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# Chemical Reduction of U(VI) by Fe(II) at the Solid−Water Interface Using Natural and Synthetic Fe(III) Oxides

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Abiotic reduction of 0.1 mM U(VI) by Fe(II) in the presence of synthetic iron oxides (biogenic magnetite, goethite, and hematite) and natural Fe(III) oxide-containing solids was investigated in pH 6.8 artificial groundwater containing 10 mM $NaHCO_3$. In most experiments, more than 95% of added U(VI) was sorbed to solids. U(VI) was rapidly and extensively (≥80%) reduced in the presence of synthetic Fe(III) oxides and highly Fe(III) oxide-enriched (18−35 wt % Fe) Atlantic coastal plain sediments. In contrast, long-term (20−60 d) U(VI) reduction was less than 30% in suspensions of six other natural solids with relatively low Fe(III) oxide content (1−5 wt % Fe). Fe(II) sorption site density was severalfold lower on these natural solids (0.2−1.1 Fe(II) $nm^{-2}$) compared to the synthetic Fe(III) oxides (1.6−3.2 Fe(II) $nm^{-2}$), which may explain the poor U(VI) reduction in the natural solid-containing systems. Addition of the reduced form of the electron shuttling compound anthrahydroquinone-2,6-disulfonate ($AH_2DS$; final concentration 2.5 mM) to the natural solid suspensions enhanced the rate and extent of U(VI) reduction, suggesting that $AH_2DS$ reduced U(VI) at surface sites where reaction of U(VI) with sorbed Fe(II) was limited. This study demonstrates that abiotic, Fe(II)-driven U(VI) reduction is likely to be less efficient in natural soils and sediments than would be inferred from studies with synthetic Fe(III) oxides.

## Introduction

Uranium(VI) is stable in oxic environments and typically exists as soluble carbonate complexes in aerobic groundwaters at circumneutral pH. The formation of anionic U(VI)-carbonate complexes (e.g., $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$) has been known to increase the U(VI) mobility (*1*). In contrast, uranium(IV) is stable in anoxic environments, including most environments that contain Fe(II). U(IV) forms sparingly soluble minerals such as uraninite ($UO_{2(s)}$) (*2*), and the reductive immobilization of uranium has been studied for remediation of subsurface contamination by U(VI) (*3*, *4*). Uranyl ions and possibly polymeric species and carbonato complexes of uranyl adsorb to Fe(III) oxides and other mineral surfaces in circumneutral pH groundwaters (*5*−*11*). Sorption of U(VI) to mineral surfaces is likely to play a critical role in governing the overall behavior of uranium in contaminated subsurface environments, even in the presence of substantial levels of dissolved inorganic carbon. Desorption of U(VI) from mineral surfaces (e.g., in highly contaminated source zones) represents a potential long-term source of uranium input to groundwaters (*12*, *13*), analogous to the slow release of chlorinated hydrocarbon from dense nonaqueous phase liquid (DNAPL) source zones (*14*).

It has been suggested that the mobility of uranium in soil and groundwater environments could be decreased by the combination of in situ bioreduction of soluble and sorbed U(VI) by dissimilatory metal-reducing bacteria (DMRB) and chemical reduction of sorbed U(VI) by biogenic solid-associated Fe(II). If sorbed U(VI) can be reduced to an immobile U(IV) phase (i.e., uraninite) via abiotic reaction with Fe(II), then stimulation of DMRB activity in source zones may provide an effective means [by producing biogenic Fe(II)] for abiotic U(VI) reduction, providing a long-term biogenic redox barrier for prevention of far-field U(VI) migration (*15*). Biological U(VI) reduction by DMRB has received considerable attention (*3*, *4*, *16*−*18*). The potential for abiotic reduction of sorbed U(VI) has been also recognized but has not been as well studied. Abiotic reduction of sorbed U(VI) by Fe(II) sorbed onto Fe(III) oxide surfaces (*19*), or by structural Fe(II) in green rust (*20*) and magnetite (*21*), was observed at pH 6−7.5 in the absence of carbonate species. Abiotic reduction of U(VI) on the surface of goethite has also been demonstrated in carbonate-containing experimental media (*4*). However, abiotic reduction of U(VI) did not occur in the presence of several heat-killed, Fe(II)-rich (i.e., bioreduced) natural solids (*3*, *18*, *22*). Given that homogeneous U(VI) reduction by aqueous Fe(II) does not occur (*19*), Finneran et al. (*18*) attributed these results to poor sorption of U(VI) to the natural solids. Abiotic reduction of Fe(III) oxide was also less effective for natural sediments than for synthetic Fe(III) oxide (*23*), and enzymatic reduction of Fe(III) oxides in the presence of U(VI) was slower for natural sediments than for synthetic Fe(III) oxides (*24*). An important unanswered question with regard to abiotic U(VI) reduction by sorbed Fe(II) is whether sorbed U(VI) to natural solids is subject to efficient reduction, as is the case for sorbed U(VI) to synthetic iron oxides (*4*, *19*, *20*).

The purpose of this research was to investigate the potential for abiotic reduction of sorbed U(VI) to natural solids by sorbed Fe(II) in circumneutral pH groundwater environments. A parallel study evaluated the potential for biological U(VI) reduction (*25*), with the overall goal of determining whether biotic or abiotic processes are likely to dominate U(VI) reduction activity in circumneutral pH groundwater environments supporting the activity of DMRB. This investigation also focused on the comparison of U(VI) reduction in suspensions of synthetic Fe(III) oxides versus natural Fe(III) oxide-containing solids, which revealed the potential influence of sorption site heterogeneity on abiotic U(VI) reduction.

