University of Nebraska - Lincoln

DigitalCommons@University of Nebraska - Lincoln

US Department of Energy Publications

U.S. Department of Energy

2009

Heterogeneous reduction of Tc(VII) by Fe(II) at the solid–water interface

T. Peretyazhko

Pacific Northwest National Laboratory, tetyana.peretyazhko@pnl.gov

John M. Zachara

Pacific Northwest National Laboratory, john.zachara@pnl.gov

S.M. Heald

Argonne National Laboratory

B.-H. Jeon

Yonsei University

Ravi K. Kukkadapu

Pacific Northwest National Laboratory, ravi.kukkadapu@pnl.gov

See next page for additional authors

Follow this and additional works at: <https://digitalcommons.unl.edu/usdoepub>

Part of the [Bioresource and Agricultural Engineering Commons](#)

Peretyazhko, T.; Zachara, John M.; Heald, S.M.; Jeon, B.-H.; Kukkadapu, Ravi K.; Liu, C.; Moore, D.; and Resch, C.T., "Heterogeneous reduction of Tc(VII) by Fe(II) at the solid–water interface" (2009). *US Department of Energy Publications*. 163.

<https://digitalcommons.unl.edu/usdoepub/163>

This Article is brought to you for free and open access by the U.S. Department of Energy at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in US Department of Energy Publications by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.

Authors

T. Peretyazhko, John M. Zachara, S.M. Heald, B.-H. Jeon, Ravi K. Kukkadapu, C. Liu, D. Moore, and C.T. Resch

Heterogeneous reduction of Tc(VII) by Fe(II) at the solid–water interface

T. Peretyazhko^{a,*}, J.M. Zachara^a, S.M. Heald^c, B.-H. Jeon^b, R.K. Kukkadapu^a,
C. Liu^a, D. Moore^a, C.T. Resch^a

^a Pacific Northwest National Laboratory, P.O. Box 999, MS K8-96, Richland, WA 99354, USA

^b Yonsei University, Kangwon-Do 220-710, Republic of Korea

^c Argonne National Laboratory, Argonne, IL 60439, USA

Received 7 September 2007; accepted in revised form 11 January 2008; available online 26 January 2008

Abstract

Experiments were performed herein to investigate the rates and products of heterogeneous reduction of Tc(VII) by Fe(II) adsorbed to hematite and goethite, and by Fe(II) associated with a dithionite–citrate–bicarbonate (DCB) reduced natural phyllosilicate mixture [structural, ion-exchangeable, and edge-complexed Fe(II)] containing vermiculite, illite, and muscovite. The heterogeneous reduction of Tc(VII) by Fe(II) adsorbed to the Fe(III) oxides increased with increasing pH and was coincident with a second event of Fe²⁺_(aq) adsorption. The reaction was almost instantaneous above pH 7. In contrast, the reduction rates of Tc(VII) by DCB-reduced phyllosilicates were not sensitive to pH or to added Fe²⁺_(aq) that adsorbed to the clay. The reduction kinetics were orders of magnitude slower than observed for the Fe(III) oxides, and appeared to be controlled by structural Fe(II). The following affinity series for heterogeneous Tc(VII) reduction by Fe(II) was suggested by the experimental results: aqueous Fe(II) ~ adsorbed Fe(II) in phyllosilicates [ion-exchangeable and some edge-complexed Fe(II)] ≪ structural Fe(II) in phyllosilicates ≪ Fe(II) adsorbed on Fe(III) oxides. Tc-EXAFS spectroscopy revealed that the reduction products were virtually identical on hematite and goethite that were comprised primarily of sorbed octahedral TcO₂ monomers and dimers with significant Fe(III) in the second coordination shell. The nature of heterogeneous Fe(III) resulting from the redox reaction was ambiguous as probed by Tc-EXAFS spectroscopy, although Mössbauer spectroscopy applied to an experiment with ⁵⁶Fe-goethite with adsorbed ⁵⁷Fe(II) implied that redox product Fe(III) was goethite-like. The Tc(IV) reduction product formed on the DCB-reduced phyllosilicates was different from the Fe(III) oxides, and was more similar to Tc(IV) oxyhydroxide in its second coordination shell. The heterogeneous reduction of Tc(VII) to less soluble forms by Fe(III) oxide-adsorbed Fe(II) and structural Fe(II) in phyllosilicates may be an important geochemical process that will proceed at very different rates and that will yield different surface species depending on subsurface pH and mineralogy.

© 2008 Elsevier Ltd. All rights reserved.

1. INTRODUCTION

⁹⁹Technetium (⁹⁹Tc) is a long-lived ($t_{1/2} = 2.13 \times 10^5$ years) fission product of ²³⁵uranium, and an important subsurface contaminant at nuclear reprocessing sites (Wildung et al., 1979). Its speciation, solubility and sorption behavior is strongly dependent on its valence state. Under oxic conditions, Tc exists in its most oxidized form as the

pertechnetate [TcO₄[−]] anion which is weakly sorbed under circumneutral and basic pH conditions (Lieser and Bauscher, 1987; Holta et al., 1992; Wildung et al., 2004). It is consequently highly mobile in groundwaters (Schroeder et al., 1993) and soils with potential for uptake into the food chain as a sulfur analog (Wildung et al., 1979; Bennett and Willey, 2003). The reduced form of technetium, Tc(IV), is stable in anoxic environments and forms sparingly soluble phases primarily TcO₂·*n*H₂O_(s) (Bondietti and Francis, 1979; Rard et al., 1999; Wildung et al., 2000).

* Corresponding author. Fax: +1 509 376 3650.

E-mail address: tetyana.peretyazhko@pnl.gov (T. Peretyazhko).

The reduction of Tc(VII) may occur directly through biologic enzymatic pathways (Lloyd et al., 2000; Wildung et al., 2000) and/or indirectly by Fe(II) and S^{2-} (Wharton et al., 2000; Fredrickson et al., 2004; Wildung et al., 2004). The relative importance of these different reduction pathways depends on environmental conditions. For instance, in non-sulfidogenic sediments, Tc(VII) reduction is controlled by reactive Fe(II) or by direct microbial reduction when Fe(II) is not present in stoichiometric excess [Fe(II):Tc(VII) = 3:1; (Lloyd et al., 2000; Wildung et al., 2004; Burke et al., 2005)]. Ferrous iron is produced in soils, sediments, and subsurface materials by chemical (Stumm and Sulzberger, 1992; Roden, 2004; Szecsody et al., 2004; Anschutz and Penn, 2005; Hyacinthe et al., 2006; Larsen et al., 2006) or biological (Fredrickson et al., 1998; Zachara et al., 1998; Kukkadapu et al., 2001, 2006; Roden, 2004; Komlos et al., 2007; Stucki et al., 2007) reductive dissolution of Fe(III) (hydr)oxides and/or reduction of phyllosilicate Fe(III), which exert an important influence on Tc valence speciation.

