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Structural and chemical modification of nontronite associated with microbial Fe(III) reduction: Indicators of “illitization”

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ABSTRACT

The smectite-to-illite reaction, termed *illitization*, is a ubiquitous process in siliciclastic sedimentary environments and plays a significant role in biogeochemical cycling, plant nutrition, petroleum maturation/migration, particle dispersion–aggregation, and contaminant uptake. The change in the redox state of structural Fe in smectite as a consequence of microbial Fe respiration, in part, controls the physicochemical properties of smectite, but knowledge of the chemical/structural modification at a nanoscale, particularly the reversibility of the structure and K fixation at various Fe-redox states that could control illitization, is limited. The present study focused on measuring indicators of illitization at a nanoscale, utilizing transmission electron microscopy (TEM) with energy dispersive X-ray spectroscopy (EDS) and terahertz time-domain spectroscopy (THz-TDS), as well as chemical analysis, including cation exchange capacity (CEC) and Fe(III) reduction. Nontronite (NAu-1) of the size fraction less than 0.2 μm was inoculated with the Fe-reducing bacteria *Shewanella oneidensis* MR-1 in M1 medium with structural Fe(III) in NAu-1 as the sole electron acceptor and Na-lactate as the electron donor. Incubation continued for up to 12 months in an anaerobic chamber. Two sets of microbial structural Fe(III) reduction experiments were performed, and then one set was re-oxidized by bubbling pure oxygen gas through an autoclaved needle for 24 h. The reaction was stopped at various time points by freezing the samples with liquid N_2. The extent of Fe(III) reduction reached 26%; 5% of residual Fe(II) was detected upon re-oxidation. TEM and X-ray diffraction (XRD) analyses confirmed the presence of an illite-like packet with collapsed 10-Å basal spacing in the Fe-reduced nontronite sample and permanently fixed K after long-term incubation. The proportion of K fixation in the interlayer increased with the extent of Fe(III) reduction and the amount of residual Fe(II) upon re-oxidation. The values of CEC increased corresponding to the extent of Fe(III) reduction; the CEC was not restored after re-oxidation, most likely due to the increase in residual Fe(II), secondary phase mineral (vivianite) precipitation, and permanent K fixation. Nondestructive THz-TDS depicted the chemical/structural modification of bioreduced nontronite and its reversibility. In the present study, true illite was not formed because of the low value of Al/Si; however, the progressive increase in K/(K + 2Ca) and Al/Si in the packets of 10-Å layers as well as the chemical/structural irreversibility upon re-oxidation with increasing incubation time strongly suggested illitization.

1. Introduction

The smectite-to-illite (S–I) reaction is a ubiquitous diagenetic process in shale and mudstone upon increasing temperature (Hower et al., 1976), time (Pytte and Reynolds, 1989), K concentration (Huang et al., 1993), and water/rock ratio (Whitney, 1990). The S–I reaction has been extensively studied over the last four decades, specifically in the Texas Gulf Coast area as a classical type of burial digenesis (Eberl and Hower, 1976; Hower et al., 1976; Ahn and Peacor, 1986), because the degree of the S–I reaction, called “illitization,” is closely linked to oil exploration (Weaver, 1960; Burst, 1969; Bruce, 1984; Pevear, 1999). The S–I reaction is also related to the modification of petrophysical properties of sediments, including permeability, porosity, and swelling property (Boles and Franks, 1979; Freed and Peacor, 1989a,b; Bjorkum and Nadeau, 1998; Brown et al., 2001), and the strength of the sediment structure (Tolhurst et al., 2002).

The S–I transformation is considered to be entirely abiotic and to require burial, heat, and time. The variable geological conditions, including redox state, fluid composition (Kaufhold and Dohrmann, 2009, 2010), and organic matter (Dong et al., 2009), have also been considered in order to understand the mechanism of S–I transformation either

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by a layer-by-layer reaction (Hower et al., 1976) or dissolution/reprecipitation (Ahn and Peacor, 1989; Veblen et al., 1990; Kim et al., 1995; Dong et al., 1997; Stixrude and Peacor, 2002).

