

Detecting oxidation of redox-active contaminants: a case study with $^{238}\text{U}/^{235}\text{U}$

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Abstract

Redox reactions control the mobility of many contaminants that endanger sources of potable water. Detecting these reactions through only aqueous concentrations of contaminants is often problematic as other reactions and transport effects can also affect these concentrations. For example, detection of U(IV) oxidation is difficult through U(VI) concentrations alone. Uranium (U) occurs naturally as soluble U(VI) and relatively insoluble U(IV). Reduction of U(VI) to insoluble U(IV) can decrease aqueous U concentrations, but oxidation of U(IV) remobilizes U. We have developed an isotope technique using the ratio of $^{238}\text{U}/^{235}\text{U}$ of U(VI) to monitor groundwater systems for U(IV) oxidation. Through several field experiments with different oxidation strategies on locations with distinct initial U(IV) content, we measured changes in $^{238}\text{U}/^{235}\text{U}$ ratios of U(VI) during U(IV) oxidation and determined that detecting U(IV) oxidation through $^{238}\text{U}/^{235}\text{U}$ ratios is feasible. Isotope ratios of other redox-sensitive elements, such as selenium and chromium, could also be utilized to detect remobilization of these contaminants in the future.

Introduction

Contamination by heavy metals and metalloids threatens our water resources. Many of these elements including chromium, selenium, mercury, arsenic, and uranium are redox-active, occurring naturally in multiple oxidation states. Through oxidation and reduction reactions, their chemical behavior can change dramatically. For example, uranium (U) has two primary oxidation states: soluble and mobile U(VI) and sparingly soluble U(IV). Through natural or induced U(VI) reduction to U(IV) that precipitates or adsorbs strongly to sediments, U pollution may be remediated (Anderson et al., 2003; Williams et al., 2011; Long et al., 2015). Similar strategies have been applied to chromium and selenium, which are also less soluble in their reduced states. The reduced forms of chromium, selenium, and uranium are often assumed to be stable, remaining in the solid phase. However, oxidation can remobilize these contaminants, compromising the effectiveness of reduction as a remediation strategy.

Detecting oxidation through aqueous concentrations alone can be difficult and can produce erroneous conclusions. U(VI) concentrations may be affected by transport effects and adsorption/desorption, not redox reactions alone, so an increase in U(VI) concentrations could not unequivocally be attributed to U(VI) oxidation. Thus, another method of detecting oxidation of redox-sensitive elements is necessary.

We have developed the isotopic ratio of $^{238}\text{U}/^{235}\text{U}$ as an indicator of oxidation of U(IV) in groundwater systems. ^{238}U and ^{235}U are the two main U isotopes and can be treated as stable under remediation timescales. Oxidation may be detected by small shifts in $^{238}\text{U}/^{235}\text{U}$ ratios of aqueous U(VI) due to the processes that fractionate the U isotopes. $^{238}\text{U}/^{235}\text{U}$ ratios are often reported relative to an isotopic standard in delta notation:

$$\delta^{238}\text{U} = \left[\frac{\left(\frac{^{238}\text{U}}{^{235}\text{U}} \right)_{\text{sample}}}{\left(\frac{^{238}\text{U}}{^{235}\text{U}} \right)_{\text{CRM-112A}}} - 1 \right] \times 1000\text{‰}$$

Adsorption of U(VI) has a minor effect with ^{235}U preferentially adsorbing to aquifer minerals, leaving the remaining aqueous U(VI) slightly enriched in ^{238}U (Brennecke et al., 2011; Jemison et al., 2016). Abiotic reduction of U(VI) to U(IV) by iron(II) sulfides, green rust, aqueous iron(II), and sulfide appears to produce

little to no isotopic shift (Stylo et al., 2015). However, microbial reduction of U(VI) preferentially involves ^{238}U , which produces U(IV) with a higher $^{238}\text{U}/^{235}\text{U}$ ratio and can significantly decrease the $^{238}\text{U}/^{235}\text{U}$ ratio of the remaining U(VI) (Basu et al., 2014; Stylo et al., 2015). Oxidation of U(IV) induces little to no isotopic fractionation (Wang et al., 2015), but oxidation of U(IV) previously produced by microbial reduction with a high $^{238}\text{U}/^{235}\text{U}$ ratio can increase the $^{238}\text{U}/^{235}\text{U}$ ratio of aqueous U(VI) as the ^{238}U -enriched U(IV) is incorporated into the U(VI) pool (Figure 1). We have conducted several field experiments to investigate how $^{238}\text{U}/^{235}\text{U}$ ratios can be applied to detect U(VI) oxidation. This research may be applied to detect oxidation of other redox-sensitive elements in the future.