Iron(II) in anoxic subsurface environments affects the distribution, transport, and biogeochemistry of redox-sensitive chemical contaminants by sorption onto mineral surfaces and by heterogeneous reduction. Sorbed Fe(II) is a stronger reducing agent than dissolved Fe(II) (Jolivet et al., 1990; Stumm and Sulzberger, 1992; Haderlein and Pecher, 1999; Liger et al., 1999; Silvester et al., 2005). Iron(II) sorbed on various Fe(III) oxides enhances the reduction rates of nitrite (Sorensen and Thorling, 1991; Hansen et al., 1996; Coby and Picardal, 2005), hexavalent uranium (Liger et al., 1999; Behrends and Van Cappellen, 2005; Jeon et al., 2005), chromate (Buerge and Hug, 1999), and various organic species (Klausen et al., 1995; Charlet et al., 1998; Kim and Picardal, 1999; Amonette et al., 2000; Pecher et al., 2002; Hofstetter et al., 2003; Strathmann and Stone, 2003; Elsner et al., 2004; Gregory et al., 2004; Chun et al., 2006; Colon et al., 2006). The molecular nature and redox properties of surface Fe(II) responsible for heterogeneous reduction is still under active investigation and debate (e.g., Williams and Scherer, 2004; Silvester et al., 2005). Structural Fe(II) in magnetite, green rusts, and phyllosilicates can also be an effective reductant of redox-sensitive inorganic and organic molecules (Cui and Eriksen, 1996a; Hansen et al., 1996; Hofstetter et al., 2003, 2006). Generalizing the redox reactivity of mineral associated Fe(II) in surface-complexed, surface-precipitated, and structural states on different mineral phases with different aqueous oxidants has been found to be difficult (e.g., Strathmann and Stone, 2003; Elsner et al., 2004).

The reduction of Tc(VII) by sorbed or structural Fe(II) has been observed in reduced sediments (Fredrickson et al., 2004; Wildung et al., 2004), and with mineral sorbents (Cui and Eriksen, 1996a; Cui and Eriksen, 1996b; Lloyd et al., 2000; Pepper et al., 2003). Beyond these studies, heterogeneous reduction has not been systematically investigated to identify the influence of variables such as pH, sorbed Fe(II) concentration and effective redox potential, and nature of solid surface on Tc(VII) reduction rate or products. Fredrickson et al. (2004) noted large differences in the heterogeneous reduction rate of Tc(VII) in a sediment with sig-

nificant amounts of Fe(III) oxides as compared to one dominated by phyllosilicates, but did not identify the primary causes for this behavior. An improved understanding of the geochemical factors controlling heterogeneous reduction is thus necessary to assess the valence stability of Tc in various environments, and for predicting Tc(VII) migration in natural and engineered systems.

This communication extends a recent study of Tc(VII) reduction by aqueous Fe(II) (Zachara et al., 2007) to heterogeneous systems. We investigate the rates and extent of heterogeneous Tc(VII) reduction by sorbed and structural Fe(II), and identify the nature of reduced, precipitated Tc(IV)-containing reaction products. Key to this investigation was a comparison between heterogeneous Tc(VII) reduction in suspensions of synthetic Fe(III) oxides with sorbed Fe(II), with a natural phyllosilicate mixture containing structural Fe(II) and variable concentrations of ion-exchangeable Fe(II). This comparison revealed that the nature of sorbed and/or structural Fe(II) can have a strong influence on the kinetics and products of heterogeneous Tc(VII) reduction.

2. MATERIALS AND METHODS

2.1. Kinetic experiments

All experimental work was performed in a 97% Ar/3% H_2 atmosphere inside an anaerobic chamber (Forma Scientific, OH) that was equipped with a palladium catalyst to remove trace O_2 . Despite these precautions, it was discovered that the chamber contained up to 4×10^{-7} atm O_2 [corresponding to 0.29 ppm O_2 in the chamber atmosphere (Jeon et al., 2004)]. The presence of this trace amount of O_2 resulted in significant oxidation of Fe(II) in circumneutral pH solution open to the glove box atmosphere. Consequently, all experiments with Fe(II) were conducted using a low-temperature oxygen trap described by (Jeon et al., 2004). The O_2 trap bottles contained 0.9 mmol L^{-1} Fe(II) and 23.3 mmol L^{-1} Fe(III) as hydrous ferric oxide (HFO) that was buffered at pH 8.1 with 0.1 mol L^{-1} tris(hydroxymethyl)-aminomethane (TRIS). The half-time for O_2 reduction in the suspension phase of the oxygen trap was less than 0.5 s and the half-time for transfer of O_2 from the gas phase within the traps to the water phase was 6 min. The trap lowered O_2 concentrations to $<7.5 \times 10^{-9}$ atm O_2 (Jeon et al., 2004). Using this trap, solutions of Fe(II) could be maintained at pH 7 and 8 for more than 2 weeks without oxidation.

Experiments were conducted in 125 or 200 mL glass serum reaction bottles (referred to as master reactors). The solution pH in master reactors was varied from 4 to 7 using 30 mmol L^{-1} Na-acetate for pH 4.0–5.0, or 30 mmol L^{-1} PIPES (Na-1,4-piperazine *N,N*-bis 2-ethanesulfonic acid) for pH 5.5–7.0. Deoxygenated Na-acetate or PIPES buffer solution was added to the master reactors, then the reactors were capped with thick butyl rubber stoppers and crimp sealed. The master reactors were attached to the oxygen trap and deoxygenated. After 4 days of extensive deoxygenation of the reactors, isotopically enriched $^{57}Fe(II)$ solution was added first and monitored for 2–4 days to ensure stabil-

