Manipulated Clay Minerals**

There are several mechanisms for the remediation of heavy metals by clay minerals. One classical strategy is adsorption and absorption, which take advantage of the high external
and internal surface area of clay minerals. Although this strategy may be effective in the initial removal of heavy metals, it may not be permanent because these inorganic contaminants can be remobilized if the environmental conditions change. Other strategies involve the coprecipitation of metals and radionuclides into clay mineral structures (Brandt et al. 2007). This strategy may be more “permanent” as clay minerals are fairly stable under a wide range of conditions.

A more recent approach is redox manipulation facilitated by microbes. It is assumed that Fe(II) in smectite, possibly produced via the biological reduction of structural Fe(III), reduces oxidized forms of heavy metals, such as Tc(VII), according to the following general reaction (Jaisi et al. 2009):

\[
\text{structural Fe(II)} + \text{Tc(VII)} \rightarrow \text{structural Fe(III)} + \text{Tc(IV)}
\]

A number of studies have examined the interactions of clay-associated Fe(II) with heavy metals and radionuclides, including Tc (Jaisi et al. 2009; Bishop et al. 2011), U (Zhang et al. 2009, 2011), and Cr (Taylor et al. 2000). Even when excess Fe(II) is available in an experimental protocol, not all Fe(II) is reactive. Fe(II) reactivity depends on the crystalchemical environment of Fe(II) in clay minerals. For Tc(VII) reduction, Fe(II) in smectite is the most reactive, and Fe(II) in illite the least (Bishop et al. 2011). Differences in surface area, surface charge, layer expandability, and layer charge between smectite and illite are important factors in accounting for this difference (Bishop et al. 2011). For this reason, any transformation of smectite to illite has an adverse effect on metal reduction and immobilization. Conversely, any method to reverse the S-I reaction would be of benefit. Not only does smectite reduce and immobilize Tc(VII), but the reduced Tc(IV) resides inside the mineral matrix, minimizing the potential for remobilization (Jaisi et al. 2009).

Reduced structural Fe(II) in smectite is an effective reductant for Cr(VI) as well. Sorption of Cr(VI) onto a clay mineral surface appears to be a prerequisite for subsequent reduction. Unlike Tc(VII) and Cr(VI), U(VI) reduction by clay-associated Fe(II) is kinetically slow. For some clay minerals, such as nontronite, redox chemistry may favor the oxidation of U(IV) by Fe(III), which is opposite to the direction of the Tc(VII) reduction reaction. Because of the rapid oxidation of U(IV) by structural Fe(III) in nontronite, uranium can serve as an electron shuttle for microbial reduction of structural Fe(III) in chlorite (Zhang et al. 2009), with the implication that Fe(II) in nontronite may not reduce and immobilize U(VI).

**Organic-Contaminant Degradation**

In addition to heavy metal remediation, reduced smectites have been found to be effective in degrading organic compounds, including pesticides, 2,4,6-trinitrotoluene, nitroaromatics, carbon tetrachloride, chlorinated and nitroaliphatic compounds (Stucki and Kostka 2006 and references therein; Fialips et al. 2010). Because reduced smectites remove these compounds from aqueous solution much faster and to a greater extent than their oxidized counterparts (supposed to have similar surface area and adsorption capacity), the removal mechanism appears to be by degradation. The detection of various degradation products further supports such a mechanism.

**Advantages of Microbially Mediated Clay Minerals in Remediating Inorganic and Organic Contaminants**

Coupled with microbial activity, clay minerals exhibit certain properties that can be explored for waste disposal. First, iron-bearing clay minerals help establish the physical/hydrogeological conditions of redox transition zones because of their small size and limited hydraulic conductivity. Because typical clay minerals in soils and sediments, such as smectite, provide a solid-phase reservoir of Fe(III) and Fe(II) (3–5% total iron, with the ferric/ferrous ratio depending on redox state; Stucki 2006), they can buffer the redox conditions through the transition zone and minimize any chance of reoxidizing reduced heavy metals and radionuclides.

Second, because iron redox cycling largely occurs in the solid state, especially when the extent of cycling is small, Fe(III) produced from the reduction of heavy metals or the degradation of organic compounds can be recycled back to Fe(II), generating a renewable source of electrons. Methods have been discovered for the in situ reduction of Fe(III) within soil or sediments by stimulating indigenous Fe-reducing bacteria through the addition of a carbon source and an electron donor, such as ethanol or glucose (Stucki et al. 2007).

Third, because of low permeability and rapid particle aggregation, clay minerals are ideal matrices to immobilize metals and radionuclides for long-term disposal. Secondary contamination can be minimized because of low oxygen penetration (Jaisi et al. 2009).

**OUTLOOK**

Despite the past 20 years of research, challenges and many unanswered questions still remain. Much of our understanding of microbially mediated clay mineral transformation is qualitative. It is still poorly known to what extent these mineral reactions are mediated by microbial activity in nature. What is the relative importance of abiotic versus biotic effects in mineral evolution? How do clay–microbe interactions evolved through geological history? To what extent do such interactions contribute to ocean chemistry and atmospheric composition?

Our knowledge of microbe–clay interactions is largely derived from laboratory experiments that are greatly simplified relative to what happens in nature. For example, typical bioreduction experiments use pure microbial cultures and pure clay minerals in a defined buffer or medium, mostly at room temperature and pressure, in static batch reactors. However, in nature, microbes exist in communities, and they may cooperate or compete in their interaction with minerals. Furthermore, several clay
minerals may be present, often mixed with various Fe oxides and other silicates. Aqueous media such as ground-water aquifers are often complex, with various types of organic matter present. Natural systems are usually dynamic, with varying rates of flow. How can laboratory-based results be extrapolated to complex field applications? What possible issues are involved in spatial and temporal scaling? These questions are especially relevant to the microbiologically catalyzed S-I reaction model, as it is not yet clear how widely this model is applicable to the overall picture of clay diagenesis. The laboratory-optimized conditions may be satisfied only in certain geological environments. The lack of these conditions may be the reason why smectite in soils and sediments persists despite the presence of active microbial processes (mostly non-iron-reducing activity). Likewise, illite in modern sediments is mostly derived from the erosion of sedimentary rocks and is not necessarily biogenic in origin. Future studies should focus on the identification of these conditions in natural settings and quantitatively assess the relative importance of the biotic versus abiotic effects on the S-I reaction.

Reduced smectites have shown great promise in contaminant remediation. Although the degradation of organic compounds by reduced smectites has been well established, the application of reduced smectites to heavy metal and radionuclide remediation is at an early stage. How can such a strategy be implemented at the field scale? How do clay mineral redox manipulations impact aquifer porosity and permeability and, subsequently, metal transport behavior? Would clay minerals enhance, rather than retard, metal transport?

As interest in this field is growing, we can anticipate that answers to these questions will be forthcoming. Certainly there are many opportunities and challenges facing researchers who are dedicated to studying clays and microbes. I hope that this review will encourage collaboration among clay mineralogists, soil scientists, microbiologists, and environmental engineers.

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