Abiotic U(VI) reduction by aqueous sulfide

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Abstract

Reactions with aqueous sulfide are important in determining uranium (U) geochemistry under sulfate reducing conditions. This paper reports on abiotic reduction of U(VI) by aqueous sulfide under a range of experimental conditions using batch reactors. Dissolved U concentration was measured as a function of time to study the effects of chemical variables including pH, U(VI), S(-II), total dissolved carbonate ($\text{CARB} = \text{H}_2\text{CO}_3^* + \text{HCO}_3^- + \text{CO}_3^{2-}$), and Ca^{2+} concentration on the U(VI) reduction rate. Solid phase reaction products were characterized using X-ray diffraction, X-ray absorption spectroscopy, and transmission electron microscopy. The chemical variables had impacts on the solid phase U(VI) reaction products as well as the reduction rates by aqueous sulfide. The solid U reaction product at circumneutral pH was identified as uraninite ($\text{UO}_{2+x(s)}$). Under basic pH conditions, whether a precipitate occurred depended on Ca^{2+} and CARB concentrations. U(VI) reduction was faster under higher S(-II) concentrations but was slowed by increased dissolved Ca^{2+} or CARB concentration. In the

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absence of dissolved CARB and Ca^{2+} , a rapid decrease in dissolved U concentration occurred at circumneutral pH, while virtually no decrease was observed at pH 10.7 within the experimental timeframe of two days. The U(VI) reduction rate was proportional to the total concentration of free uranyl plus its hydrolysis complexes even at minor to trace concentrations. Dissolved Ca^{2+} and CARB slow abiotic U(VI) reduction by forming stable Ca-U(VI)-carbonato soluble complexes that are resistant to reaction with aqueous sulfide. U(VI) reduction was slow in a synthetic solution representative of groundwater at a uranium mill tailings site. This study illustrates that abiotic U reduction by aqueous sulfide can significantly vary under typical ranges of chemical conditions in groundwater and newly demonstrates the importance of dissolved Ca^{2+} in the abiotic U(VI) reduction by aqueous sulfide. The results contribute to our understanding of the impact of sulfate reducing conditions on U speciation in groundwater systems undergoing bioreduction conversion of U(VI) to less mobile U(IV) solid phases.

Keywords: uranium(VI); abiotic reduction; aqueous sulfide; Ca^{2+} ; carbonate

1. Introduction

Redox chemistry of uranium (U) needs to be considered in reactive transport models that are used for long-term assessment of U migration in contaminated aquifers. Under sufficiently reducing conditions, the more mobile U(VI) in the form of dissolved uranyl ion species can be reduced to less mobile U(IV) solid phase species. To facilitate this transformation, injection of a carbon source into contaminated groundwaters has been used to stimulate iron or sulfate reducing conditions (Anderson et al., 2003; Qafoku et al., 2009; Moon et al., 2010). Under sulfate reducing conditions, microbiological and chemical reduction of U may occur simultaneously (Boonchayaanat et al, 2010; Hua et al., 2006; Lovley and Phillips, 1992), complicating the assessment of each contribution. For example, sulfate reducing

1 microorganisms have been shown to directly reduce U(VI) to U(IV) as part of their metabolic
2 processes (Lovley and Phillips, 1992; Lovley et al., 1993; Pietzsch et al., 1999). Alternatively,
3 the sulfide produced by microbial activity under natural or stimulated sulfate reducing conditions
4 at U contaminated sites may subsequently react with U(VI) and reduce it to U(IV) or react with
5 iron to form ferrous sulfide precipitates that may reduce U(VI) to U(IV) (Hua et al., 2006; Hua
6 and Deng, 2008; Hyun et al., 2012).

7   The research presented here focuses on the chemical reactions responsible for abiotic U
8 redox transformations under sulfate reducing conditions. Field-scale biostimulation experiments
9 have been carried out at a DOE U-contaminated site (U mill tailings site in Rifle, CO) by
10 intermittently injecting acetate into the shallow aquifer and monitoring groundwater chemistry
11 and microbial community changes (Yabusaki et al., 2007). The results have shown that iron
12 reducing bacteria effectively immobilized U (Anderson et al., 2003). However, once the terminal
13 electron acceptor, Fe(III), was effectively depleted, sulfate reduction became predominant, but
14 acetate-oxidizing sulfate-reducing bacteria appeared to be not as effective at U(VI)
15 immobilization (Anderson et al., 2003; Lovley et al., 1993; Williams et al., 2011). A recent *in*
16 *situ* column study has shown that U immobilization under sulfate reducing conditions occurs
17 mainly by U reduction to “molecular” U(IV) species (Bernier-Latmani et al., 2010). Yet, the
18 relative contributions that are due to biotic or abiotic processes are still not clear. A better
19 understanding of U redox transformations under sulfate reducing conditions therefore requires
20 isolating the chemical processes from microbial metabolic U redox processes, and, in particular,
21 the role of aqueous sulfide as a reducing agent over a range of environmentally relevant
22 conditions.

