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Low-temperature feldspar and illite formation through bioreduction of Fe(III)-bearing smectite by an alkaliphilic bacterium

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ABSTRACT

Biogenic mineral assemblages that form from circumneutral microbial reduction of iron in smectite have been suggested as biosignatures in the geological record. However, mineralogical transformation of smectite mediated by microbes under extreme pH condition is still poorly known. The objective of this study was to understand the reduction capacity of structural Fe(III) in iron-rich smectite (nontronite, NAu-2) by a novel anaerobic alkaliphile (strain CCSD-1) isolated from the deep subsurface, and associated mineralogical changes. The experiments with CCSD-1 were conducted in a growth medium containing the electron shuttle anthraquinone-2,6-disulfonate (AQDS) at pH 9.4. The Fe(II) concentration was monitored over the course of the experiment via wet chemistry, and unreduced and reduced nontronites were characterized with X-ray diffraction (XRD), and scanning and transmission electron microscopy (SEM and TEM). The results indicate that strain CCSD-1 utilizes proteinaceous substrates (yeast extract and tryptone) to reduce structural Fe(III) in smectite with the maximum reduction extent of 26.2%. Mineralogical analysis confirmed that biogenic plagioclase (Na–Ca feldspar) and illite were formed after bioreduction. Our work shows that the interaction between alkaliphile and iron-bearing smectite could account for low-temperature feldspar and illite formation and these minerals may be used as biosignatures in sedimentary rocks.

1. Introduction

Microorganisms are important agents in catalyzing surficial geochemical reactions, such as mineral formation, rock decomposition (weathering), elemental redox cycles, and other geological processes (Falkowski et al., 2008; Gadd, 2010). Among these biogeochemical reactions, the field of microbe–mineral interaction has attracted much attention in the last two decades (Banfield and Nealson, 1997; Dong, 2010; Gadd, 2010). Microorganisms play a passive or active role in (trans)formation of various minerals (e.g., oxides, carbonates, silicates, phosphates and others) (Banfield and Nealson, 1997; Konhauser and Urrutia, 1999; Dong et al., 2009; Gadd, 2010). In comparison to chemically-formed minerals, biogenic minerals may possess unique chemical, structural, or morphological signatures (Fortin, 2004; Javaux and Benzerara, 2009). Therefore, it is believed that biogenic minerals, especially those that form at ambient temperature, can be used as biosignatures to infer past life activities on Earth (Fortin and Langley, 2005; Chan et al., 2011; Li et al., 2011; Crosby et al., 2014) and beyond (Pósfai et al., 1998; Thomas-Keprta et al., 2000; Banfield et al., 2001). Dolomite is a well-studied example. Dolomite is common in sedimentary record, yet efforts to synthesize dolomite at low temperatures (<80 °C) have resulted in little progress. Mounting evidence has suggested that certain types of microbes can overcome the kinetic energy barrier and promote dolomite formation under room temperature laboratory conditions (Mckenzie and Vasconcelos, 2009, and references therein). Notably, globule-shaped dolomite observed in microbially catalyzed bench-scale systems has been proposed as a characteristic biosignature for ancient dolomite in the geological record (Sánchez-Román et al., 2008; Mckenzie and Vasconcelos, 2009, and references therein).

Formation of low-temperature illite through the smectite-to-illite (S–I) reaction is another example showing how microbes challenge our traditional concepts of mineral transformation. The S–I reaction (also termed smectite illitization) is one of the important reactions in mudstones and shales, and accounts for abundant authigenic illite in sedimentary rocks (Dong et al., 1997; Pevear, 1999). During sediment diagenesis, the S–I reaction proceeds through mixed-layer illite–smectite (I–S) intermediates, including smectite-rich R0, ordered R1, R2, R3 I–S (R, Reichweite ordering parameter) and end-member illite (Pevear, 1999). It was believed that the S–I reaction is an abiotic process that typically requires conditions of 300–350 °C, 100 MPa, and 4–5 months to occur. Therefore, the increased value of %I in I–S had been commonly

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used as a paleo-thermometer to constrain the thermal history of a sedimentary basin (Hoffman and Hower, 1979; Pevear, 1999).

