Determination of Uranyl Incorporation into Biogenic Manganese Oxides Using X-ray Absorption Spectroscopy and Scattering

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Abstract

Uranium is a toxic and radioactive contaminant in many settings, such as groundwater and sediments. In oxidizing environments, uranyl (U(VI)) is thermodynamically the most stable oxidation state. Sorption or incorporation of U(VI) into reactive mineral phases are processes of major importance because they retard its transport. Biogenic manganese oxides are an important source of reactive mineral surfaces in the environment and may be potentially enhanced in bioremediation cases to improve natural attenuation. Experiments were performed in which U(VI) at various concentrations was present during manganese oxide biogenesis. At all concentrations there was strong uptake of U onto the oxides. Synchrotron based x-ray studies were carried out to determine the manner in which uranyl is incorporated into the oxide and how this incorporation affects the resulting manganese oxide structure and mineralogy. The EXAFS experiments show that uranyl does not appear to substitute into the lattice of the oxides, and is rather present as a strong surface complex. However, the presence of U(VI) on the Mn-oxide layers modifies the lattice constants and coherence lengths of the oxides. These results suggest a complex mechanism in which U transport is retarded by sorption and the surface area of the sorbent is increased.

1. Introduction

Uranium ore mining, processing, and manufacturing have contributed to groundwater contamination in numerous locations in the United States [1]. Uranium contamination is transported in groundwater primarily as the dissolved uranyl ion (U(VI)) which can intercept water supplies. Manganese oxide surfaces have been shown to have large capacities for heavy metal ion uptake [2–4]. In some groundwater environments, it has been shown that transuranic elements associate with manganese oxides preferentially over other mineral surfaces, including iron oxides [5]. Much of the manganese oxides found in the natural environment is considered to be of biologic origin [6–8]. Many diverse bacteria have been shown to rapidly catalyze the oxidation of the Mn(II) to Mn(III, IV) [9]. Biogenic rates of oxidation have been shown to be up to five orders of magnitude greater than abiotic rates under the same conditions [6, 8]. Thus, understanding the molecular mechanisms that are involved in the binding of uranyl to biogenic manganese oxide surfaces is critically important. This work uses x-ray techniques such as x-ray absorption spectroscopy and x-ray diffraction to examine how uranyl attaches to biogenic manganese oxides that form in the presence of the uranyl contamination and how this incorporation affects the structure of the biogenic manganese oxide.

2. Methods

Manganese oxide samples were prepared using spores of the marine bacterium Bacillus sp. strain SG-1 to catalyze the oxidation of Mn(II) to Mn(IV) [10]. Spores were added to flasks containing 400 mL of incubation solutions to a final spore concentration of 108 spores per mL. The incubation solution contained 10 mM HEPES to maintain the pH at 7.5 and 10 mM Mn(II)-triflate. Additions of Mn-triflate and U(VI)-triflate were added daily to maintain metal concentrations as the oxidation progressed. Triflate was used as the counter-ion for all metal additions in order to minimize ternary complexation of uranyl by cations such as nitrate or chloride [10]. Carbonate was not excluded from the solutions to so as to simulate natural conditions. Uranyl concentrations in the flasks ranged in concentrations from 50 nM to 100 μM to span a large range of adsorption conditions (Table I). Incubations progressed for two weeks on a shaker platform after which the supernatants were drawn off and the manganese suspensions concentrated into a pellet by centrifugation. All EXAFS and XRD measurements were performed on wet biospores to prevent oxidation state and structural changes that can be driven by sample dehydration. Mn-K and U-LIII-edge XAS spectra were collected at SSRL beamline 4-3 with a Si(220) monochromator and, in the case of Mn, a harmonic rejection mirror with a cut-off energy set at 9 keV. Samples were collected in transmission geometry if possible, or in fluorescence mode for dilute samples. Fluorescence data were collected using either a 13-element Ge array detector or a Kα-gas-filled Lytle-type ionization chamber detector equipped with 5x x-ray filters. All spectra were background subtracted and splined using the SIXPack software [12]. Linear combination fitting and EXAFS fitting were also performed with SIXPack. Oxygens and oxygens shells for U were fit initially and then subtracted from the raw data to create second-shell residual spectra. This allows a more sensitive fit of the second-shell contributions in the sample spectra without the interference of the O shells. Phase and amplitude files for the EXAFS fitting were created with FEF7 [13, 14]. Since the Debye-Waller factors (σ) correlated highly with coordination numbers (CN), CN fits for some shells were each fixed at their average values. The U=O−O−Mn transidoxy multiple scattering path [15] was included in all fits. Mn EXAFS were fit using a model based on a layered phyllosilicate structure, loosely based on that of Ressler, et al. [16]. This model also accounts for splitting of the Mn-O and Mn-Mn distances in the structure due to Jahn-Teller distortions, angular deviations from planar sheets (particularly important with Mn-Mn multiple scattering), aqueous Mn(OH)2 surface bound Mn species, and vacancies present in the Mn-layer lattice. Full details of the model are provided elsewhere [17]. This model has been tested on relevant model spectra (bismutite, α-MnO2) and found to fit the EXAFS up to R ~ 5.5 Å for samples with good data up to k of 15 Å−1.
X-ray diffraction intensity data were collected on wet solids in transmission geometry using the two-circle diffractometer on SSRL beamline 2-1 using a Bicron NaI detector equipped with Soller slits to examine the crystallinity and phases present in the biogenic Mn-oxide samples. The incident x-ray beam was tuned to 10 keV (λ = 1.24 Å) to improve beam penetration in to the wet samples and to provide Q-space access up to about 12 Å⁻¹. Wet sample slurries were placed in a custom sample cell between two lexan windows. The diffractometer was calibrated with LaB₆ and has a 0.04°/2θ fwhm resolution. Data were collected in Q-space in 0.004 Å⁻¹ intervals in dose mode of 10,000 counts per point. Several scans were added together to improve signal to noise ratios for interesting regions.