Abiotic reduction of U has been reported by Fe(II) oxyhydroxide minerals (O'Loughlin et al., 2003; Rosenspurg et al., 2009), Fe(II) sulfide minerals (Wersin et al., 1994; Moyes et al., 2000; Livens et al., 2004), adsorbed Fe(II) (Chakraborty et al., 2010; Jeon et al., 2005; Liger et al., 1999; Fox et al., 2013), and aqueous sulfide (Hua et al., 2006). Recent papers suggest that slight changes in U(VI) aqueous speciation may affect the thermodynamic feasibility of abiotic U(VI) reduction, noting the closeness of redox couples U(IV)/U(VI), Fe(II)/Fe(III) oxides, and $\text{HS}^-/\text{SO}_4^{2-}$ (Ginder-Vogel et al., 2006; Borch et al., 2010). These conclusions were originally made in the context of uraninite oxidation, but the same reasoning should apply for U(VI) reduction. It follows that chemical variables such as pH, carbonate, and calcium, which change U(VI) speciation, may have impacts on U(VI) reduction. Under sulfate reducing conditions, it is thus of practical importance to assess the feasibility of U(VI) reduction by aqueous sulfide under variable chemical conditions.

In this study, abiotic U(VI) reaction with aqueous sulfide was investigated over a range of chemical conditions, including U(VI), S(-II), total dissolved carbonate (hereafter CARB, equals $\text{H}_2\text{CO}_3^* + \text{HCO}_3^- + \text{CO}_3^{2-}$), and Ca^{2+} concentrations under circum-neutral pH conditions (pH 6.7, 7.1, and 7.3). The research questions addressed were: 1) what are the U(VI) reaction products with aqueous sulfide over a range of environmentally relevant conditions?; and 2) what conditions promote abiotic U(VI) reduction by aqueous sulfide? Related to the first questions, previous studies report different reaction products from aqueous sulfide reduction of U(VI), depending on experimental conditions. For example, several have reported a partially reduced mixed-valent U solid phase forms (Wersin et al., 1994; Moyes et al., 2000; Livens et al., 2004), while others found uraninite precipitation when U(VI) was reacted with ferrous sulfide or aqueous sulfide in Ca-free systems (Hua et al., 2006; Hua and Deng, 2008). In more recent

investigations, “molecular” U(IV) species formed as a reaction product, contrary to the long-held belief that U(IV) quickly forms *extremely* insoluble reduced U solid phases (Bernier-Latmani et al., 2010; Fletcher et al., 2010; Sivawamy et al., 2011). Regarding the second question, Hua et al. (2006) reported that the U reduction rate by aqueous sulfide was proportional to the sum of the U(VI)-hydroxide species concentrations, suggesting a strong influence of U(VI) aqueous speciation on the reduction rate. However, these authors used pH buffers (12.5mM PIPES and TRIS), and very high dissolved carbonate concentrations (up to 30mM), and Ca^{2+} was absent in their experiments. These results may not be directly applicable to natural systems. The work presented here includes a wider range of chemical conditions, and concentrations more representative of natural and U contaminated groundwater sites.

2. Materials and Methods

2.1. Batch U(VI) reaction with aqueous sulfide.

Batch reactor reduction experiments were performed under N_2 atmosphere (with 4% H_2 for O_2 scavenging) in an anaerobic chamber. Solutions were prepared using anoxic Milli-Q water (18.3 M Ω -cm) inside the anaerobic chamber. All the glassware and plastic bottles were stored in the anaerobic chamber at least 2 days before use to ensure that O_2 molecules possibly adsorbed to the vessel walls were exchanged and removed under the N_2 atmosphere. Abiotic reactions of aqueous U(VI) with aqueous sulfide were carried out in 150mL batch reactors in the anaerobic chamber, following Beyenal’s method (Beyenal et al., 2004). In the simplest aqueous phase system, a 180 μM uranyl nitrate solution (as U(VI)) was reacted with 1mM sodium sulfide solution (as S(-II)) without CARB and Ca^{2+} . In a second experiment, Ca^{2+} and CARB were

1 added to the sulfide solution (1mM S, 1mM CARB, and 5mM Ca²⁺) and reacted with the 180μM
2 uranyl nitrate solution to get a preliminary assessment of their impact on U(VI) reduction by
3 sulfide. After this, U(VI) was reacted with 10mL solution of sulfide in 15mL polypropylene
4 conical tubes in solutions containing various other specific concentrations of CARB and Ca²⁺ to
5 see the trends of changes in U speciation and reduction. The desired reaction pH was obtained
6 by adding appropriate amounts of hydrochloric acid. No pH buffer was used, but the pH was
7 well buffered in the presence of CARB. During the course of reaction, the batch reactor tubes
8 were continuously mixed on an end-over-end rotator (60rpm). At each time point, the final
9 solution pH in the reactor tube was measured and then the solution was filtered with a 0.1μm
10 nylon syringe filter (GE Cameo) using a lubricant-free plastic disposable syringe (National
11 Scientific). Dissolved U in the solution was measured by inductively coupled plasma mass
12 spectrometry (Perkin-Elmer Elan). Chemical conditions were systematically varied to test the
13 effect of each variable on U(VI) reduction rates. The experimental ranges were chosen to
14 encompass the conditions observed for Rifle groundwater (Hyun et al., 2009), where the field-
15 scale biostimulation experiments were run (Yabusaki et al., 2007). Initial U(VI) concentration
16 ranged between 3.5×10^{-7} and 10^{-4} M, dissolved sulfide between 1 and 10mM, CARB between 1
17 and 5mM, and Ca²⁺ between 0 and 5mM. The synthetic solution used to simulate the Rifle
18 aquifer groundwater contained [Na⁺] = 10mM, [K⁺] = 0.4mM, [Mg²⁺] = 4mM, [Ca²⁺] = 4.8mM,
19 CARB = 7.7mM, [Cl⁻] = 3mM, [SO₄²⁻] = 8.8mM, and pH = 7. Three different initial U
20 concentrations (4×10^{-7} , 4×10^{-6} , and 4×10^{-5} M) were used for the experiments using synthetic
21 groundwater. Equilibrium aqueous U(VI) speciation was calculated using Visual MINTEQ
22 (ver.3.0). The NEA database (Guillaumont et al., 2003) was used for U species, with Ca_x-UO₂-

