



Isotope fractionation during oxidation of tetravalent uranium by dissolved oxygen

Xiangli Wang*, Thomas M. Johnson, Craig C. Lundstrom

Department of Geology, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

Received 20 June 2014; accepted in revised form 4 December 2014; available online 13 December 2014

Abstract

We conducted laboratory experiments to investigate isotopic fractionations during oxidation of tetravalent uranium, U(IV), by dissolved oxygen. In hydrochloric acid media with the U(IV) dissolved, the $\delta^{238}\text{U}$ value of the remaining U(IV) increased as the extent of oxidation increased. The $\delta^{238}\text{U}$ value of the product U(VI) paralleled, but was offset to $1.1 \pm 0.2\%$ lower than the remaining U(IV). In contrast, oxidation of solid U(IV) by dissolved oxygen in 20 mM NaHCO_3 solution at $\text{pH} = 9.4$ caused only a weak fractionation ($\sim 0.1\%$ to 0.3%), with $\delta^{238}\text{U}$ being higher in the dissolved U(VI) relative to the solid U(IV). We suggest that isotope fractionation during oxidation of solid U(IV) is inhibited by a “rind effect”, where the surface layer of the solid U(IV) must be completely oxidized before the next layer is exposed to oxidant. The necessity of complete conversion of each layer results in minimal isotopic effect. The weak shift in $\delta^{238}\text{U}$ of U(VI) is attributed to adsorption of part of the product U(VI) to the solid U(IV) surfaces.

© 2014 Elsevier Ltd. All rights reserved.

1. INTRODUCTION

Uranium mining and other applications in the energy and weapons industries over the past decades have caused contamination of groundwater and soils in many places around the world. This has raised public health concerns due to the chemical toxicity (mainly nephrotoxicity) of U (Bleise et al., 2003).

U is a redox sensitive element, with two main valence states being stable in nature: U(VI) (hexavalent) and U(IV) (tetravalent). U(VI) is stable as dissolved uranyl ion (UO_2^{2+}) under a wide range of pH and often complexed by carbonate ions and other ligands in natural waters. In contrast, U(IV) is highly soluble only at very low pH (< 2) in aqueous media (Langmuir, 1978). Thus, at circumneutral pH conditions, the reduction of mobile U(VI) to immobile U(IV) offers an efficient *in situ* method of mitigating U contamination (Bopp et al., 2010; Shiel et al., 2013). U(VI) can

be reduced by both artificial and natural reductants, including Fe(II) species and microorganisms (Lovley et al., 1991; O’Loughlin et al., 2003; Hua et al., 2006; Du et al., 2011). In both cases, reduction needs to be monitored. Recent field and laboratory studies (Bopp et al., 2010; Basu et al., 2014) show that reduction of U(VI) causes a systematic shift in $\delta^{238}\text{U}$ that appears to be caused by a nuclear volume effect (Schauble, 2007; Abe et al., 2008). This allows the use of $^{238}\text{U}/^{235}\text{U}$ to monitor and potentially quantify reduction of U(VI).

However, studies have shown that the U(IV) product deposited by reductive remediation can be quickly reoxidized by natural oxidants such as oxygen and nitrate (Beller, 2005; Moon et al., 2009). Potential isotope fractionation during oxidation may complicate the application of $^{238}\text{U}/^{235}\text{U}$ measurements to indicate reduction.

Besides environmental applications, $^{238}\text{U}/^{235}\text{U}$ measurements have recently been used to trace ocean/atmosphere redox states (Montoya-Pino et al., 2010; Brennecka et al., 2011a; Kendall et al., 2013). The long residence time of uranium in the ocean (about 500 ky) (Klinkhammer and

* Corresponding author.

E-mail address: xiangli.wang1@gmail.com (X. Wang).

Palmer, 1991) leads to homogeneous U concentration and isotopic composition of the open seawater (Delanghe et al., 2002; Stirling et al., 2007; Weyer et al., 2008). Therefore, $\delta^{238}\text{U}$ potentially offers a redox proxy on global scales.

The global U cycle on Earth is very sensitive to the oxygen content in the atmosphere. U in continental rocks is present mainly as U(IV), residing in feldspars, zircon, apatite, sphene, and uraninite (Speer et al., 1981). U(IV) in minerals can only be oxidized to soluble U(VI) and carried to the ocean when the atmosphere O_2 is above a certain level. Absence of oxidative weathering leads to extremely small dissolved U concentrations in the ocean, given extremely low solubilities of U(IV) minerals under reducing conditions (Langmuir, 1978). Under these conditions, the global U cycle is dominated by sedimentary fluxes of reduced U contained in detrital grains, leading to essentially invariant marine sedimentary U isotope composition (Kendall et al., 2013). With the onset of oxidative weathering, the increased U inventory in the ocean allows for partial reduction of U(VI), making $^{238}\text{U}/^{235}\text{U}$ variations possible. Therefore, variation of marine sedimentary U isotope composition may be used to trace paleoredox perturbations in earth's early surface environments.