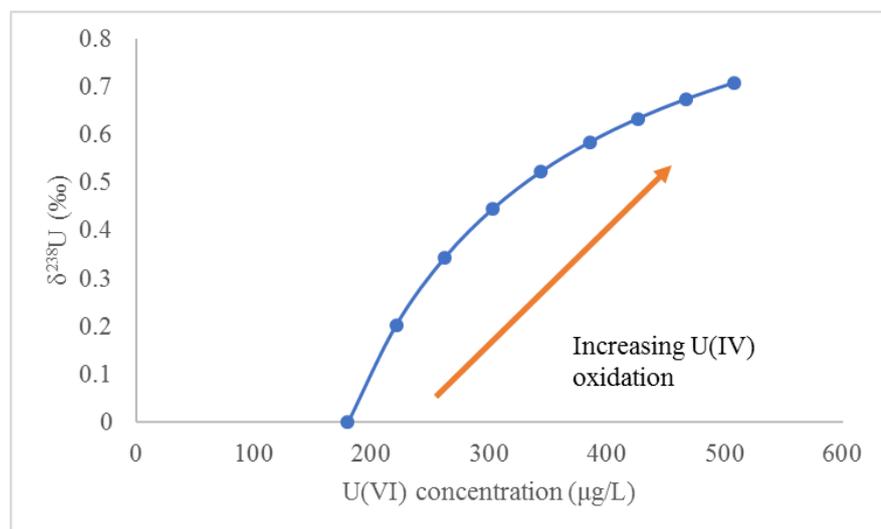


Figure 1: Theoretical model of the increase in U(VI) concentration ($\mu\text{g/L}$) and $\delta^{238}\text{U}$ (‰) as oxidation of ^{238}U -enriched U(IV) occurs.

Methods

Field site

Our experiments to test the use of $^{238}\text{U}/^{235}\text{U}$ ratios to detect U(IV) oxidation were performed at a U-contaminated site in Rifle, CO. The Rifle site is a former U mill that processed U ore from 1924 to 1958 (Williams et al., 2011). Leaching of U from mill tailings into the groundwater produced high U concentrations ($\sim 180 \mu\text{g/L}$). The Department of Energy took control of the Rifle site, installing hundreds of monitoring wells, which allows researchers to conduct spatially precise experiments. Several biostimulation experiments have been performed at the Rifle, CO site (Anderson et al., 2003; Williams et al., 2011; Long et al., 2015). These experiments involved injecting an organic electron donor, such as acetate, into the groundwater, which stimulates microbes to reduce U(VI) to U(IV) that accumulates near the injection wells. U(IV) is also found in naturally reduced zones (NRZs) across the Rifle, CO site and other U-contaminated sites. NRZs have low permeability and contain high amounts of organic matter that promotes microbial U(VI) reduction (Campbell et al., 2012; Janot et al., 2016).

The stability of U(IV) within these areas is a major controlling factor in U(VI) concentrations over time. If U(IV) from biostimulated areas oxidizes relatively rapidly, other remediation strategies may be needed. In addition, NRZs have been identified as a likely culprit of the prolonged U(VI) contamination occurring in Rifle, CO, as U(VI) can be slowly oxidized and leached into the aquifer.

Experiments

We performed several experiments on the “JB” NRZ, an NRZ intersected by several groundwater wells in Rifle, CO (Janot et al., 2016), to gain understanding of oxidation processes occurring in NRZs. Core material from two wells intersecting the “JB” NRZ were subsampled at ~ 10 depths each for U concentrations and $^{238}\text{U}/^{235}\text{U}$ ratios. Sediments were leached with 3M nitric acid to release U derived from contamination due

to milling activities and not natural U within mineral matrices. U(IV) within these NRZ sediments is susceptible to natural oxidation.

We artificially stimulated U(IV) oxidation with the addition of dissolved O₂ to the aquifer, to test if a significant change in ²³⁸U/²³⁵U ratios occurred. Two injections of groundwater with elevated dissolved O₂ concentrations occurred in the “JB” NRZ to induce U(IV) oxidation and measure ²³⁸U/²³⁵U ratio shifts of aqueous U(VI). For one injection, a baffle system was used to direct the injection primarily to the center of the NRZ. The other injection did not use a baffle system, which allowed groundwater with elevated dissolved oxygen to be injected throughout the entire NRZ and some of the surrounding aquifer. Groundwater was collected from the injection well for ²³⁸U/²³⁵U ratios as U(VI) concentrations increased due to U(VI) oxidation, then decreased as the slug of groundwater with high dissolved oxygen advected downgradient from the injection well. Sediment and groundwater samples were purified using extraction chromatography (Weyer et al., 2008), and purified U was analyzed on a Nu Plasma MC-ICPMS at University of Illinois- Urbana Champaign following the methods described by Bopp et al. (2010). ²³⁸U/²³⁵U were reported relative to the U isotopic standard CRM 112-A in delta notation.