Table 1
Summary of experimental conditions and kinetic analyses

	pH	Solid concentration (g L ⁻¹)	Tc(VII) _{added} (μmol L ⁻¹)	Intrinsic Fe(II) ^a (mmol L ⁻¹)	Fe(II) _{added} (mmol L ⁻¹)	Nominal sorbed Fe (II) ^b (mmol L ⁻¹)	<i>k</i> _{obs} (h ⁻¹)	<i>k</i> _{obs} /Fe(II) _{sorbed}
Hematite	4.0	4.5	10.3 ± 0.1	0	0.10	0.0052 ± 0.0004	4 × 10 ⁻⁴	0.08
	4.5	4.5	10.3 ± 0.1	0	0.10	0.0049 ± 0.0002	0.01	2.04
	5.0	4.5	10.3 ± 0.1	0	0.10	0.0102 ± 0.0004	0.1	9.80
	5.6	4.5	10.2 ± 0.0	0	0.12	0.030 ± 0.004	6.06	202
	5.8	4.5	10.2 ± 0.0	0	0.12	0.033 ± 0.001	6.81	206
	6.1	4.5	10.2 ± 0.0	0	0.12	0.038 ± 0.001	11.91	313
	6.5	4.5	10.2 ± 0.0	0	0.10	0.038 ± 0.002	15.14	398
	7.0	4.5	10.3 ± 0.0	0	0.12	0.070 ± 0.002	>16.0	>228
Goethite	7.0	9.0	20.5 ± 0.0	0	0.23	0.160 ± 0.007	>16.0	>100
	7.0	1.5	10.3 ± 0.0	0	0.12	0.078 ± 0.001	>16.0	>205
FRC-dcb	7.0	3.0	20.5 ± 0.0	0	0.23	0.169 ± 0.002	>16.0	>94
	6.0	10.0	10.0 ± 0.2	0.114 ± 0.023	0	0	0.19	
	6.5	10.0	10.3 ± 0.0	0.100 ± 0.014	0	0	0.15	
	7.0	20.0	10.2 ± 0.1	0.154 ± 0.027	0	0	0.15	
	7.0	10.0	10.1 ± 0.0	0.093 ± 0.003	0.10	0.094 ± 0.006	0.18	1.91
FRC-dcb-HCl	7.0	20.0	10.1 ± 0.0	0.183 ± 0.014	0.20	0.198 ± 0.012	0.19	0.96
	7.0	20.0	10.6 ± 0.0	0	0	0	nr ^c	
	7.0	10.0	10.4 ± 1.2	0	0.10	0	nr	
	7.0	20.0	20.7 ± 0.0	0	0.20	0	nr	

^a Experimentally determined by 2 h 0.5-mol L⁻¹ HCl extraction.

^b Difference in dissolved Fe(II) concentration before and after sorbent spiking.

^c No reduction.

ity against oxidation or precipitation. Solid [Fe(III) oxide or phyllosilicate isolate] was added and 2 days equilibration time was allowed for Fe(II) adsorption. The suspensions were continuously and gently stirred using a Teflon-coated magnetic stirring bar. Tc(VII) was added to the master reactors after Fe(II) had reached adsorption equilibrium. Dissolved Fe(II), total Fe(II) and dissolved Tc(VII) concentrations were monitored from this point onward. The conditions of the reduction experiments are summarized in Table 1. The Tc(VII) aqueous concentrations used (10–20 μmol L⁻¹) were within the range of those observed in porewaters of Hanford's BC-crib complex (Serne and Mann, 2004; Ward et al., 2004) where over 400 Ci were released to the vadose zone.

2.2. Solid phases

Synthetic medium surface area (55 m² g⁻¹ by N₂-BET analysis) goethite (α-FeOOH) was produced by adjusting 0.4 mol L⁻¹ FeCl₃·6H₂O solution to pH 13 with 4 mol L⁻¹ NaOH and incubating the suspension at 70 °C for 16 h (Schwertmann and Cornell, 2000). The goethite was washed by centrifugation until the Cl⁻ concentration was <0.5 mmol L⁻¹, freeze-dried, and then passed through a 100-μm sieve. Hematite (α-Fe₂O₃) was purchased from J.T. Baker and had a specific surface area of 9 m² g⁻¹ by N₂-BET method and average particle diameter of 1.0 μm as determined by SEM particle counting.

A weathered shale–limestone saprolite (designated FRC) was obtained from the U.S. Department of Energy's (DOE) Environmental Remediation Sciences Division

(ERSD) Field Research Center (FRC) background site located in West Bear Creek Valley of DOE's Oak Ridge Site in eastern Tennessee. The FRC sample was air-dried and passed through a 2-mm sieve. The surface area measured by N₂-BET method was 32 m² g⁻¹.

The FRC sediment was treated with dithionite–citrate–bicarbonate (DCB; Stucki et al., 1984; Hofstetter et al., 2003) to reduce and remove Fe(III) and Mn(III/IV) oxides. This treatment yielded a natural phyllosilicate mixture with Fe(II/III) ratio significantly higher than the pristine sediment (Kukkadapu et al., 2006). A portion of DCB-treated FRC was further treated with 0.5 mol L⁻¹ HCl for 2 h. The weak-acid extraction partially remove Fe(II) from some reduced phyllosilicates (Kukkadapu et al., 2006), presumably from the smallest phyllosilicate size fraction of FRC (e.g., <0.2 μm) and edge-complexed Fe(II) (Hofstetter et al., 2003, 2006). All subsequent manipulations of the reduced phyllosilicates were performed in a controlled atmosphere glove box. The DCB-treated FRC (FRC-dcb) and DCB-0.5 mol L⁻¹ HCl-treated FRC (FRC-dcb-HCl) materials were washed extensively with anoxic distilled and ionized water (ADDW) to solubilize residual extractant and bicarbonate until the conductivities of the final centrifuges were ~10 μmho cm⁻¹. The FRC-dcb suspension was then washed 3× with anoxic 0.5 mol L⁻¹ CaCl₂ to displace ion-exchangeable Fe(II) (Charlet and Tournassat, 2005), and then a final 3× with anoxic 30 mmol L⁻¹ PIPES buffer at pH 7 to partially remove edge-complexed Fe(II). The FRC-dcb-HCl was treated identically to yield suspensions with the same initial condition. Subsequent analyses of the FRC-dcb showed that it contained a particle size distribu-

tion (by hydrometer method) of 24% sand, 43% silt, and 33% clay; a cation exchange capacity of $551 \mu\text{equiv g}^{-1}$ (by ammonium chloride extraction), and a surface area of $19 \text{ m}^2 \text{ g}^{-1}$ (by N_2 -BET analysis).

All solid materials were suspended in either 30 mmol L^{-1} Na-acetate at pH 5.0 or PIPES at pH 7.0 buffer solutions to obtain final concentrations of 200 g L^{-1} hematite, 50 g L^{-1} goethite, or 400 g L^{-1} FRC-dcb and FRC-dcb-HCl. The suspensions were prepared in serum bottles, capped with thick butyl rubber stoppers, crimp sealed, and degassed using the oxygen trap in the anoxic chamber.