3. Results and Discussion

Incubation samples with large concentrations of U(VI) in the solution (>4 µM) visually appeared to inhibit manganese oxide formation. This was apparent by the decrease in amount of biogenic product in the centrifuged slurry at the end of the incubation experiment. The extreme case occurred in the highest U(VI) sample (100 µM) in which no manganese oxidation occurred.

Mn K-edge EXAFS spectra change substantially as the amount of U(VI) in the sample increase, indicating that the local structure around Mn changes significantly as shown in Figure 2. At the highest U(VI) concentration, the spectra are similar to those for todorokite, a 3 × 3 tunnel structure tecktomangantate. Tunnel structures can be fit using the phyllomanganate EXAFS layer model (Figure 1). Doing so produces apparently high dihedral angles in the manganese octahedral plane and an abnormally high percentage of vacancies, which can be used to distinguish todorokite from true phyllomanganates. Table I shows the summary of major fitted EXAFS parameters for the sample series, including a metal-free biogenic manganese oxide and todorokite. The fit derived parameters for the samples progresses from those typical of well-defined layer structures at low metal concentrations, to value indicating a highly bent or pseudo-tunnel structure at high U(VI) concentrations. The transition from a layer to tunnel-like structure begins to occur at U(VI) concentrations around 4 µM and appears to be complete at 20 µM.

Table I. Summary of model parameters from the Mn K-edge EXAFS fitting results for each of the uranyl-manganese oxide incubations. *Describes the fraction of the total Mn sites in the octahedral layer that are unoccupied. Large numbers of edge sites due to small particles will also affect this parameter. †Describes the out-of-plane bend of the manganese octahedral layer in the direction parallel to the a-axis. ‡Describes the out-of-plane bend of the manganese octahedral layer in the direction parallel to the b-axis.

| Sample | U(VI) added (%DM) | Vacancies (%M) | Angle (a-axis) | Angle (b-axis) |
|--------|------------------|----------------|---------------|---------------|
| No metal | N/A | 0 | 0 | 0 |
| A | 50 µM | 30 | 1 | 0 |
| B | 100 µM | 30 | 1 | 0 |
| C | 500 µM | 28 | 1 | 0 |
| D | 1 µM | 26 | 1 | 0 |
| E | 4 µM | 60 | 6 | 0 |
| F | 10 µM | 56 | 12 | 7 |
| G | 20 µM | 65 | 5 | 20 |
| Todorokite | N/A | 40 | 6 | 19 |

Figure 2: X-ray diffraction data for the 001 basal plane reflections for the uranyl incubation samples.

XRD (Figure 2) shows that at low U(VI) concentrations, the XRD structure of the metal incubated oxides is dominated by a 7.5 Å phyllomanganate basal plan reflection typical of himesseitike phases and very similar to that of biooxides formed in the absence of U(VI). The breadth and low intensity of the peaks indicates very small particle size as well as structural disorder. The two sharp peaks at 9.4 and 10.1 Å are due to diffraction from the spores. As the concentration of U(VI) in the incubation increases, the intensity of the phyllomanganate basal plan reflection decreases. At the same time, a new broad peak at 9.8 Å is observed, indicating a phase with differing long-range structure, possible similar to todorokite. The change from 7.5 to 9.8 Å phases occurs at sample E, which is the same region in which EXAFS indicated significant changes in the Mn local structure were occurring.