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**TABLE 1. Characteristics of Synthetic Fe(III) Oxide and Natural Fe(III) Oxide-Bearing Soil**

| solid phase | C/D Fe(III)[a] ($\mu$mol g$^{-1}$) | Fe weight%[b] | surface area[c] (m$^2$ g$^{-1}$) | Fe(II) sorption site density Fe(II) per nm$^2$ (ref) | dominant Fe(III) oxide phase (ref) |
|---|---|---|---|---|---|
| synthetic hematite | 12 300 ± 1900 | 68.8 | 9.0 | 2.5 (*41*) | hematite (*32*) |
| synthetic goethite | 11 100 ± 300 | 62.1 | 55.2 | 1.6 (*42*) | goethite (*33*) |
| Abbot's Pitt sand (APS) | 520 ± 17 | 2.9 | 45.3 | 0.5[d] | goethite (*34*, *35*) |
| oyster sand (OS) | 825 ± 18 | 4.6 | 64.3 | 0.9[e] | goethite (*34*, *35*) |
| field research center (FRC) | 345 ± 41 | 1.9 | 31.0 | 0.5[e] | goethite (*36*) |
| natural hematite (NH) | 6300 ± 16 | 35.1 | 25.7 | 3.2[d] | hematite (*37*) |
| natural goethite (NG) | 3143 ± 15 | 17.5 | 27.1 | 2.8[e] | goethite (*38*) |
| Cecil/Pacolet (CP) | 574 ± 47 | 3.2 | 15.9 | 1.1[e] | goethite (*39*) |
| Holston/Cloudland (HC) | 691 ± 47 | 3.9 | 19.0 | 0.9[d] | hematite (*39*) |
| Paleosol | 140 ± 34 | 0.8 | 19.3 | 0.2[d] | hematite (*40*) |

[a] One-hour extraction with C/D; mean ± SD of triplicate determinations, corrected for 0.5 M HCl-extractable Fe(II). [b] On the basis of total C/D-extractable Fe. [c] Determined by multipoint BET $N_2$ adsorption. [d] Estimated by a separate Fe(II) adsorption measurement (Figure 1). [e] Estimated in the heat-killed suspension with biogenic Fe(II) produced by 8−10 days of Fe(III) bioreduction.

## Materials and Methods

**Microorganism and Culture Conditions.** The DMRB *Geobacter sulfurreducens* (*26*, *27*) was used to produce biogenic Fe(II)-containing materials for abiotic U(VI) reduction experiments. Procedures for the cultivation and handling of *G. sulfurreducens* are described in ref *25*.

**Aqueous Phase.** A Pipes-buffered (10 mM) artificial groundwater (PBAGW) was used for all abiotic (and biotic) reduction experiments. The major element composition of PBAGW was as follows (mM): $CaCl_2$ (0.62), KCl (0.2), $MgCl_2 \cdot 6H_2O$ (0.25), and $Na_{1.5}$-Pipes (10.0). The Pipes buffer maintained solution pH values between 6.7 and 6.9 in all experiments. In the abiotic reduction experiments with heat-killed bioreduced materials (see below), the medium was supplemented with vitamin and trace mineral solutions (*28*) as well as small quantities of inorganic nutrients (10−50 $\mu$M $KH_2PO_4$, 100−500 $\mu$M $NH_4Cl$) to facilitate growth/maintenance of the DMRB. Speciation calculations [using MINEQL+ (*29*)] employing aqueous uranyl-carbonate, uranyl-hydroxide, and uranyl-phosphate stability constants from Grenthe (*30*) indicated that the aqueous phase remained undersaturated with respect to U(VI) mineral phases such as schoepite, $\beta$-$UO_2(OH)_2$, and $(UO_2)_3(PO_4)_2$.

**Fe(III) Oxide Phases.** Synthetic medium surface area (ca. 55 m$^2$ g$^{-1}$) goethite ($\alpha$-FeOOH) was produced as previously described (*25*). Biogenic magnetite (BM) was prepared allowing bioreduction of HFO by *G. sulfurreducens* (*31*) in Pipes-buffered artificial groundwater supplemented with vitamin and trace mineral solutions for 8 d and used for experiments without further treatment. Hematite ($\alpha$-$Fe_2O_3$) was purchased from J. T. Baker and identified by XRD and Mössbauer spectroscopy with greater than 99% purity (*32*).

Selected properties of several previously characterized natural Fe(III) oxide-containing materials used in this study are provided in Table 1. Details regarding the origin and characteristics of these materials are provided in ref *25* and references therein. The majority of the Fe(III) oxide content of the natural materials was in the form of crystalline phases, as indicated by the ratio of 0.5 M HCl-extractable to total citrate/dithionite-extractable Fe(III), which ranged from ca. 0.3 to 8.1% (*25*). All the natural solids were wet-sieved (100 $\mu$m) and freeze-dried except for the Paleosol which was wet-sieved (2 mm) and air-dried. Portions of the APS (Abbot's Pitt Sand) and NH (Natural Hematite) materials (Atlantic Coastal plain sediments with different Fe(III) oxide abundance; see Table 1) were treated with a citrate/dithionite (C/D) reagent (50 mg mL$^{-1}$ Na-dithionite + 0.2 M citrate in 0.35 M acetic acid) to remove Fe(III) oxides; the Fe(III) extraction procedure was modified from the method by Loeppert and Inskeep (*43*). The Fe(III) oxide-removed APS and NH were then treated three times with 3% $H_2O_2$ to oxidize residual reductants (*44*), including residual dithionite as well as structural Fe(II) in clay minerals (*45*) that may have been reduced during Fe(III) extraction. The Fe(III)-removed materials were subsequently washed extensively with deionized water.