2.3. Analytical techniques

Syringes, needles, glass vials, and plastic tubes were used for sample processing. All glassware and plastic bottles were acid washed with 1% HNO_3 , rinsed several times with distilled and deionized water (DDW), and purged with O_2 -free Ar/H_2 before use.

All chemicals were reagent grade or better, unless otherwise described. ADDW was stored in the anoxic chamber for preparation of all solutions and suspensions. ^{99}Tc was purchased as NH_4TcO_4 (Perkin-Elmer Life Sciences Inc., Boston, MA) and diluted in ADDW to produce a 5-mmol L^{-1} stock solution. All stock solutions and acids/bases were stored in serum bottles that were extensively deoxygenated using the oxygen trap before the addition to the master reactors. All samples that contained Fe(II) were kept inside the chamber at all times.

For dissolved Fe(II) analysis, samples were filtered ($0.2 \mu\text{m}$) and $0.1\text{--}0.5 \text{ mL}$ of the filtrate was added to 5 mL ferrozine reagent (1 g L^{-1} ferrozine in 50 mmol L^{-1} HEPES buffer, pH 7.0) in the anaerobic chamber. After 15 min, the samples were removed and the absorbance at 562 nm was determined with a Shimadzu UV-1240 spectrophotometer. Total Fe(II) was determined by adding a 1.5-mL aliquot of suspension to 1.5 mL of 1 mol L^{-1} HCl. The sample was then extracted for 2 h in the anaerobic chamber. The samples were filtered ($0.2 \mu\text{m}$) and analyzed using the ferrozine method. Samples for dissolved Tc(VII) were filtered ($0.2 \mu\text{m}$) and 1 mL of the filtrate was added to 9 mL anoxic scintillation cocktail in the anaerobic chamber. Radioanalysis was performed with a Packard 2500TR liquid scintillation counter (Packard Instrument Co., Meriden, CT, USA); the minimum quantifiable Tc_{aq} concentration was $5.9 \pm 0.24 \times 10^{-9} \text{ mol L}^{-1}$ (Zachara et al., 2007). Solution pH was measured using an Orion 250A+ pH meter with a combination pH/temperature probe.

2.4. X-ray absorption (XAS) spectroscopy

2.4.1. Mineral, valence, and speciation standards

$\text{TcO}_2 \cdot n\text{H}_2\text{O}$ precipitate was prepared by the reduction of Tc(VII) to Tc(IV) using sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) inside a controlled atmospheric chamber (Hess et al., 2004). To reduce the Tc(VII) using the desired reductant to Tc(VII) ratio, 0.18 mL of 0.29 mol L^{-1} Tc(VII) was added to 4.12 mL of 0.195 mol L^{-1} $\text{Na}_2\text{S}_2\text{O}_4$. The pH was then adjusted to 12 using NaOH. A black precipitate quickly

formed which was aged for 72 h. The precipitate was then washed $3\times$ using 20 mL freshly prepared 0.01 mol L^{-1} $\text{Na}_2\text{S}_2\text{O}_4$ and then ADDW. The remaining solid was collected by filtration and then dried in an oxygen-scrubbed dessicator in the glove box.

A stock suspension of ferrihydrite was prepared according to Schwertmann and Cornell (2000). The ferrihydrite suspension was allowed to remain for 48 h inside the chamber. Excess Na^+ and NO_3^- were removed from the ferrihydrite by dialysis in DDW. The ferrihydrite concentration was determined by gravimetric and Fe analyses. Aliquots were dried under anoxic conditions for XAS standards yielding 5–6 line ferrihydrite according to X-ray diffraction analysis.

A subsample of the $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ precipitate (20 mg of ^{99}Tc) was added to 900 mL of 2 mol L^{-1} HCl and allowed to dissolve to steady state. The Tc(IV) solution was filtered through a $0.45\text{-}\mu\text{m}$ filter under anoxic conditions and the ^{99}Tc concentration quantified in the filtrate. A Tc(IV)–ferrihydrite coprecipitate reference phase with 1 mol % Tc(IV) was prepared by mixing a predetermined volume of acidic Tc(IV) solution with an appropriate volume of ferrihydrite suspension; this mixing lead to the dissolution of all of the ferrihydrite. The acidic Tc(IV)/Fe(III) solution was then adjusted to pH 7 ($<1 \text{ h}$) to form the coprecipitate. The resulting solid was aged for 2 h, washed with ADDW, and dried under strictly anoxic conditions. The dried solid yielded an X-ray diffraction pattern of 2-line ferrihydrite with traces of a 6-line structure.

Technetium(IV)–hematite and Tc(IV)–goethite reference phases were prepared by mixing aliquots of the above described, standard Tc(IV) solution with hematite or goethite stock suspensions in ADDW to obtain final concentrations of $\sim 10 \mu\text{mol L}^{-1}$ Tc(IV), 4.5 g L^{-1} hematite and 1.5 g L^{-1} goethite in 0.5 mol L^{-1} HCl. This procedure was mandated by the solubility of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ which does not increase above $10^{-8} \text{ mol L}^{-1}$ until pH < 2 . The suspension pH was then adjusted to pH 7.0–7.7 by 10 mol L^{-1} NaOH (20–30 min titration). The time that goethite and hematite experienced pH < 3 was estimated to be 5–15 min, with the possibility of some dissolution to yield $\text{Fe(III)}_{\text{aq}}$ (Jang et al., 2007). The resulting solids were aged for 4 days, washed $4\times$ with 30 mmol L^{-1} PIPES buffer at pH 7 and dried in an oxygen-scrubbed dessicator in the glove box.

2.4.2. Sample preparation

The four post-reaction mineral suspensions [FRC-dcb at 10 g L^{-1} and pH 6 contacted with $10 \mu\text{mol L}^{-1}$ Tc(VII) (FRC-dcb1); FRC-dcb at 10 g L^{-1} and pH 6.5 contacted with $10 \mu\text{mol L}^{-1}$ Tc(VII) (FRC-dcb2); goethite at 3 g L^{-1} and pH 7 contacted with 0.2 mmol L^{-1} Fe(II) and $20 \mu\text{mol L}^{-1}$ Tc(VII); and hematite at 9 g L^{-1} and pH 7 contacted with 0.2 mmol L^{-1} Fe(II) and $20 \mu\text{mol L}^{-1}$ Tc(VII)] were transferred to 50 mL Oak Ridge polycarbonate screw capped centrifuge tubes. The samples were centrifuged at 2000 rcf for 20 min, and the supernatant discarded. The solid was washed with 10–15 mL of degassed, anhydrous methanol. The samples were dried in a vacuum dessicator with Drierite, ground and packed in a Teflon sample cell with a slot $2 \text{ mm} \times 10 \text{ mm} \times 2 \text{ mm}$. Kapton adhesive

tape (1 mil, CS Hyde, Co.) was applied to one side of the holder to make a recess into which the sample was packed. Kapton tape was applied to the top of the holder. A second layer of Kapton tape was applied to seal the sample into the holder. The sample holder was sealed inside a Kapton envelope made from 2 mil Kapton film (CS Hyde Co.). The samples within the Kapton envelopes were placed inside 100 mL Wheaton glass bottles that were sealed with special plastic stoppers designed for anaerobic use for storage and shipment to the beamline.