CO₃ species from Dong and Brooks (2006), consistent with our previous work (Hyun et al., 2009).

2.2. Solid Phase Characterization.

Solid phase reaction products were characterized using X-ray diffraction (University of Michigan X-ray Microbeam Analysis Laboratory), transmission electron microscopy (University of Michigan Electron Microbeam Analysis Laboratory), and X-ray absorption spectroscopy (Stanford Synchrotron Radiation Lightsource). U *L*_{III} edge X-ray absorption spectroscopy data were collected at the Stanford Synchrotron Radiation Lightsource (SSRL). XAS samples were prepared under the same experimental conditions as the batch kinetic experiments, but scaled up to collect enough amounts of samples necessary for the XAS data collection. Fluorescence X-ray absorption data were measured at the beam lines 11-2 and 4-1 using a 30- or 13-element Ge detector or Lytle detector. The beam energy was calibrated by setting the simultaneously measured *K* edge position of a Y foil as 17038 eV. To improve the signal-to-noise ratio, multiple scans were measured using a liquid nitrogen cryostat. To minimize the higher order harmonics, the monochromator crystals were detuned 30%. The data were collected at 3GeV with beam current of 200-195 mA. A Sr-3 or Sr-6 filter was used as necessary depending on the fluorescence signal quality. EXAFS data reduction and model based fitting analyses were performed using SixPack (Webb, 2002). Feff8.10 code was used to calculate phase-shift and amplitude functions for U-backscatterer pair scattering paths (Ankudinov et al., 2002). The crystallographic input files for Feff calculation were generated using ATOMS (Ravel, 2001). The background removed, averaged EXAFS spectra were converted from energy space to the photoelectron wave vector *k* space. The fitting was performed using the Feff EXAFS fitting module typically in the range of

3< k <12. The accuracy of the bond length and coordination number was estimated to be $\pm 0.02 \text{ \AA}$ and 24% for the first shell, respectively. To obtain the best fitting results, the Debye-Waller factor (σ^2) and energy reference E_0 were floated in the fitting process, whereas the many-body factor (S_0^2) was fixed at 0.9. The R factor of SixPack was used as the goodness of EXAFS fitting to the measured data in comparing different combination of structural parameters (Webb, 2002).

3. Results

Dissolved U concentration as a function of time in the simplest model system (1mM S(-II), no CARB, no Ca^{2+}) is given in Figure 1. The equilibrium pH was stable at 10.7 without externally added acid. At this pH, the dissolved U concentration did not change as a function of time. However, when the pH was titrated down to 7 by adding 1N nitric acid, the dissolved U concentration immediately decreased to below detection limit (Fig. 1) with the appearance of a dark precipitate. In systems amended with 1mM CARB and 5mM Ca^{2+} (at 1mM total sulfide), the dissolved U(VI) concentration decreased as a function of reaction time under both circumneutral and basic pH conditions (Data not shown). However, the resulting precipitates were different under circumneutral and basic pH conditions. The precipitate formed at circumneutral pH had a dark color similar to the precipitate formed in the absence of Ca^{2+} and CARB. However, the precipitate formed at pH 10.7 had a distinctly different yellow color. Further characterization results at circumneutral pH are discussed in the following section.

3.1. Solid Phase Reaction Products.

3.1.1. Ca^{2+} - and CARB-free Model System. The solid phase reaction products in the reaction of U(VI) with aqueous sulfide were characterized using X-ray diffraction (XRD),

