



Microbial reduction of chlorite and uranium followed by air oxidation

Gengxin Zhang^a, William D. Burgos^{b,*}, John M. Senko^c, Michael E. Bishop^d, Hailiang Dong^d, Maxim I. Boyanov^e, Kenneth M. Kemner^e

^a Institute of Tibetan Plateau Research, Chinese Academy of Sciences, Beijing, China

^b Department of Civil and Environmental Engineering, The Pennsylvania State University, University Park, PA, USA

^c Department of Geological and Environmental Sciences, University of Akron, Akron, OH, USA

^d Department of Geology, Miami University, Oxford, OH, USA

^e Biosciences Division, Argonne National Laboratory, Argonne, IL, USA

ARTICLE INFO

Article history:

Received 26 July 2010

Received in revised form 24 January 2011

Accepted 25 January 2011

Available online 3 February 2011

Editor: J. Fein

Keywords:

Smectites

Phyllosilicates

Uraninite

Iron reduction

ABSTRACT

To evaluate the stability of biogenic nanoparticulate U(IV) in the presence of an Fe(II)-rich iron-bearing phyllosilicate, we examined the reduction of structural Fe(III) in chlorite CCa-2 and uranium(VI) by *Shewanella oneidensis* MR-1, and the reoxidation of these minerals (after pasteurization) via the introduction of oxygen. Bioreduction experiments were conducted with combinations of chlorite, U(VI), and anthraquinone-2,6-disulfonate (AQDS). Abiotic experiments were conducted to quantify the reduction of U(VI) by chemically-reduced chlorite-associated Fe(II), the oxidation of nanoparticulate U(IV) by unaltered structural Fe(III) in chlorite, and the sorption of U(VI) to chlorite, to elucidate interactions between U(VI)/U(IV) and Fe(II)/Fe(III)-chlorite. Solids were characterized by X-ray diffraction, scanning electron microscopy, and X-ray absorption spectroscopy to confirm Fe and U reduction and reoxidation. U(VI) enhanced the reduction of structural Fe(III) in chlorite and nanoparticulate U(IV) was oxidized by structural Fe(III) in chlorite, demonstrating that U served as an effective electron shuttle from *S. oneidensis* MR-1 to chlorite-Fe(III). Abiotic reduction of U(VI) by chlorite-associated Fe(II) was very slow compared to biological U(VI) reduction. The rate of nanoparticulate U(IV) oxidation by dissolved oxygen increased in the presence of chlorite-associated Fe(II), but the extent of U(IV) oxidation decreased as compared to no-chlorite controls. In identical experiments conducted with bioreduced suspensions of nanoparticulate U(IV) and nontronite (another iron-bearing phyllosilicate), the rate of U(IV) oxidation by dissolved oxygen increased in the presence of nontronite-associated Fe(II). In summary, we found that structural Fe(III) in chlorite delayed the onset of U(VI) loss from solution, while chlorite-associated Fe(II) enhanced the oxidation rate of U(IV) by dissolved oxygen, indicating that chlorite-associated Fe(II) could not protect nanoparticulate U(IV) from oxygen intrusion but instead increased the oxidation rate of U(IV).

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Uranium contamination of sediment and groundwater is a problem at many U.S. Department of Energy (DOE) sites and uranium ore-processing sites where soluble U(VI) has migrated into groundwater. In aerobic groundwater, U(VI) carbonate complexes are often the predominant uranium species. These anionic or neutral U species tend to sorb weakly to solid phases and, therefore, can be relatively mobile in the environment (Akca, 1998; Arnold et al., 1998). Under anoxic conditions U(VI) can be reduced to sparingly soluble U(IV) minerals and precipitated from groundwater (Lovley and Phillips, 1992). Bacterially mediated reduction of U(VI) to uraninite may be

exploited for *in situ* remediation of uranium-contaminated sites (Lovley et al., 1991; Fredrickson et al., 2000; Brooks et al., 2003).

The stimulation of indigenous dissimilatory metal-reducing bacteria (DMRB) for uranium remediation is an area of active research at several DOE field sites. Assessment of the efficacy of any one strategy (e.g., ethanol addition) is typically based on changes in aqueous geochemistry measured in monitoring wells. Interpretation of these results is often challenging due to the complex suite of redox reactions potentially operative in these subsurface environments. For example, while the addition of an electron donor will promote reducing conditions, the availability of multiple electron acceptors (e.g., nitrate, Mn(III/IV) oxides, Fe(III) oxides, or sulfate) may enhance or impede U(VI) reduction. In a related manner, the concentration and flux of electron donor addition can also impact U(VI) reduction and U(IV) reoxidation (Tokunaga et al., 2008).