2.4.3. XAS methods

Tc-extended X-ray adsorption fine structure (Tc-EXAFS) measurements were made at the Advanced Photon Source (APS) sector 20 beamlines 20-ID and 20-BM in fluorescence mode using a multi-element Ge fluorescence detector. A total of 10–20 scans were run for each of the four samples on 20-ID. The Tc(IV)-ferrihydrite, hematite and goethite standards were run on 20-BM. A Mo foil was used for energy calibration. A Si(111) monochromator was used with a 1-mm entrance slit located approximately 50 m from the source on both beamlines. The monochromator provided an energy resolution of about 4 eV at the Tc edge. At the beamline, the reduced samples were kept in a plastic container with Kapton windows under flowing nitrogen to avoid any oxygen diffusion through the Kapton of the sample cells.

The EXAFS and XANES data were analyzed using the Athena and Artemis interfaces to the IFEFFIT program package (Ravel and Newville, 2005). Theoretical models were calculated using FEFF 7 (Rehr and Albers, 2000) with the parameters refined using ARTEMIS.

2.5. ^{57}Fe Mössbauer spectroscopy

Mössbauer spectroscopy was performed on the FRC-dcb sediment before and after HCl extraction according to procedures outlined in Kukkadapu et al. (2006).

Mössbauer spectroscopy is a ^{57}Fe (natural abundance of 2.12%) specific technique. Therefore, to probe the nature of adsorbed Fe(II), measurements were performed on ^{56}Fe -goethite (Mössbauer insensitive nucleus) with adsorbed ^{57}Fe (II) before and after reaction with Tc(VII). Isotopically enriched ^{57}Fe (II) and ^{56}Fe (II) stock solutions were prepared in 0.1 mol L^{-1} HCl from 96.7% pure $^{57}\text{Fe}(0)$ and 99.94 pure $^{56}\text{Fe}(0)$ metals (Web Research Co., MN) following the procedure of Williams and Scherer (2004). Oxidation of the ^{56}Fe (II) acid solution was achieved by H_2O_2 addition. Goethite was synthesized from a ^{56}Fe (III) solution mixed with 5 mol L^{-1} KOH and diluted with DD water (Williams and Scherer, 2004). The precipitate obtained was incubated at 70°C for three days for transformation to goethite. The resulting goethite had a specific surface area of $41\text{ m}^2\text{ g}^{-1}$ by N_2 -BET method. Scanning electron microscopy showed the presence of 500 nm acicular crystals. Suspensions [1.5 g L^{-1} ^{56}Fe -goethite, 0.1 mmol L^{-1} ^{57}Fe (II), 30 mmol L^{-1} PIPES, pH 7 with/without $10\text{ }\mu\text{mol L}^{-1}$ Tc(VII)] were prepared as described in the Sections 2.1 and 2.2. Two days of equilibration with ^{57}Fe (II) were allowed before collecting the Mössbauer sam-

ple. The remaining suspension was spiked with Tc(VII) stock solution and allowed to react for 10 days.

The goethite Mössbauer samples were prepared by withdrawing 50 mL of suspension from the master reactor. A disposable syringe filter holder (Swinnex) with a removable filter [$0.45\text{ }\mu\text{m}$ pore-size (Millipore); 1.25 cm diameter] was used. A Cu Mössbauer sample holder (0.95 cm by 1.27 cm) that was sealed at one end with clear scotch tape was half-filled with the vaseline. The filter membrane containing the precipitate was placed on top of the vaseline within the Mössbauer sample holder, the holder was then filled with vaseline and sealed with scotch tape. An oxygen impermeable polymer (aluminized Mylar stable to 4 K) was used as an outer seal on both ends of the holder. The tape and polymer were snapped into the holder with rings made of carbonized-polyetheretherketone (PEEK) polymer. The sample holders were stored in the anoxic chamber until analysis.

Mössbauer spectra for both the FRC-dcb samples and $^{57}\text{Fe}/^{56}\text{Fe}$ goethite were collected using a 50-mCi (initial strength) $^{57}\text{Co}/\text{Rh}$ source. The velocity transducer MVT-1000 (WissEL) was operated in a constant acceleration mode (23 Hz , $\pm 12\text{ mm s}^{-1}$). An Ar–Kr proportional counter was used to detect the radiation transmitted through the holder, and the counts were stored in a multichannel scalar (MCS) as a function of energy (transducer velocity) using a 1024 channel analyzer. Data were folded to 512 channels to give a flat background and a zero-velocity position corresponding to the center shift (CS or δ) of a metal iron foil at room temperature. Calibration spectra were obtained with a $25\text{-}\mu\text{m}$ -thick $\alpha\text{-Fe(m)}$ foil (Amersham, England) placed in the same position as the samples to minimize any errors due to changes in geometry. A closed-cycle cryostat (ARS, Allentown, PA) was employed for 260, 77 and 10 K measurements. The Mössbauer data were modeled with the Recoil software using a Voigt-based structural filtering routine (Rancourt and Ping, 1991).

3. RESULTS

3.1. Reactivity of sorbed Fe(II) on goethite and hematite

3.1.1. Kinetic behavior

Technetium(VII) was weakly adsorbed by Fe(III) oxides in buffered solution when Fe(II) was absent (data not shown). We found that the sorption of $10\text{ }\mu\text{mol L}^{-1}$ TcO_4^- was less than 3% to 4.5 g L^{-1} hematite even at pH 5.6, where significant positive charge density existed.