transmission electron microscopy (TEM), and X-ray absorption spectroscopy (XAS). The results for the precipitate formed at pH 7 in the Ca²⁺- and CARB-free system are illustrated in Figure 2. Both XRD (Fig. 2a) and selected area electron diffraction (Fig. 2c) confirmed that the precipitate formed by the homogeneous reaction of dissolved U(VI) and aqueous sulfide was uraninite under circum-neutral pH in this simple system with only dissolved U(VI), sulfide, nitrate, sodium, H⁺, and OH⁻ in anoxic water. XAS, which gives an independent set of information regarding the local coordination structure of U, confirms the formation of uraninite by U(VI) reaction with aqueous sulfide in the Ca²⁺- and CARB-free system (Fig. 2d and e). XANES (Fig. 2d) shows that the edge position of the U L_{III}-edge X-ray absorption spectrum shifted to 17172eV, *ca.* 2eV lower than the starting U(VI) solution, indicating U reduction to U(IV). EXAFS analysis (Fig. 2e) gives structural parameters of 6.1 nearest oxygen neighbors at the interatomic distance of 2.26Å from the central U atom and of 3.6 second shell uranium neighbors at 3.83Å. These structural parameters are consistent with the reported structure of uraninite, although the coordination number for the uranium shell is lower than that expected for a well crystalline uraninite (Wyckoff, 1978; Schofield et al., 2008). Similar observation of low coordination number for the nearest U atoms is reported to be due to the nanocrystalline nature of the uraninite precipitate in a study of U(VI) reaction with green rust or mackinawite (O'Loughlin et al., 2003). The following 1:1 stoichiometric relation between U(VI) and S(-II) is suggested from a previous study of U(VI) reduction by dissolved sulfide under similar experimental conditions (Hua et al., 2006):

Considering the aqueous speciation of U(VI), the following are the reactions for the predominant U(VI) species:

Characterization of the solid phase reaction product confirms that in the absence of Ca^{2+} and CARB, U(VI) is reduced to uraninite under the circum-neutral pH by reaction with aqueous sulfide, but U(VI) remains as dissolved U(VI) without formation of any solid phase under the basic pH condition.

3.1.2. Ca^{2+} and CARB Added Systems. The 1st derivative X-ray absorption near edge structure (XANES) spectra of the solid phases precipitated in the Ca^{2+} and CARB added systems at circumneutral pH, i.e., at pH 6.7, 7.1, and 7.3, are shown in Figure 3. The precipitates have the maximum 1st derivative points moved to a lower energy (17171.5eV), compared with 17173eV of the starting U(VI) solution. The energy position of the samples is similar to that of synthetic uraninite (Schofield et al., 2008). The minimum 1st derivative positions of the circumneutral pH samples also line up well with that of synthetic uraninite. This observation indicates that the dark precipitates formed by homogeneous reaction between aqueous U(VI) and S(-II) in the presence of Ca^{2+} and CARB under the range of circum-neutral pH conditions are a U(IV) solid. The extended X-ray absorption fine structure (EXAFS) parts of the XAS spectra were reduced and analyzed (Figure 4 and Table 1). Each of these samples had structural parameters similar to those of the uraninite model compounds (Table 1). The nearest neighbors are in a single oxygen shell instead of the starting U(VI) solution's distinct double shell composed of axial and equatorial oxygen atoms characteristic of uranyl ion (UO_2^{2+} ; Fig. 4). The interatomic distances of the first shell oxygen atoms ranged from 2.32 to 2.33 Å. These values

are in good agreement with the reported ranges for synthetic, biogenic, and hydrothermal uraninite specimens (Schofield et al., 2008; Sharp et al., 2009; Singer et al., 2009). The distinct second shell feature at 3.81-3.82Å originating from the strong backscattering by U neighbors excludes possibilities of molecular U(IV) monomers recently reported for microbial U(VI) reduction (Bernier-Latmani et al., 2010; Fletcher et al., 2010; Sivawamy et al., 2011). These EXAFS structural parameters suggest precipitation of uraninite in the homogeneous reaction of U(VI) with aqueous sulfide under circum-neutral pH in the presence of Ca^{2+} and CARB.

3.2. Factors Affecting U(VI) Reduction Kinetics.

3.2.1. U(VI) concentration. When the initial U(VI) concentration was $5.5 \times 10^{-5} \text{M}$, U reduction was clearly observed at pH 7 in the reaction with 1mM dissolved S(-II) in the presence of 1mM CARB and 5mM Ca^{2+} concentrations (Fig. 5a). When the initial U(VI) concentration was lowered to $3.5 \times 10^{-7} \text{M}$, U reduction was much slower under the same experimental conditions (Fig. 5b). At 5mM CARB, the rate of U removal from solution was much slower for both initial U concentrations (Fig. 5a and 5b). The carbonate effect is discussed below in more detail.

3.2.2. Dissolved S(-II). Presented in Fig. 5c are the results for U(VI) reactions with different aqueous sulfide concentrations as a function of time without added Ca^{2+} . The rate of U removal from solution was faster at higher dissolved sulfide concentration. When the dissolved sulfide concentration was 10 mM, the dissolved U concentration decreased to below detection within half an hour. The dissolved U concentration had a gentler slope and was below detection after ~2 h of reaction when reacted with 1mM S(-II).

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2   **3.2.3. Ca^{2+} Concentration.** Increasing Ca^{2+} concentration slowed the U(VI) removal
3 rate from solution (Fig. 5d). When the dissolved Ca^{2+} concentration was 0.3mM, dissolved U
4 concentration decreased to below detection within 2h from the start of the reaction, whereas it
5 took 10h to reach below detection when the Ca^{2+} concentration was increased to 5mM.