Similar field methods were utilized to study U(IV) oxidation from biostimulated areas, where previous experiments reduced and precipitated U(IV). Plot C, a former biostimulated area in Rifle, CO (Long et al., 2015; Shiel et al., 2016), was the setting for several induced oxidation experiments to test how ²³⁸U/²³⁵U ratios of aqueous U(VI) evolve with U(IV) oxidation. Researchers had previous induced distinct biostimulation conditions on the two sides of plot C, which likely produced different patterns of ²³⁸U/²³⁵U ratios of U(IV) between both sides. Groundwater with added nitrate to induce U(IV) oxidation was injected on both sides of plot C to investigate how biostimulation conditions affected ²³⁸U/²³⁵U of aqueous U(VI) during subsequent U(IV) oxidation. In addition, one location received two nitrate injections to determine if the δ²³⁸U shift due to oxidation waned over time. Groundwater was collected downgradient from the injection wells and was analyzed for δ²³⁸U.

Results

The nitrate injections into the biostimulated area in plot C induced a concurrent increase in U(VI) concentrations and δ²³⁸U values for all injections. The increase in ²³⁸U/²³⁵U ratios was fairly consistent between the injections at two locations, despite the differences in biostimulation conditions. The second injection at the one injection site produced an increase in ²³⁸U/²³⁵U ratios similar to the initial injection.

The dissolved oxygen injections into the “JB” NRZ produced less consistent increases in ²³⁸U/²³⁵U values. The first injection through the baffle system induced a large increase in U(VI) concentrations, but a muted increase in δ²³⁸U values. The second injection without a baffle system induced a smaller increase in U(VI) concentrations, but a much larger change in δ²³⁸U values. These discrepancies may be explained by the heterogeneity found in the sediment samples of the “JB” NRZ. Both cores have a similar pattern of increasing U concentrations towards the center of the NRZ where more U(IV) accumulates. However, ²³⁸U/²³⁵U values decrease towards the center of the NRZ.

Discussion

The isotopic heterogeneity of the NRZ appears to be due to reductive distillation. As U(VI) is microbially reduced on the edge of the NRZ, U(IV) begins to accumulate with a high ²³⁸U/²³⁵U. However, microbial reduction drives the remaining U(VI) to lower ²³⁸U/²³⁵U values as it is transported to the center of the NRZ. This U(VI) is then reduced to U(IV) with a lower ²³⁸U/²³⁵U ratio than U(IV) at the edges of the NRZ.

This isotopic heterogeneity appears to have an effect on the change in ²³⁸U/²³⁵U ratios during U(IV) oxidation from NRZs. The injection with dissolved oxygen with a baffle system concentrated the injection to the center of the NRZ with a high concentration of lower δ²³⁸U U(IV), which produced a muted ²³⁸U/²³⁵U increase as less ²³⁸U-enriched U(IV) was oxidized. The dissolved oxygen injection without the baffle system was spread through the entire NRZ and the surrounding aquifer, producing a small aqueous U(VI) increase

and a larger $\delta^{238}\text{U}$ increase. The low permeability of the NRZ likely prevented much of the dissolved oxygen to penetrate the NRZ and oxidize U(IV) from the center of the NRZ. Instead, U(IV) oxidation appears to have primarily occurred on the edge of the NRZ that contains U(IV) with a high $^{238}\text{U}/^{235}\text{U}$ ratio, producing a larger isotopic change in the aqueous U(VI). We would expect natural U(IV) oxidation to occur similarly, with the low permeability of the NRZ mostly preventing oxidants from penetrating to the center of the NRZ. With the oxidants reacting with U(IV) on the edge of the NRZ, natural oxidation should induce a measurable increase in $\delta^{238}\text{U}$ that can be used to identify U(IV) oxidation.

The experimental results from the biostimulated area suggest that $^{238}\text{U}/^{235}\text{U}$ ratios are a promising tool for detecting U(IV) oxidation from biostimulated areas. Oxidation of U(IV) produced primarily microbial reduction with a high $^{238}\text{U}/^{235}\text{U}$ induced a fairly consistent increase in $\delta^{238}\text{U}$ of aqueous U(VI), which suggests this technique is capable of detecting U(IV) oxidation at various U contaminated sites.

We currently are developing reactive transport models to test how chemical (e.g., rate of U(IV) oxidation and U(VI) and dissolved oxygen concentrations) and physical characteristics (e.g., size of NRZs and groundwater velocity) affect the change in $^{238}\text{U}/^{235}\text{U}$ ratios during U(IV) oxidation from NRZs and biostimulated areas and investigate how broadly our experimental results may be applied. $^{238}\text{U}/^{235}\text{U}$ ratio measurements appear to provide a promising method of detecting U(IV) oxidation. The general lessons learned from this study are broadly applicable to isotope ratios of other redox-active elements that may be remobilized by oxidation.

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