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Competition between enzymatic and abiotic reduction of uranium(VI) under iron reducing conditions

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Abstract

Reduction of U(VI) under iron reducing conditions was studied in a model system containing the dissimilatory metal-reducing bacterium *Shewanella putrefaciens* and colloidal hematite. We focused on the competition between direct enzymatic uranium reduction and abiotic reduction of U(VI) by Fe(II), catalyzed by the hematite surface, at relatively low U(VI) concentrations (<0.5 μM) compared to the concentrations of ferric iron (>10 mM). Under these conditions surface catalyzed reduction by Fe(II), which was produced by dissimilatory iron reduction, was the dominant pathway for uranium reduction. Reduction kinetics of U(VI) were identical to those in abiotic controls to which soluble Fe(II) was added. Strong adsorption of U(VI) at the hematite surface apparently favored the abiotic pathway by reducing the availability of U(VI) to the bacteria. In control experiments, lacking either hematite or bacteria, the addition of 45 mM dissolved bicarbonate markedly slowed down U(VI) reduction. The inhibition of enzymatic U(VI) reduction and abiotic, surface catalyzed U(VI) reduction by the bicarbonate amendments is consistent with the formation of aqueous uranyl-carbonate complexes. Surprisingly, however, more U(VI) was reduced when dissolved bicarbonate was added to experimental systems containing both bacteria and hematite. The enhanced U(VI) reduction was attributed to the formation of magnetite, which was observed in experiments. Biogenic magnetite produced as a result of dissimilatory iron reduction may be an important agent of uranium immobilization in natural environments.
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Keywords: Enzymatic U(VI) reduction; Surface catalyzed U(VI) reduction; Iron respiration; Biogenic magnetite; Hematite; *Shewanella putrefaciens*

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1. Introduction

The reduction of uranyl to the tetravalent state has a marked effect on the mobility of uranium in the environment. Under natural conditions uraninite (UO_2(c)), pitchblende (UO_2(am)) and coffinite ($USiO_4$), the most common salts of the uranous ion U^{4+}, have much lower solubilities than salts of the uranyl ion (UO_2^{2+}) (Langmuir, 1997). Additionally, the uranyl ion forms strong aqueous complexes with carbonate (Grenthe et al., 1992; Langmuir, 1997), inhibiting precipitation or sorption of U(VI) in alka-

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line waters. Consequently, uranium reduction is a key process in risk assessment of nuclear waste repositories, the remediation of sites contaminated with uranium, the formation of uranium ore deposits, and the global cycling of this element.

Reduction of U(VI) generally coincides with microbial iron and sulfate reduction. A variety of sulfate and metal-reducing bacteria are capable of reducing U(VI) (Caccavo et al., 1992; Francis et al., 1994; Lovley and Phillips, 1992; Lovley et al., 1991; Tebo and Obraztsova, 1998; Wade and DiChristina, 2000). Incubation experiments in which U(VI) was added to groundwaters and soils taken from uncontaminated sites and sites contaminated with uranium have revealed the ubiquitous presence of uranium-reducing microbial communities (Abdelouas et al., 2000). Nonetheless, the microbial reduction mechanisms in suboxic and anoxic environments remain poorly known.

The reduction of U(VI) by the products of iron and sulfate respiration, ferrous iron (Fe(II)) and sulfide, is thermodynamically possible, while methane and hydrogen are also potential reductants (Langmuir, 1978). The abiotic reduction of U(VI) by dissolved sulfide in homogeneous solution has been demonstrated (Ho and Miller, 1986; Kosztolanyi et al., 1996; Mohagheghi et al., 1985). The homogenous reaction is favored by high temperature, high sulfide concentrations and high pH-conditions unlikely to occur in sediments and groundwaters. Wersin et al. (1994) investigated the adsorption of uranium onto galena and pyrite using spectroscopic techniques. They observed reduction of U(VI) at the solid–aqueous solution interface and suggested that heterogeneous reduction may be an important process in the genesis of roll-type uranium deposits.

Liger et al. (1999) studied the reduction of U(VI) by ferrous iron. In their experiments, they found no indication of homogeneous reduction of U(VI) by Fe^{2+} ions, but showed that the reaction is catalyzed by iron (hydr)oxides. They explained the dependency of the reduction rate on pH and ferrous iron concentration by postulating that the neutral hydroxo surface complex ($\equiv Fe^{III}OFe^{II}OH^0$) is the reactive reductant species. They proposed the following rate law for U(VI) reduction:

$$\frac{d[U(VI)]}{dt} = -k\left[\equiv Fe^{III}OFe^{II}OH^0\right][U(VI)]_{ads} \qquad (1)$$

with $k = 399 \pm 25$ M^{-1} min^{-1}, at 25 °C, and $[U(VI)]_{ads}$ is the uranyl concentration adsorbed onto the hematite surface.

Under suboxic conditions, U(VI), rather than Fe(III), is considered the preferred terminal electron acceptor for microbial respiration, due to a higher energetic yield (Cochran et al., 1986; Fredrickson et al., 2000). Wielinga et al. (2000) found that the presence of goethite and hematite did not significantly affect enzymatic reduction of U(VI) coupled to the oxidation of an organic electron donor. The presence of ferrihydrite, however, decreased the initial reduction rate of U(VI). In mixtures of goethite and ferrihydrite, the inhibition was related to the fraction of ferrihydrite. Fredrickson et al. (1998) observed no effect on the reduction of U(VI) to U(IV) when goethite was added and when U(VI) occurred predominantly as the carbonate complexes $UO_2(CO_3)_3^{4-}$ and $UO_2(CO_3)_2^{2-}$, or as the mineral metaschoepite [$UO_32H_2O(s)$]. The reduction of uranium was incomplete when U(VI) precipitated as metaschoepite or when lactate, the electron donor, was limiting. They proposed that the precipitation of $UO_2(s)$ or $Fe(OH)_3(s)$ on the metaschoepite surface physically prevented U(VI) from being reduced.

Previous experimental work clearly demonstrates the important role of the chemical speciation of Fe(III) and U(VI) in microbial reduction processes. Much of the previous work, however, was carried out at relatively high U(VI) concentrations. Fredrickson et al. (1998) and Wielinga et al. (2000), for example, performed their experiments at uranium concentrations above 100 μmol/L. While these uranium levels are relevant for contaminated sites, in non-polluted environments uranium concentrations are much lower, and the ratio between U(VI) and Fe(III) is generally much smaller than in the laboratory experiments. High Fe(III) to U(VI) ratios favor adsorption of U(VI) to ferric iron (hydr)oxides. Under these conditions, surface catalyzed reduction by Fe(II) may become the preferred reaction pathway. Rate constants measured by Liger et al. (1999) for the surface catalyzed reduction by Fe(II) indicate that this pathway could outcompete enzymatic U(VI) reduction under typical conditions encountered in suboxic environments.

In this paper, we focus on the competition between alternative pathways of uranium reduction under iron reducing conditions at relatively low U(VI) concen-

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