6
7   **3.2.4. CARB Concentration.** The CARB concentration effect observed in Fig. 5 in
8 conjunction with the U(VI) concentration was studied in more detail in the presence of 5mM
9 Ca^{2+} (Fig. 6). The initial total carbonate concentration was varied between 1 and 5mM. A rapid
10 decrease in dissolved U concentration occurred under the 1mM CARB condition, but the
11 reduction and disappearance of dissolved U was slowed as the CARB concentration increased to
12 1.5, 2.0, and 3.0mM (Fig. 6). Virtually no reduction was observed when the CARB concentration
13 was raised to 5.0mM (Fig. 6). This is an important observation given that 5.0mM and higher
14 CARB concentrations are commonly observed in groundwaters, including the Rifle aquifer
15 (Hyun et al., 2009; Fox et al., 2012).

16 17 **3.3. U(VI) Reaction with Sulfide in Synthetic Rifle Groundwater.**

18   The typical pH range of the Rifle groundwater is between 6.62 and 7.42 with the mean
19 value of 6.94 (US DOE, 1999), suggesting that abiotic U reduction by aqueous sulfide could be
20 feasible at the Rifle site if other conditions (e.g. Ca^{2+} and CARB concentrations) are favorable.
21 The results of abiotic U reduction by aqueous sulfide in a synthetic groundwater sample are
22 shown in Fig. 7. A slow decrease in the dissolved U concentration was observed as a function of
23 time under the initial U(VI) concentrations of 4×10^{-5} , 4×10^{-6} , and 4×10^{-7} M. A 1st order reduction

rate was obtained using the decrease in dissolved U concentration as a function of time. This rate was extrapolated to estimate dissolved U(VI) concentrations after two and three weeks to compare with the observed U concentration variation in field biostimulation experiments (Yabusaki et al., 2007). The extrapolation suggests that 86% and 95% of the initial U(VI) would be reduced after two and three weeks, respectively. This estimated concentration decrease is less than what was observed during the Fe(III)-reducing phase of the biostimulation experiments carried out at the Rifle site (Yabusaki, 2007), although a straightforward, direct comparison is difficult due to differences in geochemical, flow, and mixing conditions. After the initial 50 days of acetate injection, rapid U removal was observed in the field experiment, along with an increase in dissolved Fe(II) concentration in the groundwater. Sulfate reduction followed between 50 and 100 days after the start of acetate injection, but during this phase of the experiment, the dissolved U concentration slightly increased. The increase in dissolved U concentration may have occurred because of slow U(VI) desorption processes from the sediments that were greater in magnitude than U reduction by sulfate reducers (Williams et al., 2011). Our results suggest that abiotic U(VI) reduction by aqueous sulfide may also contribute to the various processes that influence dissolved U(VI) concentrations under sulfate reducing conditions, although the net result is apparent increase in dissolved U concentration.

4. Discussion

U(VI) was reduced to U(IV) by reaction with aqueous sulfide under certain combinations of experimental conditions. In general, higher S(-II), higher U(VI), circumneutral pH, lower CARB, and lower Ca^{2+} concentrations provided favorable conditions for abiotic U reduction by aqueous sulfide. At pH 7, the products of the electron transfer reaction between aqueous sulfide

(major species HS^-) and U(VI) were elemental sulfur and uraninite in the Ca^{2+} - and CARB-free system as evidenced by X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS), and transmission electron microscopy (TEM: Figure 2). XAS confirmed that the solid phases formed in the Ca^{2+} - and CARB-added systems were also uraninite (Figures 3 and 4). This is consistent with the results of Hua et al. (2006), although these authors used different experimental conditions, e.g., use of pH buffers and higher CARB concentrations and the absence of Ca^{2+} .

Thermodynamic calculations show systematic changes in U(VI) aqueous speciation as functions of the above mentioned experimental variables. U(VI) reduction rate was dependent on the solution variables, suggesting U(VI) speciation-dependent reduction. The overall reduction can be written with reactions involving the two major U(VI) aqueous species under the experimental conditions studied (Table S1):

However, no direct quantitative kinetic relation between the concentrations of the dominant U(VI) aqueous species and observed U(VI) reduction rates can be drawn from the experimental data in this case. The observed dependency of the reduction rate on each experimental variable suggests that the reduction takes a path composed of a set of parallel elementary steps involving minor U(VI) species, and thus depends on solution variables that affect their concentrations.

EXAFS characterization shows that $\text{Ca}_2\text{UO}_2(\text{CO}_3)_{3(\text{aq})}$ has the local structure of a central U(VI) atom with two axial oxygen atoms at 1.78Å as in free uranyl ion (UO_2^{2+}) (Kelley et al., 2007). This species also has six equatorial oxygen atoms at 2.45Å, shared with three carbon atoms of the carbonate neighbors located at 2.90Å from the central uranium atom, and two Ca^{2+} atoms at 4.01Å (Brooks et al., 2003). The kinetic results of this study suggest that its structure is

1 stable in water and resistant to reduction by dissolved sulfide, compared to the free uranyl ion
2 and its hydrolysis complexes. It leads to the conclusion that its filled coordination structure
3 hinders electron transfer between bisulfide ion and the central U(VI), making it an unfavorable
4 U(VI) species for reduction by aqueous S(-II). However, the concentration of this species did not
5 show a direct relationship with U(VI) reduction rate under the experimental conditions
6 investigated, given the rate of reduction of this species is much slower. Instead, the U(VI)
7 reduction rate was proportional to the concentration of U(VI) species with more favorable
8 structures for reduction, such as the free uranyl and its hydroxide complexes. Therefore, the
9 impact of the soluble Ca-U(VI)-CARB species on the abiotic reduction of U(VI) species by
10 sulfide is related to the extent to which the formation of the calcium complex lowers the
11 equilibrium concentration of U(VI)-hydroxide species (Supplementary data). Those
12 groundwater conditions that increase the initial concentration of the more reactive U(VI)
13 hydroxyl species will tend to enhance the rate of dissolved U(VI) abiotic reduction by dissolved
14 sulfide.

