



Biomining of U(VI) phosphate promoted by microbially-mediated phytate hydrolysis in contaminated soils

Kathleen R. Salome^a, Melanie J. Beazley^{b,d}, Samuel M. Webb^c,
Patricia A. Sobecky^b, Martial Taillefert^{a,*}

^a School of Earth & Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30332, United States

^b Department of Biological Sciences, University of Alabama, Tuscaloosa, AL 35487, United States

^c Stanford Synchrotron Radiation Lightsource, Menlo Park, CA 94025, United States

^d Department of Chemistry, University of Central Florida, Orlando, FL 32816, United States

Received 28 August 2015; accepted in revised form 12 October 2016; Available online 19 October 2016

Abstract

The bioreduction of uranium may immobilize a significant fraction of this toxic contaminant in reduced environments at circumneutral pH. In oxic and low pH environments, however, the low solubility of U(VI)-phosphate minerals also makes them good candidates for the immobilization of U(VI) in the solid phase. As inorganic phosphate is generally scarce in soils, the biomining of U(VI)-phosphate minerals via microbially-mediated organophosphate hydrolysis may represent the main immobilization process of uranium in these environments. In this study, contaminated sediments were incubated aerobically in two pH conditions to examine whether phytate, a naturally-occurring and abundant organophosphate in soils, could represent a potential phosphorous source to promote U(VI)-phosphate biomining by natural microbial communities. While phytate hydrolysis was not evident at pH 7.0, nearly complete hydrolysis was observed both with and without electron donor at pH 5.5, suggesting indigenous microorganisms express acidic phytases in these sediments. While the rate of hydrolysis of phytate generally increased in the presence of uranium, the net rate of inorganic phosphate production in solution was decreased and inositol phosphate intermediates were generated in contrast to similar incubations conducted without uranium. These findings suggest uranium stress enhanced the phytate-metabolism of the microbial community, while simultaneously inhibiting phosphatase production and/or activity by the indigenous population. Finally, phytate hydrolysis drastically decreased uranium solubility, likely due to formation of ternary sorption complexes, U(VI)-phytate precipitates, and U(VI)-phosphate minerals. Overall, the results of this study provide evidence for the ability of natural microbial communities to liberate phosphate from phytate in acidic sediments, possibly as a detoxification mechanism, and demonstrate the potential utility of phytate-promoted uranium immobilization in subsurface environments. These processes should be investigated in more detail with pure cultures isolated from these sediments.

© 2016 Elsevier Ltd. All rights reserved.

Keywords: Uranium biomining; Uranium bioremediation; Phytate hydrolysis; Uranium contaminated soils

1. INTRODUCTION

Since the end of the Cold War Era, the United States Department of Energy (DOE) has shifted its focus from

nuclear weapons proliferation to remediation of radionuclide and heavy metal contamination at former weapons development sites (DOE, 1997). The large number of DOE-managed facilities with a wide range of subsurface geochemical conditions, ranging from highly acidic (Oak Ridge, TN) to alkaline pH (Hanford, WA), makes developing a prescriptive bioremediation strategy appropriate for

* Corresponding author.

E-mail address: mtaillef@eas.gatech.edu (M. Taillefert).

all subsurface conditions complicated (DOE, 1997). In particular, the presence of acidic environments, where metal reduction is unfavorable, commands the development of creative *in situ* remediation solutions for environmental uranium contamination (Istok et al., 2004; North et al., 2004; Wu et al., 2006a,b; Kelly et al., 2008; Sitte et al., 2010; Van Nostrand et al., 2011).

The mobility of uranium in the subsurface is controlled by a combination of surface complexation reactions, precipitation reactions, and redox processes (Hsi and Langmuir, 1985; Langmuir, 1997; Finch and Murakami, 1999). Uranium exists primarily as U(IV) or U(VI) depending on the prevailing environmental redox conditions. In oxidizing conditions, U(VI) exists as the aqueous uranyl ion UO_2^{2+} and its hydroxyl complexes (Belli and Taillefert, 2016). Above pH 7.0, carbonates may enhance uranyl mobility by forming soluble uranyl-carbonate complexes and promoting the dissolution of U(IV) and U(VI) minerals (Langmuir, 1978, 1997). In addition, the presence of calcium at this pH may inhibit uranyl reduction or U(VI)-phosphate precipitation through formation of ternary calcium-uranyl-carbonate complexes (Brooks et al., 2003; Luo et al., 2007), though uranyl phosphate precipitation may prevail when phosphate concentrations are elevated (Salome et al., 2013). In contrast, below circumneutral pH, strong sorption to metal oxides (Hsi and Langmuir, 1985; Waite et al., 1994; Han et al., 2007; Plathe et al., 2013), clays (Bai et al., 2009; Meleshyn et al., 2009; Grabias et al., 2014), and natural organic matter (NOM) (Li et al., 2014) and the formation of highly stable and sparingly soluble precipitates with phosphate may limit uranyl mobility in the environment (Langmuir, 1997; Finch and Murakami, 1999). In reducing conditions, U(VI) may either be chemically (Wersin et al., 1994; Liger et al., 1999; Missana et al., 2003; O'Loughlin et al., 2003; Hua and Deng, 2008) or microbially (Lovley et al., 1991; Tebo and Obraztsova, 1998; Wade and DiChristina, 2000; Sanford et al., 2007) reduced to U(IV) and precipitate as uraninite (UO_2) (Langmuir, 1997; Finch and Murakami, 1999) or other non-uraninite U(IV) mineral phases (Fletcher et al., 2010; Boyanov et al., 2011; Alessi et al., 2014). However, the reintroduction of oxygen (Langmuir, 1997; Murphy and Shock, 1999; Wu et al., 2007) or the presence of NO_2^- (Senko et al., 2002, 2005a), Fe(III) (Senko et al., 2002, 2005b; Wan et al., 2005), or MnO_2 (Fredrickson et al., 2002) in reducing conditions may remobilize U(IV)-precipitates to soluble U(VI) species.