The experiments were designed to minimize the effect of homogeneous Tc(VII) reduction by dissolved Fe(II) as a parallel reaction pathway. The rates of homogeneous Tc(VII) reduction are influenced by Fe(II) concentration and pH (Zachara et al., 2007). Our previous experiments showed that less than 3% of Tc(VII) was homogeneously reduced after 5 days reaction time (i.e., the pseudo-first-order rate constant was 0.005 day^{-1}) when $11\text{ }\mu\text{mol L}^{-1}$ of Tc(VII) was reacted with 0.05 mmol L^{-1} of Fe(II) at pH 7 in 10 mmol L^{-1} PIPES solution. Based on these past observations, the dissolved Fe(II) concentrations in the heterogeneous experiments were generally maintained at ≤ 0.05

Fig. 1. Time-dependent behavior of $\text{Fe}^{2+}_{(\text{aq})}$ solutions spiked sequentially with hematite or goethite (at day -2 , concentrations noted) and Tc(VII) (20 or 10 $\mu\text{mol L}^{-1}$ at day 0, concentrations noted) for pH 7: (a) dissolved Tc(VII) with hematite, (b) dissolved Fe(II) with hematite, (c) total Fe(II) with hematite, (d) dissolved Tc(VII) with goethite, (e) dissolved Fe(II) with goethite, and (f) total Fe(II) with goethite. Data represent means ($\pm$ SD) of triplicate samples.

mmol L^{-1} [after adsorptive pre-equilibration of Fe(II) with the sorbent of interest]. Up to 0.09 mmol L^{-1} of dissolved Fe(II) was allowed in the suspensions with lower pH (between 5.6 and 6.5) where little homogeneous Tc(VII) reduction was observed even in the presence of 0.4 mmol L^{-1} dissolved Fe(II) (Zachara et al., 2007).

The heterogeneous reduction of Tc(VII) to Tc(IV) was virtually instantaneous when 10 or 20 $\mu\text{mol L}^{-1}$ of Tc(VII) was reacted in suspensions containing 0.12 or 0.23 mmol L^{-1} total Fe(II) and Fe(III) oxides at pH 7 (Fig. 1a and d), even though Tc(VII) adsorption to these phases in the absence of Fe(II) was not measurable. The adsorbed Fe(II) concentration in these experiments (Table

1) ranged from 0.08 mmol L^{-1} [for 0.12 mmol L^{-1} Fe(II)- TOT] to 0.17 mmol L^{-1} [for 0.23 mmol L^{-1} Fe(II)- TOT]. These adsorption densities correspond to 2.75 times the stoichiometric demand for complete reduction of added Tc(VII) to Tc(IV), given the differences in initial Tc(VII) concentration. The complete stability of Fe(II) before sorbent addition (from -6 to -2 days) confirmed that the experimental systems were strictly anoxic (Fig. 1c and f). The addition of hematite and goethite to the Fe(II) containing solutions caused a small decrease in 0.5 mol L^{-1} HCl recoverable total Fe(II) after 2 days of reaction time (Fig. 1c and f). This observation was consistent with previous studies (Jeon et al., 2001, 2003) that suggest surface

Fig. 2. Time-dependent behavior of $\text{Fe}^{2+}_{(\text{aq})}$ -hematite suspensions at various pH values (as noted) that were spiked with $10 \mu\text{mol L}^{-1}$ Tc(VII) at day 0: (a) dissolved Tc(VII), (b) dissolved Fe(II), and (c) total Fe(II) at pH 4.0, 4.5, and 5.0, and (d) dissolved Tc(VII), (e) dissolved Fe(II), and (f) total Fe(II), at pH = 5.6, 5.8, 6.1, and 6.5. Data represent means ($\pm$ SD) of triplicate samples.

phase formation initiated by interfacial electron transfer from sorbed Fe(II) to Fe(III) in bulk hematite or goethite. Both total and dissolved Fe(II) concentrations dropped sharply within a minute after the Tc(VII) addition (Fig. 1b, c, e, and f), consistent with the rapid reduction of Tc(VII) in all four suspensions. The decrease in the total Fe(II) was $40\text{--}50 \mu\text{mol L}^{-1}$ for $10 \mu\text{mol L}^{-1}$ Tc(VII), and $80\text{--}90 \mu\text{mol L}^{-1}$ for $20 \mu\text{mol L}^{-1}$ Tc(VII). The decrease in $\text{Fe(II)}_{\text{TOT}}$ was greater than the stoichiometric demand [$\text{Fe(II)}:\text{Tc(VII)} = 3:1$] for reduction of Tc(VII) to Tc(IV), similar to observations made for reaction of Tc(VII) with $\text{Fe(II)}_{\text{aq}}$ (Zachara et al., 2007). Heterogeneous Tc(VII) reduction was coincident with, or immediately followed by, a $\text{Fe(II)}_{\text{aq}}$ readsorption step that replenished sorbed Fe(II) (e.g., Fig. 1b and e).

The heterogeneous reduction of Tc(VII) in hematite suspensions showed pH dependency below pH 6.5 (Fig. 2). Very little Tc(VII) was reduced at pH 4 (e.g., $1.7 \mu\text{mol L}^{-1}$), while slow kinetics were observed at pH 4.5. Experiments performed between pH 5.6–6.5 displayed rapid reduction kinetics. To a first approximation, the reduction rates paralleled the adsorption density of Fe(II), Table 1, as Fe(II) adsorbs on hematite between pH 5 and 6, depending on sorbate and sorbent concentrations (Jeon et al., 2001; Liu et al., 2007).

3.1.2. Mössbauer spectroscopy of product Fe(III)

Mössbauer spectra were obtained for $^{57}\text{Fe(II)}$ adsorbed on ^{56}Fe -goethite at pH 7 to identify the nature of reactant Fe(II), and the Fe(III) oxidation product resulting from

Fig. 3. ^{57}Fe Transmission Mössbauer spectra of ^{56}Fe -goethite (1.5 g L^{-1}) that had been reacted with $^{57}\text{Fe}^{2+}_{(\text{aq})}$ (0.1 mmol L^{-1}) and then Tc(VII) ($10 \mu\text{mol L}^{-1}$) at pH 7.0: (a) room temperature and 260 K spectra and (b) 77 K spectra with Recoil modeling of site distributions.

heterogeneous reaction with Tc(VII). In the suspension studied, almost all of the added $^{57}\text{Fe}(\text{II})$ (0.1 mmol L^{-1}) was sorbed to ^{56}Fe -goethite after 2-day equilibration, and only $\sim 3 \times 10^{-3} \text{ mmol L}^{-1}$ of $^{57}\text{Fe}(\text{II})$ remained in the aqueous phase. Pertechnetate that was spiked to this suspension was completely reduced, and no aqueous Fe(II) was detected by the end of the experiment.