However, Kim et al. (2004) provided compelling evidence for the first time revealing that a dissimilatory iron-reducing bacterium (DIRB), *Shewanella oneidensis* MR-1, is capable of facilitating smectite illitization at room temperature and 1 atm within two weeks. This S–I reaction was interpreted to occur as a result of microbial reduction of structurally-coordinated Fe(III) in smectite by DIRB, reductive dissolution of smectite, and subsequent formation of illite (Kim et al., 2004). A growing body of work has subsequently suggested that a wide variety of DIRB (e.g., *Shewanella* strains: Zhang et al., 2007a; Gaines et al., 2009; Jaisi et al., 2011; Koo et al., 2014; Liu et al., 2014; *Thermoanaerobacter ethanolicus*: Zhang et al., 2006, 2007b; *Thermus scotoductus*: Jaisi et al., 2011) and sulfate-reducing bacteria (SRB) (Liu et al., 2012) catalyze illite formation via a similar mechanism. In addition to illite, some other secondary minerals have also been observed as a result of bio-reduction of iron-bearing smectite, such as amorphous silica globules (Dong et al., 2003; O'Reilly et al., 2005; Zhang et al., 2007b; Liu et al., 2011, 2014), high charge smectite with increased Al/Si ratios (O'Reilly et al., 2005; Zhang et al., 2007a; Liu et al., 2011), and other various byproducts (e.g., vivianite, siderite, calcite, and iron sulfide particle), depending on medium and buffer type (Li et al., 2004; Dong et al., 2009; Jaisi et al., 2011). Upon burial diagenesis or low-grade metamorphism, silica, high charge smectite, and iron sulfide could be transformed to more stable phases (quartz, illite, and pyrite). Consequently, certain mineral assemblages, such as low-temperature illite, quartz, calcite, and pyrite, may be used as biosignatures for the presence and activities of iron-reducing microorganisms in geological time. Several studies have successfully used this type of mineral assemblages to identify the role of iron reducing bacteria in sedimentary systems (Sanz-Montero et al., 2009; Vorhies and Gaines, 2009). However, to date most studies on clay-microbe interactions have been conducted at near-neutral pH, and the impact of alkaliphilic bacteria on smectite transformation remains poorly understood.

Alkaliphilic microorganisms, those that grow at pH in excess of 9, are widely distributed in almost all environments, particularly in soda lakes and alkaline deserts (Horikoshi, 1999). To date, several species of anaerobic alkaliphiles have been isolated and they can respire solid-phase iron oxides (e.g., Ye et al., 2004; Zhilina et al., 2009). However, it is unclear whether alkaliphilic bacteria can use structural iron in phyllosilicates, and if so, how secondary mineral assemblages differ from those formed in circumneutral environments. Even though naturally-occurring alkaline environments are not common on modern Earth, it is postulated that alkaline conditions may have predominated in large areas of the Precambrian ocean (termed soda ocean) (Kempe and Degens, 1985; Kempe et al., 1989), and even in the subsurface of Europa (Kempe and Kazmierczak, 2002). Because clay minerals are the most abundant mineral constituents of marine sediments and one of the main Fe(III) pools in sedimentary environments (Favre et al., 2006; Dong et al., 2009), they can co-exist with alkaliphilic iron-reducing microorganisms. Therefore, understanding the interaction process between clay minerals and alkaliphiles could be essential to assess the possibility of life on early Earth and other planets.

In the present study, one novel anaerobic alkaliphile, recently isolated from the borehole of the Chinese Continental Scientific Drilling (CCSD) project, was selected to test whether unique byproducts can be formed during microbially-mediated smectite reduction.