**Fe(II) and U(VI) Sorption Experiments.** Fe(II) sorption to native and Fe(III) oxide-removed NH and APS was measured in 10 mM Pipes buffer solution at pH 6.8 (±0.1) in the anaerobic chamber. Solid was added to the buffer solution contained in a 100-mL serum bottle which had been degassed with 100% $N_2$. The serum bottle was capped with thick butyl rubber stopper, crimp sealed, and degassed further connecting to an oxygen trap (*46*) to ensure removal of trace $O_2$ (e.g., $O_2$ partial pressure in the headspace is less than $7.5 \times 10^{-9}$ atm). After connecting the bottles to the trap, the headspace of the bottles was replaced 10 times with the gas phase in the oxygen trap using a syringe, needle, and stopcock. Each 10 mL of suspension was then transferred with a syringe and needle to 10-mL serum bottles which had been capped with a rubber stopper, crimp sealed, and degassed with the $O_2$ trap. Fe(II) (reagent grade $FeCl_2 \cdot 4H_2O$) was then added to 10-mL serum bottles from sterile anaerobic stock solution (prepared with 0.1 M HCl). The suspensions were equilibrated for 3 days at 22 °C on a rotary shaker. Results from a previous study on the kinetics of Fe(II) sorption to Fe(III) oxides (*47*) suggested that this time interval was sufficient to allow for complete equilibration of Fe(II) with the solid phase. More than 98% of added Fe(II) was recovered in a control experiment (Fe(II) added to solution without solids), indicating success in maintaining the strict anoxic conditions. Aqueous Fe(II) concentrations were determined as described below, and these data were used to construct Fe(II) sorption isotherms in which the concentration of sorbed Fe(II) was determined by subtracting the concentration of aqueous Fe(II) from the total amount of Fe(II) added to each bottle.

U(VI) sorption kinetic and isotherm experiments were conducted with sterile, anaerobic suspensions of APS or synthetic goethite in 10 mM Pipes buffer solution containing 10 mM $NaHCO_3$ at pH 6.8 (±0.1). Preliminary studies showed that dissolved inorganic carbon concentrations in $NaHCO_3$-amended PBAGW (determined by acidifying a portion of the aqueous phase in a sealed vial and determining the $CO_2$ content of the vial headspace by gas chromatography) were ca. 9 mM. U(VI) (uranyl-acetate, Spectrum, Gardena, CA) was added from sterile anaerobic stock solutions (prepared with 0.1 M HCl). The suspensions were equilibrated for up to 2 days on the rotary shaker.

**Abiotic U(VI) Reduction Experiments.** Synthetic or natural Fe(III) oxides were added to $N_2$-sparged PBAGW containing 10 mM $NaHCO_3$ in the anaerobic chamber. The experimental bottles were capped with thick butyl rubber stoppers, crimp sealed, and autoclaved (121 °C, 20 min). Sterilized suspensions of Fe(III) oxide in PBAGW were further degassed connecting to the $O_2$ trap. Fe(II) and U(VI) were then added to initial concentrations of 0.6−4.0 mmol $L^{-1}$ and 0.1 mmol $L^{-1}$, respectively. The pH of the suspensions was adjusted to 6.8 (±0.1) with small amounts of sterile and anaerobic 1.0 M HCl or 1.0 M NaOH as needed. The amount of U(VI) added to the reaction systems was comparable, when normalized to Fe(III) oxide abundance, to the high range of uranium contamination present in subsurface sediments at the Y-12 site at Oak Ridge National Laboratory (*48*). The suspensions were incubated statically at 22 °C in the anaerobic chamber, and concentrations of Fe(II) and U(VI) were monitored over time.

**Heat-Killed Experiments.** Biological Fe(III) reduction was allowed to proceed for 8−10 d in U(VI)-free Fe(III) oxide suspensions (PBAGW with 10 mM $NaHCO_3$) to generate abundant surface-associated Fe(II). Briefly, the culture bottles were prepared in the anaerobic chamber, capped with thick butyl rubber stoppers, crimp sealed, and autoclaved. Washed *G. sulfurreducens* cells were added to obtain a cell density of approximately $10^8$ cells $mL^{-1}$ (ca. 40 mg dry weight $L^{-1}$). Sodium acetate (10 mM) served as the electron donor for biological reduction of Fe(III). The cultures were incubated statically at 22 °C in an anaerobic chamber, and total Fe(II) concentration was monitored. The suspensions were then divided in half, and one of the suspensions was pasteurized (80 °C) for 15 min. U(VI) was then added (0.1 mmol $L^{-1}$), and concentrations of Fe(II) and U(VI) were monitored over time. In one experiment, pasteurized suspensions were amended with 2.5 mM $AH_2DS$. $AH_2DS$ is the reduced form of the quinone-bearing humic analogue AQDS (*49*, *50*), which was shown in previous studies to efficiently reduce U(VI) associated with enzymatically inaccessible soil surfaces (*25*). The $AH_2DS$ was produced by exposing 20 mM AQDS (Sigma, St. Louis, MO) in 10 mM Pipes buffer to a 100% $H_2$ headspace for several days in the presence of several palladium-coated silica pellets (Sigma, St. Louis, MO) (*50*).