15   Standard and conditional half-cell potentials for possible major U(VI) aqueous species
16 are given in Table S2 (in Supplementary data). For example, at 4×10^{-5} M U(VI), 5mM Ca^{2+} ,
17 5mM total carbonate, and pH 7, the half-cell potential values indicate that $\text{Ca}_2\text{UO}_2(\text{CO}_3)_{3(\text{aq})}$ has
18 the least favorable and the uranyl ion the most favorable free energy for reduction to uraninite.
19 The conditional half-cell potential values at pH 7 show that 4×10^{-7} M U(VI), 5mM Ca^{2+} , and
20 5mM total carbonate are the least favorable set of conditions for $\text{Ca}_2\text{UO}_2(\text{CO}_3)_{3(\text{aq})}$ reduction to
21 uraninite of those investigated here. The rate trends observed in this study in which higher
22 U(VI), lower Ca, and lower CARB concentration lead to faster U(VI) reduction by sulfide are
23 consistent with the thermodynamic favorability of reduction.

Similar results have been reported by others. For example, in a study of the bioreduction of U(VI) in the presence of carbonate and calcium, Brooks et al. (2003) reported that calcium caused a significant decrease in bacterial U(VI) reduction by *Schewanella putrefaciens* strain CN32, *Desulfovibrio desulfuricans*, and *Geobacter sulfurreducens*. Ulrich et al. (2011) studied the relationship between U(VI) bioreduction kinetics and U(VI) aqueous speciation. They too reported systematic correlations between the rate constant, Gibbs free energy of reaction, and Eh in the bioreduction of U(VI) by *Shewanella onedensis* strain MR-1, with the reduction rate increasing with conditions that favored overall free energy of reduction. They reported the fastest reduction with U(VI)-hydroxyl and U(VI)-organic species, slower reduction of the U(VI)-carbonate group, and much slower reduction of the Ca-U(VI)-carbonate group. These trends are also supportive of our results, even though they investigated rates of microbiological processes; they did not consider abiotic reduction of U(VI) as a possible pathway.

In the present paper we report for the first time, the inhibition of Ca^{2+} on *abiotic* U(VI) reduction by sulfide. As mentioned earlier, Hua et al. (2006) reported the inhibition of dissolved carbonate on abiotic U(VI) reduction by dissolved sulfide through the formation of uranyl carbonate complexes, but did not consider Ca^{2+} impacts. In the absence of Ca^{2+} , they concluded that U(VI)-hydroxyl species were favorably and relatively rapidly reduced by sulfide, in contrast to the dominant U(VI)-carbonate species. By including Ca^{2+} , we have extended the range of conditions to those more representative of groundwater, and the potentially even more significant inhibition by Ca^{2+} .

Visual MINTEQ calculations show that $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ and $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ constitute more than 99% of the total dissolved U(VI) present in the Ca and carbonate added systems (Table S1), with the relative abundance of each being dependent on U(VI), Ca^{2+} , and CARB

concentrations and pH. The calculations also show that the concentrations of uranyl hydroxide species have dependency on the same variables. For instance, free UO_2^{2+} is $5.90 \times 10^{-11} \text{M}$ and $4.84 \times 10^{-13} \text{M}$ under 1mM and 5mM total carbonate conditions, respectively. The sum of free uranyl and uranyl-hydroxide species is $4.91 \times 10^{-9} \text{M}$ at 1mM total carbonate compared with $3.72 \times 10^{-11} \text{M}$ at 5mM carbonate.

The thermodynamic considerations show that $\text{Ca}_2\text{UO}_2(\text{CO}_3)_{3(\text{aq})}$ is the most abundant but the least favorable U(VI) aqueous species to be reduced by aqueous sulfide in our experimental systems. It is not practical to determine the reduction rate for individual U(VI) species due to the complexity of U(VI) aqueous chemistry under the experimental conditions considered (See Supplementary data). Nonetheless, it is instructive to establish an empirical relation, although not strictly derivable from elementary reaction steps, from the data we have obtained. Assuming the reaction order of 0.54 for HS^- as in Hua et al. (2006), the following empirical relation fits the abiotic U(VI) reduction rate data by aqueous sulfide under the conditions with $\text{S}(-\text{II})=1\text{mM}$ and $\text{Ca}^{2+}=5\text{mM}$:

$$-\frac{d[\text{U(VI)}]}{dt} = 3 \times 10^{-11} \{\Sigma[\text{CARB}]\}^{-3.402} [\text{U(VI)}]_{\text{Tot}} [\text{HS}^-]^{0.54} \quad (6)$$

where $\Sigma[\text{CARB}]$ is the sum of all the dissolved carbonate species and $[\text{U(VI)}]_{\text{Tot}}$ is the total dissolved U(VI) concentration. U(VI) reduction rate has a strong dependency on CARB concentration, which in turn has a systematic negative correlation with the sum of the equilibrium concentrations of free uranyl and its hydroxyl complexes, a similar tendency observed by Hua et al. (2006) for their Ca-free model systems. The above empirical relation well explains the observation that the rate of abiotic U(VI) reduction by aqueous sulfide is dependent on the concentrations of free uranyl and uranyl hydrolysis complexes, even though they are minor or trace species under the experimental conditions (Fig. 8).