While considerable research has been conducted on uranium interactions with iron (oxyhydr)oxides (e.g., Jeon et al., 2005; Ginder-

* Corresponding author at: Dept. of Civil and Environmental Engineering, The Pennsylvania State University, 212 Sackett Building, University Park, PA 16802-1408, USA. Tel.: +1 814 863 0578; fax: +1 814 863 7304.

E-mail address: wdb3@psu.edu (W.D. Burgos).

Vogel et al., 2006), much less research has focused on uranium interactions with iron-bearing clay minerals (Stucki et al., 2007). Iron-bearing clay minerals are widely distributed in soils and sediments (Stucki et al., 2007) and often account for about half of the Fe mass in soils and sediments (Favre et al., 2006). Specifically, at the Old Rifle and Oak Ridge DOE field sites, the mass of iron associated with clay minerals is higher than the mass of iron associated with oxide minerals (Stucki et al., 2007; Komlos et al., 2008). In addition, chlorite is a common clay mineral at the DOE Hanford site (Schmeide et al., 2000; Baik et al., 2004; McKinley et al., 2007).

Compared to iron oxides which dissolve during reduction, the majority of reduced Fe(II) in iron-bearing clays is retained in the clay structure (Kostka et al., 1999; Dong et al., 2009). Fe(II) sorbed to mineral surfaces may be a more facile reductant compared to structural Fe(II) in clay minerals (Hofstetter et al., 2003, 2006), however, structural Fe(II) will not be flushed from a biostimulated reduction zone by advection. Thus, structural Fe(II) in clay minerals may be an important long-term reactant in maintaining anoxic conditions. The stability of U(IV) is, ultimately, the key criterion for determining success of any reductive immobilization strategy. The intrusion of oxidants such as oxygen or nitrate may be countered by a large reservoir of solid-phase reductants such as Fe(II)-bearing clay minerals.

In a recent, related study we measured the concomitant bioreduction of structural Fe(III) in the clay mineral nontronite and U(VI) by *Shewanella oneidensis* MR-1 (Zhang et al., 2009). From those experiments we found that uranium served as an effective electron shuttle to enhance the reduction of structural Fe(III) in nontronite but that delayed the onset of U(VI) loss from solution. In this current study, we not only report on the bioreduction of structural Fe(III) in the clay mineral chlorite CCa-2 and U(VI) but also measure the stability of bioreduced U(IV) in the presence of chlorite-associated Fe(II) and nontronite-associated Fe(II) upon oxygen intrusion. These two iron-bearing phyllosilicates were selected because they represent mineralogical end-members with respect to Fe(III) and Fe(II) content. Nontronite NAu-2 contains 4.2 mmol Fe/g with the majority of the structural iron as Fe(III) (Jaisi et al., 2007), while chlorite CCa-2 contains 3.4 mmol Fe/g with the majority of the structural iron as Fe(II). The objectives of this research were to study the interactions between U(VI) and the iron-rich ripidolite chlorite CCa-2 during their concomitant biological reduction, and then to further investigate the stability of bioreduced U(IV) and chlorite-associated Fe(II) in the presence of dissolved oxygen.

2. Experimental

2.1. Cell cultivation

S. oneidensis MR-1 was cultured in a chemically defined minimal medium as described previously (Burgos et al., 2008). Cells were harvested by centrifugation (15 min and 20 °C at 3,500 g), washed three times with anoxic 30 mM NaHCO₃ (pH 6.8, prepared under an 80:20% N₂:CO₂ atm) and resuspended in the same buffer.

2.2. Mineral preparation

CCa-2, an iron-bearing ripidolite chlorite from Flagstaff Hill (El Dorado County, CA, USA), was purchased in two separate batches from the Source Clays Repository (West Lafayette, IN). One batch was used for all the laboratory experiments and the second batch was used to produce a chlorite standard for Fe XANES. The chemical formula of this chlorite has been reported as (Mg_{5.5}Al_{2.48}Fe²⁺_{3.02}Fe³⁺_{0.94}Ti_{0.01}Mn_{0.01})(Si_{5.33}Al_{2.66}O₂₀)(OH)₁₆ as determined by electron microprobe analysis (Brandt et al., 2003). Clay fractions (0.5–2.0 μm) were suspended in 1 M NaCl for one week, separated in distilled water by centrifugation, washed repeatedly until no Cl⁻ was detected by