The ^{57}Fe -Mössbauer spectrum of the samples before and after reaction with Tc(VII) were virtually identical at all measurement temperatures, and only the post-reaction sample is shown (Fig. 3). There was no Fe(II) doublet signal in either sample, or sign of a paramagnetic doublet characteristic of ferrihydrite at temperatures above 77 K (Murad and Cashion, 2004). The samples displayed a weak, incipient, collapsed sextet at RT (Fig. 3a); a jagged, irregular, but more resolved asymmetric sextet features at 260 K (Fig. 3b) that was fully resolved at 77 K. The Mössbauer spectrum

did not significantly change in either resolution or peak refinement with further temperature reductions below 77 K (data not shown). The 77-K spectrum could be fit by three components (sites A, B and C): [isomer shift (δ) 0.48, 0.49 and 0.55 mm s^{-1} , quadrupole shift parameter (ϵ) 0.04, -0.17 , and -0.19 mm s^{-1} , and hyperfine field (B_{hf}) 48.9, 48.5 and 45.9 Tesla (T) , for sites A, B, and C, respectively]. The derived parameters of all the three sextets are similar to goethite. The noted differences in Mössbauer parameters between the three sextets are due to slight variation in their symmetries. The distribution of the three components changed slightly with Tc(VII) reaction, but these changes were within the uncertainty of measurement and the applied model. Our 77 K spectra for both Fe(II)-sorbed and Tc(VII)-reacted goethite were similar to those reported for this same temperature by Silvester et al. (2005) for sorbed $^{57}\text{Fe}(\text{II})$ on natural goethite.

Fig. 4. (a) Tc-EXAFS spectra (Fourier-transform radial distribution function) for TcO₂·nH₂O, Tc(IV) coprecipitated with ferrihydrite, heterogeneously precipitated Tc(IV) (20 $\mu\text{mol L}^{-1}$) by sorbed Fe(II) (0.2 mmol L^{-1}) at pH 7 on both hematite (9 g L^{-1}) and goethite (1.5 g L^{-1}); and Tc(IV)-goethite and -hematite standards. (b) A comparison of experimental and modeled Tc-EXAFS spectra for heterogeneously precipitated Tc(IV) on goethite and hematite. The model assumed a ferrihydrite-like surface phase as parameterized in Table 2.

3.1.3. EXAFS spectroscopy of product Tc(IV)

XANES analyses showed that Tc associated with goethite and hematite after heterogeneous reaction was entirely in the Tc(IV) valence state [energy shift for the Tc(VII)-reduced samples relative to TcO₄[−] was consistent with Tc(IV) species (−5.3 to −5.6 eV, Lukens et al., 2002), data not shown]. Radial transforms of the Tc-EXAFS data for Tc(IV) on both goethite and hematite were almost identical (Fig. 4a), with the exception of small outer shell peaks at 3.4 and 3.8 Å for Tc-hematite. These spectra, in turn, were very similar to the Tc(IV)-ferrihydrite standard, which was the originally hypothesized product of Tc(VII) redox reaction with sorbed Fe(II) (Charlet et al., 1998). The radial transforms for these three, similar samples contrast markedly with that for abiotically precipitated TcO₂·nH₂O, showing the presence of far less Tc–Tc bonding in the second shell (e.g., at 2.3 Å, Fig. 4a).

A closer inspection of the sample and reference EXAFS spectra revealed uncertainty in the nature of the Fe(III) sur-

face phase and inability to precisely resolve the Fe(III)–Tc(IV) structural environment. The reference spectra for the Tc(IV)-ferrihydrite coprecipitate was virtually identical to that for adsorbed Tc(IV) on goethite, and these, in turn were very similar to the heterogeneous Tc(IV)-goethite sample (Fig. 4a). It is possible that Fe(III) dissolved from goethite at low pH during reference sample synthesis, and that this Fe(III)_{aq} hydrolyzed and coprecipitated with Tc(IV) to yield ferrihydrite upon neutralization. The heterogeneous Tc(IV)-hematite sample was intermediate in character between the hematite and ferrihydrite Tc(IV) standards (Fig. 4a), but all three were quite similar overall. Minimal Fe(III) dissolution was expected at low pH with hematite.

The data for heterogeneous Tc(IV) precipitates on both goethite and hematite were modeled with an edge sharing octahedral model that was previously successfully applied to the Tc(IV)-ferrihydrite standard as described by Zachara et al. (2007). This model was justified because the structural state of Fe(III) in the heterogeneous precipitates was not

well constrained by the EXAFS measurements, and the Tc(IV)-ferrihydrite standard was most representative of heterogeneous Tc(IV) in both systems (Fig. 4a). It consists of a variable length chain of Tc-O octahedra bonded in an edge sharing fashion to an Fe-O octahedron located on the surface of the host Fe(III) oxide substrate. In this model the first two shells of neighbors are independent of the structure of the substrate. The details of the substrate is expected to only affect the bonds past about 3 Å (2.7 Å in the radial transforms where the peaks are shifted to lower R by the EXAFS phase shifts). The primary objectives of this modeling were to provide insights on the average number of Tc(IV)–Tc(IV) bonds and the amount of Fe(III) in the second coordination sphere of the redox precipitates (both on Fe(III) oxides and the phyllosilicate mixtures). We note and will later discuss that this host phase is different from that implied by the ^{57}Fe Mössbauer measurements on goethite (Fig. 3).

If the attached Tc–O chains consist of a single octahedron (monomers) there would only be Tc–Fe neighbors in the second shell. Initial calculations indicated that the transform data for heterogeneous Tc(IV) precipitates on both goethite and hematite (Fig. 4a) was best fit with a combination of Tc(IV) and Fe(III) in the second shell indicating on average the length of the Tc chains is greater than one. For the third peak in the transform (near 3 Å) the dominant contributions come from the axial oxygens of the neighboring octahedra, and more distant Fe bonds of the substrate. For ferrihydrite, the neighboring Fe sites are only partially filled and we would expect the Tc directly bonded to the surface to have three of these more distant bonds. For more ordered materials such as hematite, the number of these bonds could be as large as six. This number is not well constrained by the EXAFS fitting, and based on the similarity of the transforms to the ferrihydrite standard, it was fixed at three in the fitting. Based on previous fits and to minimize the fitting parameters, second-shell bond distances were also fixed at Tc–Fe = 2.59 Å and Tc–Tc = 2.57 Å.