This study aims to provide experimental data on U isotope fractionation during oxidation of dissolved U(IV) and synthetic solid U(IV). Laboratory experiments were designed with simplicity in mind, to obtain clear initial results with few complications.

2. EXPERIMENTAL AND ANALYTICAL METHODS

2.1. Synthesis of U(IV)

Tetravalent U is extremely sensitive to oxygen; therefore, U(IV) was protected from air by serum bottles and/or an glove box filled with nitrogen gas. A U(VI) stock solution, from which all U-bearing solutions and solids were created, was obtained by dissolving the metal U standard CRM 112a (New Brunswick Laboratory, U.S. Department of Energy) in concentrated nitric acid. Following previously reported methods (Ondrejcin, 1961), dissolved U(VI) was then reconstituted in 1 M sulfuric acid and reduced to U(IV) by zinc metal. The produced U(IV) was then precipitated in excess 1 M ammonium hydroxide. Ammonium hydroxide was preferred over sodium hydroxide because the latter introduces matrix cations. The U(IV) precipitate was centrifuged and washed three times with O_2 -free 20 mM bicarbonate buffer (pH 7) to remove sulfate and Zn ions. The bicarbonate buffer solution was deoxygenated by passing mixed N_2 - CO_2 gas through a 20 mM bicarbonate solution. The purpose of this bicarbonate solution was to buffer pH, to minimize adsorption, and to simulate natural conditions. About half of the solid U(IV) was resuspended in O_2 -free 20 mM bicarbonate buffer as the stock for the experiments focusing on oxidation of solid U(IV). The remainder was dissolved in O_2 -free 4.5 M HCl as the stock for the experiments focusing on oxidation of dissolved U(IV). The synthesized solid U(IV) particles were stored in anaerobic serum bottles (pure N_2 headspace for the dissolved U(IV) stock and CO_2 - N_2 mix gas for the solid

U(IV) stock) for 2 weeks so that the particle surfaces were relatively stable and less prone to aging effects during the experiments. XRD analysis suggested that the synthesized U(IV) particles are ~ 4 nm uraninite (Fig. 1). Concentrations of the starting U(VI) solution, reduced U(IV) solution and solid U(IV) suspension were determined to be 0.2 M, 0.1 M, and 1.2 mM, respectively. Since all experimental suspensions were homogenized by constant mixing, we reported molarity as the concentration unit for solid suspension for the sake of easy comparison with experiments on oxidation of dissolved U(IV). Isotopic compositions of the starting U(VI) solution, the reduced U(IV) solution and the solid U(IV) suspension were determined to be the same ($0.05 \pm 0.06\text{‰}$, expressed as $\delta^{238}\text{U}$ relative to CRM112a). This indicates that the reduction and precipitation processes used to make the starting materials did not fractionate U isotopes.

2.2. Experiment procedures

Two duplicate experiments examining oxidation of dissolved U(IV) (experiments 1 and 2) were conducted in 0.1 N HCl at room temperature in an anaerobic glove box with <1 ppm O_2 in order to facilitate immediate processing of the samples without exposure to air. A small measured amount of the dissolved U(IV) stock was added to 50 mL oxygenated 0.1 M HCl in 100 mL serum bottles sealed with butyl stoppers with air headspace and immediately mixed thoroughly. Solutions were sampled by withdrawing 0.5 mL volumes with needles and syringes at 0.1–3 day intervals. The sampled volume was replenished with an equal volume of air. Experimental solutions were shaken at each sampling event but left standing the rest of the time. Immediately after sampling, 0.7 mL O_2 -free 7.5 M HCl was added to the sampled 0.5 mL solutions to bring the HCl concentration to 4.5 M before separation of U(IV) and U(VI) by anion exchange (see below).

Two duplicate experiments examining oxidation of the synthetic, solid U(IV) oxide (experiments 3 and 4) were

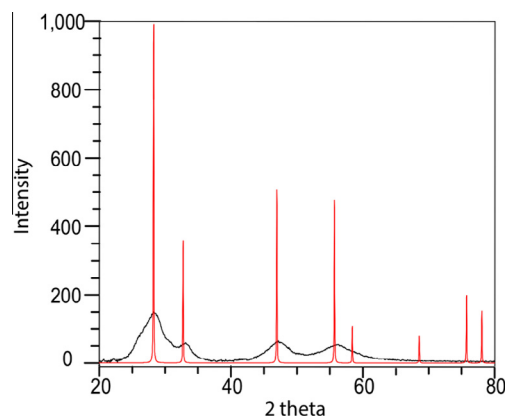


Fig. 1. XRD result for the synthesized U(IV) particles. The high, narrow peaks represent standard uraninite; the low, wide peaks represent synthesized U(IV) particles. This XRD pattern, including the missing peaks at high angles, is consistent with nano-crystalline uraninite (Singer et al., 2009). The XRD analysis also gives a rough estimate of the crystal size of ~ 4 nm.

Download English Version:

<https://daneshyari.com/en/article/4701989>

Download Persian Version:

<https://daneshyari.com/article/4701989>

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