**Analytical Techniques.** Samples for dissolved Fe(II) were filtered (0.2-$\mu$m syringe filter), and an aliquot of the filtrate was added to 5 mL of ferrozine reagent (1 g $L^{-1}$ ferrozine in 50 mM Hepes) in the anaerobic chamber. After 10 min, the samples were removed and the absorbance at 562 nm was determined with a Shimadzu UV-1201V spectrophotometer. Total Fe(II) was determined by adding a 0.5-mL aliquot of suspension to 5 mL of 0.5 N HCl. The solution was then removed from the anaerobic chamber and extracted on a rotary shaker for 1 h. The samples were filtered (0.2 $\mu$m) and analyzed using ferrozine. Dissolved and total U(VI) concentrations were analyzed with a Kinetic Phosphorescence Analyzer (KPA; Chemcheck Instruments, Richland, WA). Samples for dissolved U(VI) were filtered (0.2 $\mu$m) and acidified (0.01 N $HNO_3$ final concentration) in the anaerobic chamber. For total U(VI), a 1-mL aliquot of suspension was dispensed into 9 mL of anoxic 100 mM bicarbonate solution, and the samples were placed on a rotary shaker for more than 1 h. The samples were then filtered, acidified, and analyzed with the KPA. Preliminary studies showed that the 100 mM $NaHCO_3$ extraction recovered 93.8 ± 7.2% ($n = 18$), 95.8 ± 7.7 ($n = 18$), and 98.6 ± 3.3% ($n = 12$) of U(VI) added to sterile suspensions of synthetic goethite, synthetic hematite, and APS [50 mmol $L^{-1}$ as Fe(III)] over a 6-d incubation period. In addition, a previous study demonstrated that uranium redox speciation [i.e., the ratio of U(VI) to U(IV)] in reduced sediments determined by $NaHCO_3$ extraction and KPA analysis was similar to that determined by U $L_3$ edge XANES analysis (*25*)

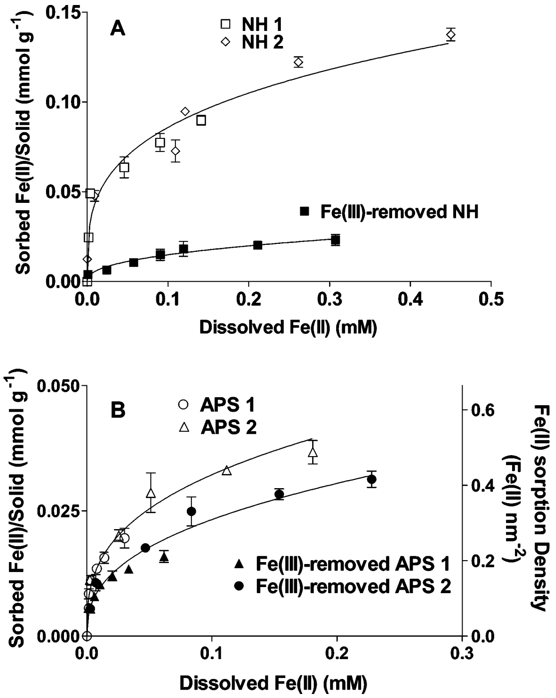

**FIGURE 1. Fe(II) sorption isotherms to NH and Fe(III) oxide removed NH (A) and to APS and Fe(III) oxide-removed APS (B) at pH 6.8 in 0.01 M Pipes solution. [NH] = 4 g $L^{-1}$ (25 mmol Fe(III) $L^{-1}$) and [APS] = 8.7 g $L^{-1}$ (4.9 mmol Fe(III) $L^{-1}$). The labels 1 and 2 correspond to separate experiments. Error bars represent standard deviation of triplicate measurements. Solid lines are nonlinear least-squares regression fits of the data to the Freundlich equation: $q = K_fC^n$, where $q$ and $C$ are the concentration of Fe(II) on the solid (mmol $g^{-1}$) and in the aqueous phase (mM), respectively. The estimated values of $K_f$ and $n$ are listed in Table S1, Supporting Information, along with $r^2$ values for the nonlinear regression analyses.**

## Results

**Fe(II) and U(VI) Sorption.** Fe(II) sorption isotherms to NH, Fe(III) oxide-removed NH, APS, and Fe(III) oxide-removed APS showed a wide range of Fe(II) sorption density among the investigated solid phases at pH 6.8. The maximum Fe(II) sorption density to NH was 3.2 sites per $nm^2$ while the maximum Fe(II) sorption densities to APS, Fe(III) oxide-removed APS, and Fe(III) oxide-removed NH were 0.5, 0.4, and 0.5 sites per $nm^2$, respectively (see Figure 1 and Table 1). The sorption density on NH was comparable to sorption on synthetic hematite and goethite, estimated to be 2.5 sites per $nm^2$ at pH 6.8 (*41*) and 1.6 sites per $nm^2$ at pH 7.0 (*42*). Removal of C/D Fe(III) from NH (initially rich in Fe(III) oxide) decreased the maximum sorption of Fe(II) from 3.2 to 0.5 sites per $nm^2$ while removal of C/D Fe(III) from APS resulted in only a 20% decrease in maximum sorption of Fe(II). Most of the sorbed Fe(II) in APS was attached to non-Fe(III) oxide phases in the APS material.

U(VI) sorbed rapidly to APS and goethite. More than 95% of the total amount of U(VI) that sorbed after 20 d was sorbed within the first 8 h (Figure 2A), in agreement with previous observations (*9*) for sorption of U(VI) on several natural materials from U.S. DOE sites. U(VI) showed a much higher sorption affinity to synthetic goethite than to natural solids on the basis of unit mass or surface area (see Figure 2 legend for mass and surface area loadings for the different systems) under the investigated conditions. U(VI) sorption was nonlinear (Figure 2B) and the magnitude of U(VI) sorption to APS was not significantly lowered by the removal of Fe(III) oxide up to 30 $\mu$M of equilibrium U(VI) concentration (see Figure 2B). Most of our U(VI) reduction experiments were conducted using equilibrium U(VI) concentration below 5