2. Materials and methods

2.1. Site description

The CCSD drilling site is located in Donghai County, Lianyungang City, Jiangsu Province, at the eastern part of the Dabie-Sulu ultra-high pressure (UHP) metamorphic belt (Zhang et al., 2007b). The CCSD project started in June 2001 and ended in January 2005, with the main aim to reconstruct the formation and evolution of UHP metamorphic terrain in eastern China (Xu, 2004). The main drillhole of the CCSD project reached a depth of 5518 m. According to previous studies, the UHP index mineral coesite was found in many sections of the main hole, strongly suggesting that the crystalline basement in this area was subjected to UHP metamorphism (Xu, 2004).

2.2. Bacterial enrichment and isolation

A drilling mud sample recovered from ca. 880-m depth of the CCSD main hole was enriched for microbial growth in the presence of additional carbohydrates. Given the in-situ high pH of the sample (pH ≈ 9.4), the following basal medium for anaerobic alkaliphiles was used (g/L): $(NH_4)_2SO_4$, 1; NH_4Cl, 0.4; $Na_2S_2O_3$, 0.1; K_2HPO_4, 0.5; $MgSO_4 \cdot 7H_2O$, 0.1; $CaCl_2 \cdot 2H_2O$, 0.05; NaCl, 10; tryptone 0.25; yeast extract, 0.25; trace element DSMZ 141 (Deutsche Sammlung von Mikroorganismen und Zellkulturen, Braunschweig, Germany) solution, 10 mL; vitamin DSMZ 141 solution, 10 mL; $NaHCO_3$, 2.2; Na_2CO_3, 2.2. The medium was dispensed into 120-mL serum bottles. After adjusting pH to 9.4 with 1 M NaOH, the bottles were purged with ultra-pure N_2 and sealed with thick butyl rubber stoppers, and capped with aluminum caps. After the bottles were autoclaved, approximately 2 g of the mud sample were added into the bottles in an anaerobic chamber (filled with 98% N_2 and 2% H_2, Coy Laboratory Products, Grass Lake, Michigan). The serum bottles inoculated with the mud sample were incubated in the dark at 35 °C. The growth was monitored by visual observation of cell turbidity and precipitation. When growth was evident, transfer to fresh enrichment bottles was carried out. After five transfers, the primary enrichments were then successively pipetted into fresh media to make serial dilutions. An aliquot of 0.5-mL diluted inoculum was added into a roll tube with agar-solidified medium (2 g/L agar) as previously described (Zhang et al., 2006). After approximately 3 weeks of incubation, single colonies were picked and again spread onto agar-solidified medium. This process was repeated until one colony type was observed.

2.3. Growth studies

An isolate, designated strain CCSD-1, was selected as a representative for further experiments. The effects of temperature and pH on cell growth were investigated in batch cultures. Growth was determined by measuring the optical density of the culture with a spectrophotometer at 600 nm.

2.4. Sequence analysis of the 16S rRNA gene

The genomic DNA of strain CCSD-1 was obtained using the FastDNA SPIN Kit for soil (MP Biomedicals, Solon, OH, USA). 16S rRNA gene was amplified using bacterial universal primers (27F and 1492R). Sequencing and phylogenetic analysis of the 16S rRNA gene were performed as previously described (Zhang et al., 2006).

2.5. Mineral preparation

Nontronite NAu-2, an iron-rich smectite from the Uley Graphite Mine in Australia, was purchased from the Source Clays Repository of the Clay Minerals Society (West Lafayette, IN, USA). Bulk NAu-2 was gently ground and saturated in 0.5 mM NaCl solution overnight. The 0.02–0.5 μm size fraction of NAu-2 was subsequently collected by centrifugation using Stokes' settling law. Once the size fraction of 0.02–0.5 μm was obtained, excess chloride anion was removed by repeated washing in doubly distilled water and its completed removal was confirmed with $AgNO_3$. Previous studies have shown that NAu-2 contains 23.40% iron by weight, of which 99.40% is Fe(III), and its structural formula can be expressed as $M_{0.72}(Si_{7.55}Al_{0.16}Fe_{0.29})(Al_{0.34}Fe_{3.54}Mg_{0.05})O_{20}(OH)_4$ (M represents