Thus far, *in situ* bioremediation of uranium contaminations has primarily focused on the formation of various reduced uranium mineral products via microbially-catalyzed reduction of U(VI), known as bioreduction (Lovley et al., 1991; Wade and DiChristina, 2000; Istok et al., 2004; North et al., 2004; Wu et al., 2006b; Kelly et al., 2008; Bernier-Latmani et al., 2010; Sharp et al., 2011). Unfortunately, the low pH, elevated nitrate, and oxidizing conditions present in some contaminated areas inhibit this process (Finneran et al., 2002; Wu et al., 2006a,b), making the precipitation of U(VI)-phosphate minerals a potentially appealing alternative to bioreduction. As orthophosphate directly amended to the subsurface is

rapidly immobilized thus limiting its transport (Wellman et al., 2006), research has focused on the addition of organophosphates to subsurface sediments to promote microbially-mediated organophosphate hydrolysis coupled to the chemical precipitation of sparingly soluble U(VI)-phosphate minerals in a process termed biomineralization (Macaskie et al., 1994; Beazley et al., 2007, 2009, 2011; Shelobolina et al., 2009). To fulfill their phosphorus requirement when faced with nutrient limitations, microorganisms encode genes for various phosphohydrolase (phosphatase) enzymes that catalyze the hydrolysis of organophosphates and release orthophosphate (Macaskie et al., 1994). In addition, uranium stress may induce microbial phosphatase expression as a metal detoxification mechanism (Macaskie et al., 1994; Barnett et al., 2002; Knox et al., 2008). Although previous research has demonstrated that microbial hydrolysis of synthetic organophosphates immobilizes more than 98% of U(VI) as U(VI)-phosphate minerals in both oxic (Beazley et al., 2007, 2009; Beazley et al., 2011; Martinez et al., 2007; Shelobolina et al., 2009) and suboxic (Beazley et al., 2009; Shelobolina et al., 2009; Salome et al., 2013) conditions, the potential of naturally-occurring organophosphates as a source of inorganic phosphorus to promote U(VI)-phosphate biomineralization has not been examined.

Inositol hexaphosphate (IP_6), also known as phytate, is a phosphorylated inositol with six attached phosphate groups (Fig. S1) that is widely synthesized by plants for phosphorus storage and may represent the dominant organophosphate compound in terrestrial environments (Turner et al., 2002), with concentrations as high as 1 g P/kg soil (Turner, 2007). The accumulation of IP_6 in soils suggests that it is relatively unavailable for biological uptake or that its bioavailability depends on the presence of specific enzymes (Turner et al., 2002). Although IP_6 is chemically stable above pH 1 and is not hydrolyzed by conventional phosphohydrolases (Turner et al., 2002), phytase enzymes may catalyze its hydrolysis to lower inositol derivatives (IP_x , $x=1-5$) and inorganic phosphate (Irving and Cosgrove, 1974). Phytase enzymes are substrate-specific phosphatases (Oh et al., 2004) that include both bacterial histidine acid phosphatases (HAP) (activated between pH 2 and 6) and bacterial β -propeller phytases (activated at or above pH 7.0) (Oh et al., 2004). Acidic phytase enzymes are inhibited by divalent cat/ions (especially Ca^{2+}) (Oh et al., 2004), whereas alkaline phytases require Ca^{2+} for enzymatic function (Ha et al., 2000). Because of its highly negative charge above pH 2 (Fig. 1A), phytate interacts strongly with soils (Degroot and Golterman, 1993; Johnson et al., 2012) and efficiently chelates metals to form sparingly soluble complexes (Martin and Evans, 1987; Turner et al., 2002). Although calcium phytate was demonstrated to chemically precipitate U(VI) by ion exchange (Nash et al., 1998; Seaman et al., 2003; Knox et al., 2008), the microbially-facilitated precipitation of U(VI)-phosphate minerals by phytate-mineralizing bacteria has yet to be examined. The objectives of this study were to investigate the ability of the natural microbial community in uranium-contaminated sediments of the ORFRC to metabolize phytate, examine the dependence of this

Download English Version:

<https://daneshyari.com/en/article/4701703>

Download Persian Version:

<https://daneshyari.com/article/4701703>

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