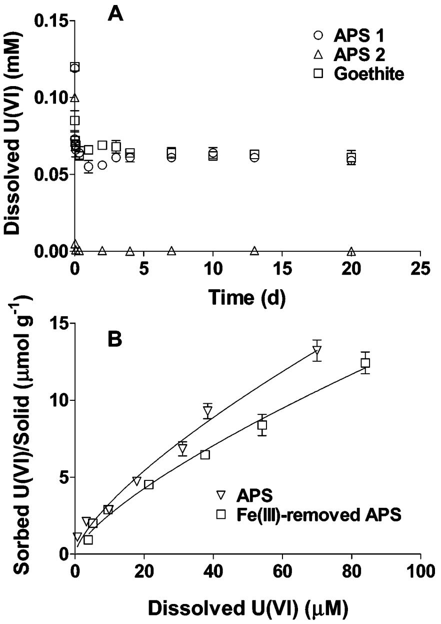

**FIGURE 2. (A) U(VI) sorption kinetics to APS and goethite at pH 6.8 in 0.01 M Pipes solution in the presence of 0.01 M bicarbonate. Experiment APS 1: [U(VI)] = 0.12 mmol L$^{-1}$, [Fe(III)] = 4.5 mmol L$^{-1}$ (394 m$^2$ L$^{-1}$); experiment APS 2: [U(VI)] = 0.1 mmol L$^{-1}$, [Fe(III)] = 45 mmol L$^{-1}$ (3941 m$^2$ L$^{-1}$); goethite experiment: [U(VI)] = 0.12 mmol L$^{-1}$, [Fe(III)] = 11.3 mmol L$^{-1}$ (55.2 m$^2$ L$^{-1}$). (B) U(VI) sorption isotherms to APS and Fe(III)-removed APS ([solid] = 8.9 g L$^{-1}$). Error bars represent standard deviation of triplicate measurements. Solid lines are nonlinear least-squares regression fits of the data to the Freundlich equation. The estimated values of $K_f$ and $n$ are listed in Table S2, Supporting Information, along with $r^2$ values for the nonlinear regression analyses.**

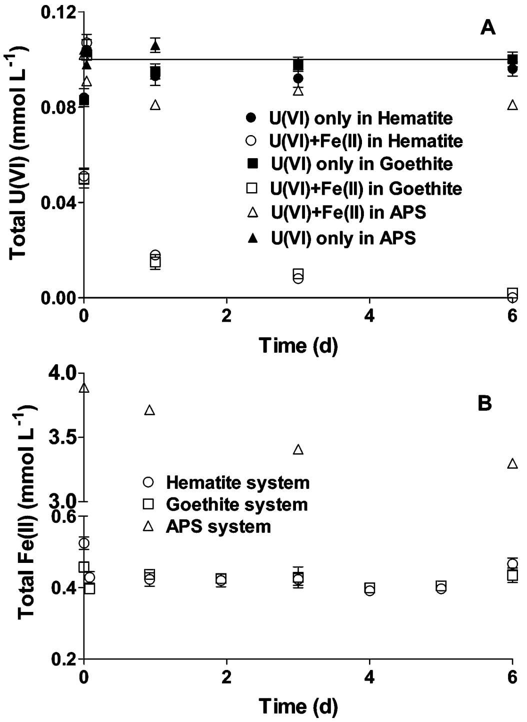

**FIGURE 3. Abiotic reduction of U(VI) (A) and recovery of Fe(II) (B) in Fe(II)-spiked Fe(III) oxide suspensions. [U(VI)] = 0.1 mmol L$^{-1}$; [Fe(II)] = 0.6 mmol L$^{-1}$ for hematite and goethite or 4.0 mmmol L$^{-1}$ for APS; [goethite] = 22.5 mmol L$^{-1}$, [hematite] = 62.5 mmol L$^{-1}$ as Fe(III), and [APS] = 50 mmol L$^{-1}$ as Fe(III) (89 g L$^{-1}$). Error bars represent standard deviation of triplicate measurements. Data points for APS system represent the mean of duplicate measurements. The dashed horizontal line in A represents the added amount of U(VI) (0.1 mmol L$^{-1}$).**

μM, at the low end of the experimental range shown in Figure 2B. A substantial decrease (up to 20%) in U(VI) sorption to Fe(III) oxide-removed APS was observed for the higher equilibrium U(VI) concentrations compared with the sorption of U(VI) to APS, which may imply U(VI) adsorption to different types of sites as a function of surface loading (*9*).

**Abiotic U(VI) Reduction in Fe(II)-Amended Systems.** More than 95% of added 0.1 mM U(VI) was sorbed within 3 h in suspensions of synthetic hematite, goethite, and natural Fe(III) oxide-containing APS (data not shown). Rapid and complete reduction of sorbed U(VI) was observed in the Fe(II)-spiked [0.6 mmol L$^{-1}$ total Fe(II)] synthetic goethite [0.29 mmol L$^{-1}$ of sorbed Fe(II)] and hematite [0.19 mmol L$^{-1}$ of sorbed Fe(II)] suspensions (Figure 3A).The total Fe(II) content of the suspensions (0.5 M HCl extraction) declined by ca. 0.17 mmol L$^{-1}$ (Figure 3B) within 1 d, close to the 0.2 mmol L$^{-1}$ that was expected on the basis of 1:2 stoichiometry between U(VI) and Fe(II). In contrast to the results obtained with synthetic hematite and goethite, less than 20% of U(VI) was reduced within 6 d in the Fe(II)-spiked APS suspension (Figure 3A). Reaction time up to 20 d did not result in an increase in abiotic reduction of U(VI) (data not shown). The poor U(VI) reduction in APS suspension was not due to lack of U(VI) sorption, as more than 95% of added 0.1 mmol L$^{-1}$ U(VI) was sorbed within 3 h (Figure 2A), nor was it due to lack of sorbed Fe(II), as more than 80% of the added Fe(II) [3.3 mmol L$^{-1}$ of sorbed Fe(II)] was rapidly adsorbed by APS surfaces. Moreover, in all Fe(II) amended suspensions, the amount of added Fe(II) was enough to saturate the available sorption sites on the solids. Although total Fe(II) concentrations decreased by ca. 0.5 mmol L$^{-1}$ during the 6-d experiment (Figure 3B), Fe(II) remained in vast excess relative to U(VI). The decrease in total 0.5 M HCl-extractable Fe(II) can be attributed to conversion to magnetite or other mixed Fe(II)−Fe(III) phases (*32*, *47*), to oxidation by manganese(IV) oxide in some natural materials (*51*), or to the presence of other unidentified electron sinks in the natural materials.