A comparison with Hua et al. (2006)'s rate constants determined in Ca-free systems was made to illustrate the suspected importance of the Ca^{2+} - UO_2 -carbonate species in slowing the kinetics of U(VI) reduction by aqueous sulfide. The reduction of U(VI) in $\text{Ca}_2\text{UO}_2(\text{CO}_3)_{3(\text{aq})}$ or $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ estimated by this approach is significantly slower than U(VI) reduction observed for U(VI)-carbonate complexes, consistent with the conclusion of Brooks et al. (2003). The extrapolation of the empirical relation of this study ($k = 3 \times 10^{-11} [\Sigma \text{CARB}]^{-3.402}$) gives the reduction rate constant k value of $0.0043 \text{ [mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}]$ for 4mM CARB condition used by Hua et al. (2006), along with $[\text{U(VI)}] = 168.3 \mu\text{M}$, $[\text{HS}^-] = 1 \text{ mM}$, and $\text{pH} = 6.89$. This value is about 40% of the value reported by Hua et al. (2006), i.e., k of $0.0103 \text{ [mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}]$ in their kinetic equation ($-\frac{d[\text{U(VI)}]}{dt} = 0.0103 [\text{U(VI)}] [\text{S}^{2-}]_T^{0.54}$) obtained under Ca^{2+} -free conditions. This comparison supports the implied importance of Ca-U(VI)-carbonate species in slowing U(VI) reduction by aqueous sulfide.

5. Summary and Conclusions

The results of this study show that abiotic reduction of U(VI) to uraninite by aqueous sulfide can occur to a significant extent under certain sets of chemical conditions. Under higher U(VI), higher S(-II), lower CARB, and lower Ca^{2+} conditions, rapid U(VI) reduction was observed at pH 7. If U(VI) is present in higher concentrations of free uranyl or its hydrolysis complexes, abiotic U(VI) reduction by aqueous sulfide is accelerated. However, at the 5mM CARB and $4 \times 10^{-7} \text{ M}$ dissolved U(VI) concentrations, which are within the typical range of the Rifle groundwater system, significant U reduction was not observed within 48h, but could contribute to U reduction over a longer period of time. The dominance of Ca-U(VI)-carbonate soluble complexes and their stability in water slow abiotic reduction by S(-II). Thus,

groundwater geochemical variables can have significant impacts on the abiotic U reduction rate by changing U(VI) aqueous speciation. The findings of this study suggest that abiotic reduction by aqueous sulfide is an important process to consider in assessing U redox chemistry under sulfate reducing conditions achieved either naturally or by biostimulation, and this process needs to be considered in developing field-scale U reactive transport models.

In conclusion, this study reports the reaction of U(VI) with aqueous sulfide under a range of experimental conditions including pH, dissolved U(VI), Ca^{2+} , and CARB concentrations. The following results are found in this study:

- U(VI) is abiotically reduced to uraninite by aqueous sulfide under certain combinations of geochemical conditions.
- Geochemical conditions including pH, dissolved U(VI), Ca^{2+} , and carbonate concentrations have impacts on the abiotic U(VI) reduction by aqueous sulfide.
- Ca^{2+} affects the abiotic U(VI) reduction by aqueous sulfide by changing the dominant U(VI) aqueous speciation.

Acknowledgment

This research was funded by the U.S. Department of Energy (DOE) Office of Science, Environmental Remediation Sciences Program (ERSP) via two projects “The Integrated Field-scale Subsurface Research Challenge (IFRC) Site at Rifle, Colorado, USA” and “Assessing the Role of Iron Sulfides in the Long Term Sequestration of Uranium by Sulfate-Reducing Bacteria,” and in part by KIGAM’s Basic Research Project (14-3218). Portions of this research were carried out at the Stanford Synchrotron Radiation Lightsource, a Directorate of SLAC National Accelerator Laboratory and an Office of Science User Facility operated for the U.S. Department of Energy Office of Science by Stanford University. The SSRL Structural Molecular Biology

Program is supported by the DOE Office of Biological and Environmental Research, and by the National Institutes of Health, National Center for Research Resources, Biomedical Technology Program (P41RR001209).

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 22

1 Table 1. Structural parameters extracted from the EXAFS analysis (N : coordination number of
2 backscatterer atoms around the absorber U atom, R : interatomic distance (in Å) of the absorber-
3 backscatterer pair, σ^2 : Debye-Waller factor (in Å²) of the absorber-backscatterer pair. The
4 subscript stands for the kind of backscatterer). ^a: U(VI) samples reacted with aqueous sulfide at
5 CARB=1mM, Ca²⁺=5mM, S(-II)=1mM, and U(VI)=0.1mM under circum-neutral but slightly
6 different pH conditions.