Recent observations suggest that illite formation can be promoted by microbial Fe(III) respiration under anaerobic conditions (Kim et al., 2004; Zhang et al., 2007a,b; Dong et al., 2009; Jaisi et al., 2011). Numerous studies have demonstrated that dissimilatory Fe(III)-reducing bacteria (DIRB) are capable of reducing the structural Fe(III) of clay minerals coupled with the oxidation of organic carbon (Kostka et al., 1996; Lovley et al., 1998; Kostka et al., 1999a,b; Jaisi et al., 2005; Seabaugh et al., 2006; Stucki, 2006; Jaisi et al.,2007a,b, 2011). Recently, other metabolic types of microorganisms, including sulfate-reducing bacteria (Li et al., 2004; Liu et al., 2012) and methanogens (Liu et al., 2011; Zhang et al., 2012; Zhang et al., 2013), were shown to be effective Fe reducers through a direct or indirect metabolic process. Vorhies and Gaines (2009) reported that microbial Fe(III) reduction in smectite is one possible mechanism for Fe liberation in marine sediments. These findings of smectite dissolution by microbial Fe(III) reduction in a natural environment may suggest that microbial activity could catalyze the S–I reaction under natural diagenetic conditions. For example, the illitization rate of smectite was enhanced in organic matter (OM)-rich black shale compared to OM-poor bentonite at Nankai Trough under the same diagenetic conditions (Masuda et al., 2001).

Microbial Fe(III) reduction in smectite results in a variety of consequences, such as the formation of illite (Kim et al., 2004; Zhang et al., 2007a,b; Jaisi et al., 2011) and physical and chemical modifications of smectite, for example, decreased swelling pressure, smaller specific surface area, increased cation exchange capacity, and a decrease in mean layer spacing (Stucki et al., 1984; Wu et al., 1989; Khaled and Stucki, 1991; Shen et al., 1992; Gates et al., 1998; Stucki and Kostka, 2006). Furthermore, the chemical and structural modifications of smectite that result in the formation of K-nontronite or illite at various redox states greatly influence Fe liberation to the ocean (Canfield, 1989; Vorhies and Gaines, 2009), the Fe cycle in sediments (Luther et al., 1992; Cappellen and Wang, 1996), contaminant uptake (Hofstetter et al., 2003; Yang et al., 2012), and the preservation of the possible biosignature in Al–Si minerals (Bishop et al., 2013). This has prompted a surge of interest among clay mineralogists in relating the redox states of structural Fe to the modification of the smectite structure. The changes in physicochemcial properties of bioreduced smectite associated with microbial Fe(III) reduction showed an increase in the amount of residual Fe(II) and K fixation upon Fe redox cycles (Stucki, 2011; Yang et al., 2012), indicating that Fe redox cycles directly affect S–I transformation. Nonetheless, the relationships of the changes in physicochemical properties of bioreduced smectite at various redox states to structural modification at a nanoscale have not been fully taken into account.

In the present study, the modification of smectite properties with respect to illitization associated with microbial Fe(III) reduction in a nontronite (NAu-1) structure by *Shewanella oneidensis* MR-1, and re-oxidation by bubbling O_2 gas were investigated using various techniques. The reduced and re-oxidized nontronite were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) with energy dispersive X-ray spectroscopy (EDS) at a nanoscale, and wet chemistry analysis, including cation exchange capacity (CEC) and the extent of Fe(III) reduction. Furthermore, structural as well as chemical modifications were monitored simultaneously using nondestructive terahertz time-domain spectroscopy (THz-TDS). The progress of chemical changes in the nontronite during microbial Fe(III) reduction/re-oxidation and its resultant structural and physicochemical modifications are discussed.

2. Materials and methods

2.1. Clay mineral preparation

Nontronite (NAu-1) ($M^{+}_{1.05}[Si_{6.98}Al_{1.02}]\,[Al_{0.29}Fe_{3.68}Mg_{0.04}]O_{20}(OH)_4$), purchased from the source clays repository of the Clay Minerals Society, has a total Fe content of 16.4%, where 99.6% of the total Fe is ferric (Jaisi et al., 2005) and Ca is a dominant interlayer cation (M^+) (Keeling et al., 2000). The clay size fraction less than 0.2 μm was separated by gravitational settling in a distilled water column and then freeze dried to produce a homogeneous nontronite sample (Keeling et al., 2000). The collected clay powder was transferred to a sterilized bottle in a clean bench to minimize the possible contamination by environmental bacteria.