**Reduction of U(VI) in Biogenic Fe(II)-Rich Heat-Killed Systems.** A series of experiments were conducted using heat-killed suspensions of both synthetic Fe(III) oxides and natural materials that contained Fe(II) produced by *G. sulfurreducens*. The suspensions were pasteurized prior to addition of U(VI) to terminate enzymatic reduction activity. Preliminary studies verified that pasteurization effectively stopped metal reduction by *G. sulfurreducens* and had no major influence on the relative abundance of aqueous versus solid-associated Fe(II). More than 95% of the added U(VI) rapidly (<3 h) associated with the solid phases, despite "presaturation" of sorption sites with biogenic Fe(II). This result indicates that anionic U(VI)-carbonate might occupy different sorption sites than those occupied by cationic Fe(II).

The rate and extent of U(VI) reduction in bioreduced hematite and goethite systems was comparable to results obtained in FeCl$_2$-spiked systems (compare Figure 3A and 4A). U(VI) reduction in heat-killed biogenic magnetite (BM) suspension was instantaneous, presumably because of the reducing capacity both by sorbed Fe(II) (*4*, *19*) and by structural Fe(II) (*20*, *21*). The behavior of uranium in heat-killed suspensions of microbially reduced APS and OS (and other natural materials; see below) was surprising: rapid U(VI) reduction occurred during the first few days of incubation, followed by regeneration of U(VI) for both natural materials (Figure 4A). A second cycle of U(VI) reduction and U(IV) oxidation was observed between days 30 and 50. A vast excess of sorbed Fe(II) was present throughout the apparent uranium redox cycles (Figure 4B).

To confirm the results obtained with the coastal plain sediments, APS and OS (oyster sand), six other natural

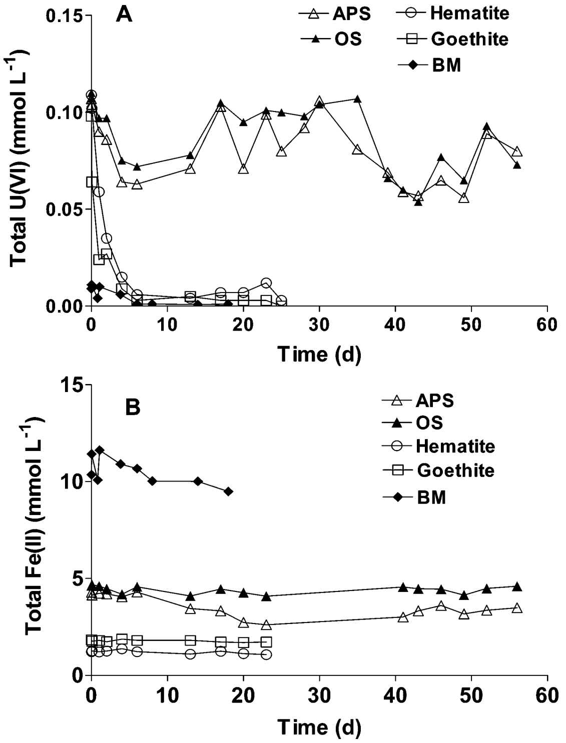

FIGURE 4. Abiotic reduction of U(VI) in the suspension of heat-killed synthetic Fe(III) oxides and natural materials. Each suspension contained a bulk Fe(III) oxide concentration of 50 mmol $L^{-1}$. Fe(III) oxide bioreduction by *G. sulfurreducens* ($10^8$ cell $mL^{-1}$) was allowed to proceed for 8−10 d prior to addition of U(VI). Data points show the mean of duplicate measurements.

Fe(III) oxide-bearing materials were used for U(VI) reduction experiments in heat-killed systems (Figure 5A). Rapid and complete U(VI) sorption took place with all of the materials, except the Hanford Paleosol, which sorbed only 35% of added U(VI) after 1 week of reaction. The behavior of added U(VI) was significantly different in the hematite-enriched (NH) and goethite-enriched (natural goethite, designated NG) sediments from Eatontown, NJ, compared to the other suspensions. Rapid and extensive U(VI) reduction occurred in these suspensions (Figures 5A) similar to results obtained with heat-killed suspensions of microbially reduced synthetic crystalline Fe(III) oxides (Figure 4A), although the extent of U(VI) reduction in the NG suspension was lower than in the synthetic goethite system.

The behavior of uranium in heat-killed suspensions of the other microbially reduced natural materials was analogous to that observed in the APS and OS suspensions: U(VI) was partially reduced during the first 5 days of incubation, followed by repetitive cycles of oxidation and reduction (Figure 5A). Virtually no U(VI) reduction occurred in the heat-killed Paleosol suspension, possibly because of poor sorption of U(VI) or the formation of nonreducible calcium/uranium carbonate complexes. High concentration of dissolved calcium (ca. 2.5 mM $Ca^{2+}$ compared to <0.3 mM $Ca^{2+}$ in the other suspensions) was observed in the Paleosol suspension. The addition of calcium at neutral pH reportedly resulted in inhibition of enzymatic reduction of both sorbed and dissolved U(VI) (*25*, *52*) and may by analogy inhibit abiotic, Fe(II)-driven U(VI) reduction. When 2.5 mM $AH_2DS$ was added to heat-killed systems, a significant decline in U(VI) concentration (≥70% loss) occurred within 14 d (Figure 5C). The major decline in U(VI) took place following a sharp increase in Fe(II) abundance associated with reduction of residual Fe(III) oxides by $AH_2DS$ (Figure 5C and 5D).