Sample Shell		pH 7.3 ^a	pH 7.1 ^a	pH 6.7 ^a	U_Stock (1000 ppm uranyl solution)	Uraninite (Wyckoff, 1978) From XRD	Uraninite Synthetic (Hyun et al., 2012)	Uraninite Biogenic (Hyun et al., 2012)	UO _{2.00(s)} Synthetic (Schofield et al., 2008)	Uraninite Biogenic (Schofield et al., 2008)
O	N	5.8(8)	6.5(0)	6.1(4)		8	6.5(5)	7.2(8)	8	8
	R	2.32(3)	2.33(0)	2.32(5)		2.3678	2.25(5)	2.33(4)	2.354(7)	2.347(7)
	σ^2	0.0105	0.0109	0.0098		0	0.0164	0.0122	0.0046(7)	0.0103(6)
U ^{IV}	N	5.3(8)	5.4(5)	5.3(4)		12	2.5(2)	4.8(8)	12	6(1)
	R	3.81(0)	3.81(9)	3.81(8)		3.8666	3.84(4)	3.83(7)	3.867(4)	3.846(5)
		0.0079	0.0069	0.0062		0	0.0071	0.0105	0.0029	0.0055(7)
O _{ax}	N				2.4(5)					
	R				1.77(0)					
	$\frac{1}{2} \sigma$				0.0030					
O _{eq}	N				4.8(3)					
	R				2.42(3)					
	$\frac{1}{2} \sigma$				0.0061					
C	N									
	R									
	$\frac{1}{2} \sigma$									
R-factor		0.0762	0.0787	0.0527						

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8

Figure Captions

Figure 1. Dissolved U concentration as a function of time in the reaction of 180 μ M U(VI) with 1mM S(-II) in the model system without Ca²⁺ and CARB. The first region is at pH 10.7 and the second is at pH 7.

Figure 2. U solid phase precipitated at pH 7 in the Ca²⁺- and CARB-free simple model system. (a) X-ray diffraction pattern, (b) high resolution transmission electron micrograph showing the lattice fringe image, (c) selected area electron diffraction pattern, (d) U *L*_{III} edge X-ray absorption near edge structure with the inflection point at 17172 eV, and (e) extended X-ray absorption fine structure spectrum (left) and corresponding Fourier transform magnitude function (right: circles (data) and solid line (fit)). The precipitate is uraninite.

Figure 3. The 1st derivative U *L*_{III} edge XANES spectra of solid samples precipitated under different pH conditions in the Ca²⁺ and CARB added systems along with those of the U(VI) solution and synthetic uraninite model compounds (CARB=1mM, Ca=5mM, S=1mM, and U=0.1mM).

Figure 4. U *L*_{III} edge EXAFS spectra and the corresponding Fourier transform magnitude functions of the solids precipitated under different pH conditions. A) U(VI) solution model compound (without Ca²⁺ and CARB), Solid precipitated in the Ca²⁺ and CARB added systems (CARB=1mM, Ca²⁺=5mM, S(-II)=1mM, and U(VI)=0.1mM) at B) pH 6.7, C) 7.1, D) 7.3, and E) uraninite model compound (Hyun et al., 2012; circles: data, solid lines: fits).

Figure 5. Effects of geochemical variables on the U(VI) reduction kinetics by aqueous sulfide.
a) Initial U(VI)= 5.5×10^{-5} M, pH 7, Ca^{2+} =5mM, HS^- =1mM, b) Initial U(VI)= 3.5×10^{-7} M, pH 7, Ca^{2+} =5mM, HS^- =1 mM, c) Initial U(VI)= 1.9×10^{-4} M, pH 7, CARB=1 mM, no Ca^{2+} added, and d) Initial U(VI)= 5×10^{-5} M, pH 7, CARB=1mM, HS^- =1 mM.

Figure 6. Changes in dissolved U(VI) concentration as a function of time in the reaction of U(VI) with HS^- under different CARB concentration conditions: Initial U(VI)= 4×10^{-5} M, Ca^{2+} =5mM, HS^- =1mM, and pH 7.

Figure 7. U(VI) reduction kinetics by aqueous sulfide in an artificial groundwater solution (Na^+ =10mM, K^+ =0.4mM, Mg^{2+} =4mM, Ca^{2+} =4.8mM, HCO_3^- =7.7mM, Cl^- =3mM, SO_4^{2-} =8.8mM, and pH=7).

Figure 8. Comparison of U(VI) reduction rate constants (k) as a function of CARB concentration with aqueous U(VI) speciation: (A) $\Sigma(\text{U}^{\text{VI}}\text{-OH})$, (B) $\Sigma(\text{U}^{\text{VI}}\text{-CARB})$, and (C) $\Sigma(\text{Ca-U}^{\text{VI}}\text{-CARB})$.

1 Fig. 1

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1 Fig. 2

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1 Fig. 3

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1   Fig. 4

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1 Fig. 5

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1 Fig. 6

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1 Fig. 7

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1 Fig. 8

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