2.2. Bacterial culture and media preparation

S. oneidensis MR-1, a Gram-negative facultative Fe(III)-reducing bacterium (FeRB) (Myers and Nealson, 1988), was cultured in Luria–Bertani broth (LB) (2.5 g/L) liquid medium aerobically for 24 h in a shaking incubator at 150 rpm and 30 °C in order to increase the cell concentration and vitality. The culture was then washed three times with 0.1 mM NaCl solution in an anaerobic chamber to remove the residual LB medium. The washed cells were then re-cultured anaerobically for 48 h in the liquid M1 medium with Fe(III)-citrate (34.5 mM) as an electron acceptor and Na-lactate (20 mM) as an electron donor. The composition of the M1 medium followed that provided by Myers and Nealson (1988): 9 mM $(NH_4)_2SO_4$, 5.7 mM K_2HPO_4, 3.3 mM KH_2PO_4, 2 mM $NaHCO_3$, 1.01 mM $MgSO_4$, 0.485 mM $CaCl_2$, 67.2 μM Na_2EDTA, 56.6 μM H_3BO_3, 10 μM NaCl, 5.4 μM $FeSO_4$, 5 μM $CoSO_4$, 5 μM $Ni(NH_4)_2(SO_4)_2$, 3.87 μM Na_2MoO_4, 1.5 μM Na_2SeO_4, 1.26 μM $MnSO_4$, 1.04 μM $ZnSO_4$, 0.2 μM $CuSO_4$, 20 mg/L arginine, 20 mg/L glutamate, and 20 mg/L serine. The solution was buffered by HEPES to maintain pH 7. The anaerobically incubated cells were washed three times with 0.1 mM NaCl solution to remove residual Fe(III)-citrate and other salts. The final cell concentration for the Fe-reduction experiments was 1×10^8 CFU/mL, which was determined by measuring the optical density at 660 nm with UV–vis spectroscopy.

2.3. Bioreduction and re-oxidation of NAu-1

The clay fraction less than 0.2 μm was inoculated in an anaerobic chamber at 30 °C with *S. oneidensis* MR-1 in N_2-purged M1 medium with the structural Fe(III) of NAu-1 as the sole electron acceptor and Na-lactate as the electron donor. An initial cell number of 1×10^8 CFU/mL and clay concentrations of 4 mg/mL were used for the Fe(III)-reduction experiment. Controls were identical to the experiment but with heat-killed bacteria to show that bacterial components were not involved in the Fe reduction. Two identical sets of microbial Fe(III) reduction experiments were prepared, and one of them was re-oxidized after the reduction experiments by bubbling pure oxygen gas through an autoclaved needle for 24 h. The reaction was stopped at various time points of 3 h, 6 h, 12 h, 18 h, 1 day, 2 days, 4 days, 7 days, 14 days, 21 days, 2 months, 6 months, and 12 months by freezing the samples with liquid N_2. All experiments were conducted in triplicate.

2.4. Extent of Fe(III) reduction and cation exchange capacity (CEC)

The extent of Fe(III) reduction in the nontronite was measured by the 1,10-phenanthroline method (Stucki, 1981). The total structural Fe was extracted by adding 3.6 N H_2SO_4 and 48% HF to the samples (~5 mg); 1,10-phenanthroline was then applied to the sample in a boiling water bath for 30 min to increase the 1,10-phenanthroline–Fe(II) complex, which turns orange. The samples were then cooled for 15 min, and boric acid was added (Anastacio et al., 2008). The samples were covered with a black paper box to prevent any artificial color change induced by light. Two sets of tubes (triplicate) were prepared for the measurements of Fe(II) and total Fe. The content of Fe(II) in the first set was immediately calculated by Beer's law by measuring the concentration of the 1,10-phenanthroline–Fe(II) complex at $\lambda = 510$ nm using UV–vis spectroscopy (HARC DR4000UV). In the second