## Discussion

**U(VI) Reduction in the Presence of Synthetic versus Natural Fe(III) Oxide-Containing Materials.** This study demonstrated rapid and extensive chemical reduction of U(VI) because of contact with Fe(II) plus synthetic Fe(III) oxides or natural materials that contained high concentrations of Fe(III) oxides (hematite, goethite, NH, or NG). The C/D-extractable Fe was 18−69 wt % and the Fe(II) sorption site densities were more than 1.6 Fe(II) per $nm^2$ for these materials

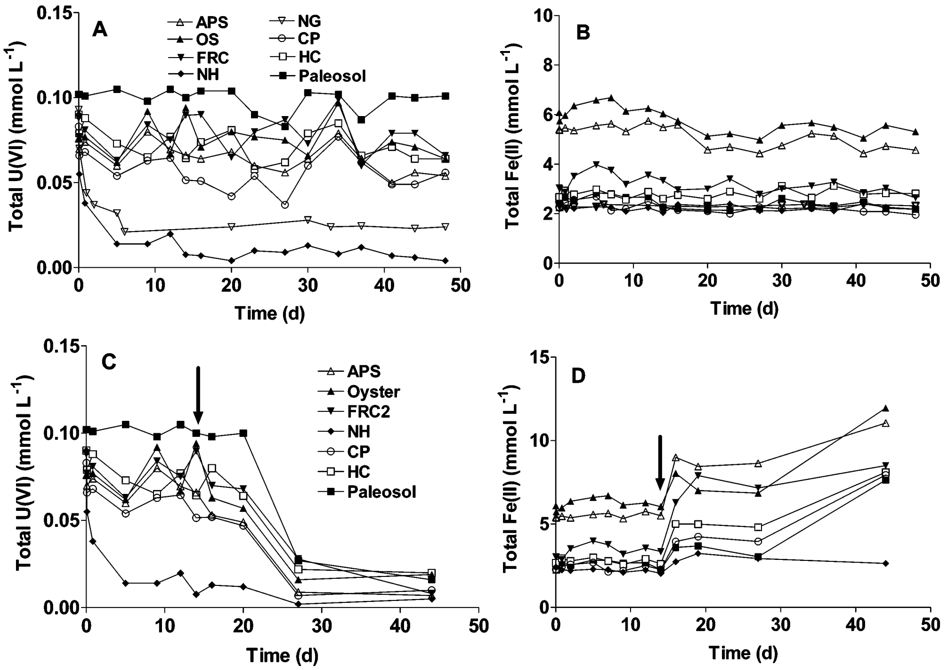

FIGURE 5. Abiotic U(VI) reduction in the suspension of heat-killed natural materials with (panels C and D) and without (panels A and B) 2.5 mM $AH_2DS$. Each suspension contained a bulk Fe(III) oxide concentration of 50 mmol $L^{-1}$. Fe(III) oxide bioreduction was allowed to proceed for 8−10 d prior to addition of U(VI). Arrow indicates time of $AH_2DS$ addition. Data points show the mean of duplicate measurements.

(see Table 1). The efficient Fe(II)-driven reduction of U(VI) in the presence of synthetic Fe(III) oxides was consistent with other recent experimental studies (*4*, *19*, *20*). In addition, rates of abiotic U(VI) reduction in these systems were comparable to rates of biological reduction of dissolved U(VI)-carbonate complexes observed in previous studies (*23*, *25*, *53*, *54*).

In contrast, the long-term net U(VI) reduction was less than 30% in abiotic suspensions of six natural solids with low Fe(III) content (APS, OS, HC, CP, FRC, and Paleosol) despite the presence of a large stoichiometric excess of either added or biogenic Fe(II). These low Fe(III) materials contained 1−5 wt % C/D extractable Fe, and Fe(II) sorption site densities ranged from 0.2 to 1.1 Fe(II) per nm$^2$ which was significantly less than the synthetic Fe(III) oxides and the natural solids that were rich in Fe(III) oxide. These findings agree with previous observations of incomplete or negligible reduction of U(VI) in Fe(II)-rich heat-killed aquatic (*3*) or aquifer (*18*, *22*) sediments.

The poor abiotic reduction of sorbed U(VI) by Fe(II) sorbed to the natural Fe(III) oxide-containing materials suggests the possibility that surface site heterogeneity of the sorbent may control the potential for abiotic U(VI) reduction by sorbed Fe(II) in natural sedimentary environments. Natural soils and sediments contain a wide variety of sorption sites and other ion exchange sites (e.g., on secondary soil minerals such as kaolinite and montmorillonite) (*55*) which have different sorption affinities for metal ions than Fe(III) oxides. The soluble speciation of U(VI) was dominated by carbonato complexes and U(VI)-carbonate surface complexes may also have been important in our experimental systems (*5*, *7*, *8*, *11*, *56*). The anionic U(VI) and the cationic Fe(II) sorbates would have different affinities for various sorption sites. For heterogeneous electron transfer to occur at the oxide surface, Fe(II) and U(VI) atoms must be properly coordinated so that electrons can be transferred from Fe(II) to U(VI) (*19*, *57*). If U(VI) adsorbs to surface sites where Fe(II) is either (i) not present or (ii) not properly coordinated, U(VI) may not be reduced even though Fe(II) is present in vast excess in the suspension. Significantly lower Fe(II) sorption density on natural materials (see Table 1) could potentially limit the ability of Fe(II) and U(VI) to obtain the surface coordination and subsequent orbital overlap (*57*) required for efficient electron transfer. An alternative explanation is that sorption of U(VI) within micropores could limit the access to Fe(II) or vice versa. The natural materials had 1−2 orders of magnitude greater total microporosity (<20 Å pore width) than for the synthetic hematite (*25*).