silver nitrate, and then air-dried. The clay fractions were determined by XRD and SEM to be pure chlorite without other iron minerals. The iron content of CCa-2 has been reported to range from 17.6% (Brandt et al., 2003) to 34.5% (Jaisi et al., 2007). As determined by complete dissolution in HF/H₂SO₄, we measured an iron content of 18.8% (3.35 mmol Fe g⁻¹) for the chlorite used in all the experiments, and an iron content of 30.4% (5.42 mmol Fe g⁻¹) for the chlorite used for the Fe XANES standard. The Fe(II) content of CCa-2 has been reported to range from 46% (Fe(II)/total Fe) (Jaisi et al., 2007; Singer et al., 2009a, 2009b) to 76% (Brandt et al., 2003) to 86% (Keeling et al., 2000). As determined by an HF/H₂SO₄-phenanthroline assay (described below), we measured an Fe(II) content of 78% for the unaltered chlorite used in all the experiments, and an Fe(II) content of 55% for the unaltered chlorite used for the Fe XANES standard. CCa-2 is composed of a tetrahedral–octahedral–tetrahedral (TOT) layer attached to a brucite-like sheet (Brandt et al., 2003; Zazzi et al., 2006). According to a proposed structural model for CCa-2 (Brandt et al., 2003), 66% of the total Fe is located in the TOT layer and 34% of the total Fe is located in the brucite sheet, and all of the Fe(III) is located in the TOT layer (specifically in the octahedral sheet). The BET surface area of the air-dried chlorite was determined to be 25.4 m²/g based on N₂ adsorption.

2.3. Bacterial reduction experiments

MR-1 bioreduction experiments were conducted in the presence or absence of U(VI), chlorite, or anthraquinone-2,6-disulfonate (AQDS) in 30 mM NaHCO₃ (pH 6.8) as described previously (Zhang et al., 2009). Chlorite CCa-2 was prepared in anoxic 30 mM NaHCO₃ buffer to produce a stock concentration of 100 g L⁻¹, and was sterilized by a 5-min exposure to microwave radiation (Keller et al., 1988). Chlorite and uranyl acetate were pre-equilibrated for two weeks before inoculation with MR-1. Experiments were conducted in 120 mL glass serum bottles where the chlorite concentration was 5.0 g L⁻¹ (16.8 mM Fe_T, 22% Fe(III)), uranyl acetate concentrations ranged from 0 to 1.5 mM, and AQDS concentrations were either 0 or 0.10 mM depending on the experiment. MR-1 was inoculated at 0.5*10⁸ cells mL⁻¹ (final concentration) with sodium lactate (5 mM) provided as the electron donor. After cells were added, reactors were periodically mixed and samples removed with sterile needle and syringe and HF/H₂SO₄-extractable Fe(II), ferrozine-extractable Fe(II), aqueous Fe(II), NaHCO₃-extractable U(VI), and aqueous U(VI) concentrations were measured as described below. All sample manipulations were performed inside an anoxic chamber (95:5% N₂:H₂ atm).

2.4. Experiments with U(VI) and chemically-reduced chlorite

Chlorite was reduced using the sodium citrate, bicarbonate, and dithionite (CBD) method as described by Stucki et al. (1984), and washed three times with anoxic distilled water (Hofstetter et al., 2003). CBD-reduced chlorite was dispensed into anoxic 30 mM NaHCO₃ buffer (pH 6.8) in 120 mL glass serum bottles (2.5 g L⁻¹ final concentration, 8.4 mM Fe_T, 98% Fe(II)), and equilibrated at least 3 d before uranium addition (0.20 mM). Reactors were periodically mixed and samples removed to measure ferrozine-extractable Fe(II), aqueous Fe(II), NaHCO₃-extractable U(VI), and aqueous U(VI) concentrations.

2.5. Experiments with biogenic nanoparticulate U(IV) and unaltered chlorite

Biogenic nanoparticulate U(IV) precipitates were produced separately by MR-1, pasteurized (70 °C for 30 min), concentrated by centrifugation, and resuspended in anoxic 30 mM NaHCO₃ buffer (pH 6.8). Unaltered chlorite was dispensed into anoxic 30 mM NaHCO₃ buffer in 20 mL glass serum bottles (5.0 g L⁻¹, 16.8 mM Fe_T, 22%

Download English Version:

<https://daneshyari.com/en/article/4699768>

Download Persian Version:

<https://daneshyari.com/article/4699768>

[Daneshyari.com](https://daneshyari.com)