U-LIII-edge EXAFS (Figure 3) of the incubation samples is dominated by the strong presence of equatorial and axial oxygens. Sample C and G were used as components for linear combination fits to spectra from samples D-F. Samples A and B have the same structure as C, but are significantly noisier due to the trace concentration of U in the sample. EXAFS fitting analysis of the residuals from the second shell of sample C shows contributions.
Analysis of sample G is far more complex. The residual EXAFS at low uranyl concentrations, the results show that the dominant that the altered biogenic oxides are still very poorly ordered, it tunnel structure similar to todorokite. Since the XRD suggests a transformation of the manganese oxide to a pseudo-todorokite. Additionally, the oxides 001 basal plane reflections suggest a transformation of the manganese oxide to a pseudo-todorokite manganese phase and the presence of strongly scattering Mn neighbors in the U EXAFS suggests that U is located in the tunnels of the manganese oxide.

| Sample | Shell | N   | R   | \(a^2\) |
|--------|-------|-----|-----|---------|
| C      | U-C   | 0.84| 2.84| 0.0041  |
|        | U-Mn  | 0.73| 3.30| 0.0180  |
| G      | U-C   | 1.45| 2.88| 0.0041  |
|        | U-Mn  | 0.31| 3.81| 0.0050  |
|        | U-Mn  | 0.28| 4.29| 0.0080  |
|        | U-O   | 1.31| 4.01| 0.0080  |

**Fig. 3.** U L-edge EXAFS for incubation samples. Data are represented by the solid lines, fits by the dotted lines. Samples A, B, C and G were fit in a shell-by-shell EXAFS fit, whereas samples D, E, and F were fitted as linear combinations of C and G.

From C and Mn shells, suggesting a uranyl-carbonate ternary surface complex to the manganese oxide surface. The U-Mn distance of 3.30 Å is suggestive of a bidentate surface complex. Analysis of sample G is far more complex. The residual EXAFS shows strong oscillations past \(k = 12\) Å\(^{-1}\), suggesting the presence of more than just surface complexity, with the presence of strongly scattering metal shells. This sample is best fit with U-Mn shells at 3.81 and 4.29 Å and a U-O shell at 4.01 Å. These results are summarized in Table II.

The measurements all show that at increasing U(VI) concentrations, not only does the mechanism of U(VI) uptake on the biogenic oxide change, but the structure of the oxide itself changes as well. All three of these techniques show that the onset of the transitions occurring in the manganese oxide structure and U(VI) complexion take place at the same uranyl concentrations.

At low uranyl concentrations, the results show that the dominant form of manganese oxide is poorly ordered, turbostratic layer manganate structure. Uranyl is adsorbed onto the oxide surfaces as a ternary carbonate complex, coordinated to the oxide surfaces in a bidentate fashion.

At high concentrations, the presence of U(VI) affects the manganese structure. The EXAFS model applied gives rise to larger apparent vacancies and increases in the dihedral angles along the a-b plane. This increase in angle has the effect of reducing the importance of Mn-Mn multiple scattering paths. The results are also strikingly like that of the 3 × 3 tunnel structure of todorokite. Additionally, the oxides 001 basal plane reflections of the XRD data move from 7.5 toward 9.8 Å. These items suggest a transformation of the manganese oxide to a pseudo-tunnel structure similar to todorokite. Since the XRD suggests that the altered biogenic oxides are still very poorly ordered, it is unlikely that the uranyl incorporated oxide is a typical 3 × 3 tunnel structure. These results suggest that the structure is more likely a 3 × n, where the distance between layers is consistent at 3 octahedra (9.8 Å), and the horizontal spacing is considered nearly random. The U(VI)-carbonate complex may stabilize the formation of these structures. The lack of bidentate U-Mn binding suggests that the mechanism of U incorporation into the structure is different at these high loadings as well. Further work is still required to develop a definitive model. However, the presence of a pseudo-todorokite manganese phase and the presence of strongly scattering Mn neighbors in the U EXAFS suggests that U is located in the tunnels of the manganese oxide.

**4. Conclusions**

At low U(VI) : Mn ratios, uranyl is associated with biogenic manganese oxide surfaces as a ternary carbonate complex. At higher uranyl concentrations, the manganese oxides become strongly distorted and exhibit spectral characteristics suggesting the existence of tunnel structures. Uranyl appears to be structurally incorporated in the tunnels of these biooxides. This bonding mechanism, were it to occur in the environment, implies that manganese oxides may be suitable materials for long-term in situ stabilization of U(VI). Other work has shown that elevated concentrations of other metals, such as Co and Cu can also lead to todorokite-like tunnel structures [18]. Thus the concentrations of dissolved Ca and Mg may be major controls on the existence and reactivity of tunnel-structure biooxides in the environment.

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