Extensive U(VI) reduction occurred within 2 weeks after addition of 2.5 mM AH$_2$DS in all suspensions containing natural materials (Figure 5C). Direct reduction of U(VI) by AH$_2$DS is consistent with the observed reduction of the solid-phase U(VI) mineral metaschoepite by AH$_2$DS (*4*). The reduction of U(VI) by AH$_2$DS was also demonstrated by biotic experiments in which there was complete and rapid reduction of U(VI), including U(VI) sorbed to enzymatically inaccessible surface sites (*25*). It is possible that AH$_2$DS reacted with U(VI) bound to chemically and biologically inaccessible surface sites or that a more reactive or mobile form of Fe(II) was produced upon addition of AH$_2$DS, indirectly resulting in further reduction of U(VI) (see Figure 5C and 5D). The incomplete reduction of U(VI) in the presence of the low-Fe(III) natural solids and AH$_2$DS (compare NH with other solids in Figure 5C) could be attributed to (i) competition between Fe(III) oxides and U(VI) for a limited quantity of chemical reductant (generally evidenced by the significant increase in Fe(II) abundance that took place prior to U(VI) reduction; see Figure 5C and 5D) or (ii) surface Fe/U redox cycling analogous to that observed in other abiotic reaction systems.

**Uranium Redox Cycling in Abiotic Systems.** Long-term patterns of U(VI) recovery in heat-killed, Fe(II)-rich abiotic systems containing natural materials suggested that uranium oscillated (albeit erratically) between the +6 and more reduced oxidation states over time (Figures 4A and 5A). This oscillation of total U(VI) concentration occurred only in the abiotic systems; parallel biological reduction systems (*25*) exhibited smooth decreases in residual U(VI), without the jagged curve shapes in Figures 4A and 5A. We tentatively attribute these results to the formation of new phases of Fe(III) oxide and UO$_{2(s)}$ during the course of the experiments. It has been demonstrated that some Fe(III) oxides serve as oxidants for U(IV) (*24*). This sequence of events can be summarized by the following reaction scheme:

$$2{\equiv}\mathrm{SOH} + 2\mathrm{Fe}^{2+} + 2\mathrm{H_2O} \rightarrow 2{\equiv}\mathrm{SOFe^{II}OH} + 4\mathrm{H}^+ \quad \text{(Fe(II) sorption)}$$

$$2{\equiv}\mathrm{SOH} + \mathrm{U^{VI}O_2}^{2+} \rightarrow ({\equiv}\mathrm{SO})_2(\mathrm{U^{VI}O_2}) + 2\mathrm{H}^+ \quad \text{(U(VI) sorption)}$$

$$2{\equiv}\mathrm{SOFe^{II}OH} + ({\equiv}\mathrm{SO})_2(\mathrm{U^{VI}O_2}) + 2\mathrm{H}^+ \rightarrow 2{\equiv}\mathrm{SOFe^{III}OH}^+ + 2{\equiv}\mathrm{SOH} + \mathrm{U^{IV}O_{2(s)}} \quad \text{(U(VI) reduction)}$$

$$2{\equiv}\mathrm{SOFe^{III}OH}^+ + 2{\equiv}\mathrm{SOH} + \mathrm{U^{IV}O_{2(s)}} \rightarrow 2{\equiv}\mathrm{SOFe^{II}OH} + ({\equiv}\mathrm{SO})_2(\mathrm{U^{VI}O_2}) + 2\mathrm{H}^+ \quad \text{(U(IV) oxidation)}$$

where $\equiv$SOH represents a surface sorption site, $\equiv$SOFe$^{II}$OH is sorbed biogenic Fe(II), $(\equiv SO)_2(U^{VI}O_2)$ is sorbed U(VI), $\equiv$SOFe$^{III}$OH$^+$ is sorbed Fe(III), and $U^{IV}O_{2(s)}$ represents precipitated uraninite that could be attached to the ferric oxide surface. Changes in the solubility or sorptive sites and sorption capacity of Fe(III) oxides and U(IV) oxides can result in changes in sorption site reactivity and in redox potential, possibly contributing to the observed cycling between U(IV) and U(VI). Though speculative, this mechanism may help to explain the incomplete long-term net abiotic U(VI) reduction by the bioreduced natural materials. The absence of such oscillations in biological reduction systems can be attributed to rapid reduction by DMRB activity of any amorphous Fe(III) oxide surface precipitates that might arise from surface-bound Fe(II)-catalyzed U(VI) reduction and to maintenance of a low redox potential thorough scavenging of reactive electron acceptors. Uranium redox cycling was not observed in the suspensions of synthetic Fe(III) oxides and Fe(III)-enriched natural materials (Figures 4A and 5A) which have higher Fe(II) sorption density (>1.6 Fe(II) per nm$^2$), which suggests that Fe(II) sorption density is not only important for efficient U(VI) reduction but also for regulating reoxidation of reduced uranium.

**Summary and Environmental Relevance.** This study documents a major contrast in the rate and long-term extent of abiotic Fe(II)-driven U(VI) reduction between synthetic Fe(III) oxides and natural soils and sediments with relatively low Fe(III) oxide abundance (e.g., <ca. 5 wt %) and Fe(II) sorption density (<ca. 1.1 Fe(II) nm$^{-2}$). These results demonstrate that the potential for abiotic Fe(II)-driven U(VI) reduction in natural systems cannot be accurately inferred from studies with synthetic Fe(III) oxides (*19*). A key implication of our findings is that production of Fe(II)-enriched sediments during one-time (or periodic) stimulation of DMRB activity is not likely to permit efficient long-term abiotic conversion of U(VI) to U(IV) in biogenic redox barriers designed to prevent far-field subsurface U(VI) migration (*15*). Instead, our results suggest that ongoing DMRB activity will be required to achieve maximal U(VI) reduction efficiency. Development of a detailed understanding of patterns of DMRB growth, colonization, and maintenance in physically and chemically heterogeneous subsurface environments will

therefore be required to predict the effectiveness of subsurface U(VI) bioremediation operations.

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## Supporting Information Available

Two tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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