Technetium(IV) octahedra have a tendency to polymerize in chains (Lukens et al., 2002), and this was allowed in the model through the number of Tc–Tc bonds (Tc–N). It

was assumed that the additional Tc–O octahedra were part of a chain, and therefore not directly bonded to the Fe(III) oxide substrate. As the average chain length of the Tc(IV) octahedra increased, Tc–N increased, the longer Fe coordination decreased, and axial O coordination increased. Therefore all of the coordination numbers in Table 2 were either fixed or determined by the Tc–N value with the exception of the first shell O coordination. The resulting model well described the Tc(IV) EXAFS data for both goethite and hematite (Fig. 4b), and the Tc(IV)-ferrihydrite (Zachara et al., 2007) with similar parameters (Table 2). The results gave an average chain length for Tc(IV) octahedra between monomers and dimers, although there was large uncertainty. Model fits with 100% monomer ($N = 0$) or dimer ($N = 1$) had similar total quality, but some of the parameters became unphysical indicating an intermediate value was best. The EXAFS results provide an average Tc environment. By itself EXAFS cannot distinguish between a surface with roughly similar amounts of monomers and dimers attached, and a surface with attached monomers and a few isolated long chains of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$.

3.2. Reduction of Tc(VII) by Fe(II) associated with phyllosilicates

3.2.1. Nature of the sorbent

The FRC-dcb sediment contained coarse silt-sized muscovite and quartz ($>10\text{ }\mu\text{m}$), and clay-sized illites and vermiculite ($<0.2\text{ }\mu\text{m}$) (Kukkadapu et al., 2006). Electron microprobe measurements of the phyllosilicates demonstrated significant Fe substitution in both size fractions (Kukkadapu et al., 2006). By analogy to results with specimen Fe-containing phyllosilicates extracted with DCB (Stucki et al., 1984; Bain and Smith, 1994; Hofstetter et al., 2003, 2006), we assumed that a dominant fraction (e.g., $>95\%$) of the Fe(II) remained in structural state after extraction, while the remainder ($<5\%$) was edge-complexed to hydroxylated sites. We made no attempt to extract edge-complexed Fe(II) from the FRC-dcb sediments to evaluate either its concentration or potential contribution to Tc(VII) heterogeneous reduction because of concerns of extraction specificity. Previous wet chemical studies of this reduced material have shown complex dissolution behavior in weak acid (Kukkadapu et al., 2006) that may result from the presence of Fe-containing phyllosilicates in both size fractions. The small Fe-containing phyllosilicates were readily reduced by DCB and dissolved rapidly and completely in weak acid. Distinguishing surface-complexed Fe(II) from submicron-sized phyllosilicates was not deemed feasible.

^{57}Fe -Mössbauer measurements of the FRC-dcb (Fig. 5a) indicated that most of the sample Fe existed within phyllosilicates with a $\text{Fe(II)}/\text{Fe}_{\text{TOT}}$ ratio of 0.46. A 2-h weak acid extraction of the FRC-dcb dissolved over 22% of the Mössbauer-visible Fe(II) (Fig. 5b). This removal changed the peak areas of the Fe(II) and Fe(III) doublets, but not their peak positions [e.g., the quadrupole splitting of Fe(II)].

3.2.2. Heterogeneous reduction behavior

It was hypothesized that $\text{Fe(II)}_{\text{aq}}$ added to suspensions of FRC-dcb would adsorb primarily by ion exchange and

Table 2
EXAFS fit parameters for heterogeneous Tc(IV) on goethite and hematite

Shell	N	R (Å)	σ^2 (Å ²)
<i>Goethite</i>			
1st O	5.4 (0.4)	2.00 (0.01)	0.0057 (0.001)
Fe short	0.6 (0.3)	2.59*	0.0042(0.002)
Tc	0.7 (0.3)	2.57*	0.0058 (0.002)
2nd O	2.6 (0.6)	3.04 (0.04)	0.0026 (0.003)
Fe long	1.8 (0.5)	3.50 (0.03)	0.0077 (0.003)
<i>Hematite</i>			
1st O	5.5 (0.4)	2.00 (0.01)	0.0039 (0.001)
Fe short	0.5 (0.3)	2.59*	0.0020 (0.002)
Tc	0.9 (0.3)	2.57*	0.0072 (0.002)
2nd O	2.8 (0.6)	3.02 (0.04)	0.0018 (0.002)
Fe long	1.6 (0.5)	3.47 (0.03)	0.0030 (0.002)

Parameters noted by * were fixed in the data fitting.

Fig. 5. Room temperature ^{57}Fe transmission Mössbauer spectra for the DCB-treated FRC phyllosilicate mineral isolate: (a) before and (b) after weak acid ($0.5\text{ L}^{-1}\text{ HCl}$) extraction. Recoil modeling was applied to estimate the distribution of phyllosilicate Fe(II) and Fe(III) in the two samples.

by some edge complexation, and that the heterogeneous reduction rate would increase proportionally. This hypothesis, however, was refuted by experiment where heterogeneous Tc(VII) reduction was found to be independent of added Fe(II) concentration (Fig. 6a), and slower than observed for either hematite or goethite. The FRC-dcb adsorbed all the dissolved Fe(II)_{aq} upon addition to the reactor (Fig. 6b). This adsorption approximately doubled the total Fe(II) concentration associated with the composite mineral phase (Fig. 6c). The total Fe(II) shown for days -2 to 6 is the sum of intrinsic (structural/edge-complexed) and ion-exchangeable Fe(II). For both experiments, the total amount of Fe(II) was in vast excess of the stoichiometric demand for Tc(VII) reduction (Fig. 6c), and no statistical differences in total Fe(II) could be determined before and after reduction.

The FRC-dcb functioned as a heterogeneous reductant for Tc(VII) in the absence of added Fe(II), with apparent rates that were independent of both pH and solids concentration (Fig. 7a), and that were nearly identical to those in Fig. 6. Therefore, the added Fe(II) adsorbed by ion exchange

and possibly edge complexation had no heterogeneous reduction capability for Tc(VII). Rather, the presence of appreciable weak acid extractable intrinsic Fe(II) in the FRC-dcb (Fig. 7b) lead us to speculate that structural Fe(II) associated with fine, clay-sized phyllosilicates, and an unquantified amount of edge-complexed Fe(II) were the responsible reductants. These hypotheses were further tested and affirmed (Fig. 8), where Tc(VII) reactivity was assessed in suspensions of HCl-treated FRC-dcb that were spiked with Fe(II)_{aq}. These suspensions demonstrated high-Fe(II) adsorption by ion exchange and some potential edge complexation (Fig. 8b), and no apparent reduction of Tc(VII) (Fig. 8a) or Fe(II) oxidation (Fig. 8c). The lack of any observed effect of increasing added Fe(II)_{aq} concentration on Tc(VII) reduction by the FRC-dcb-HCl (Fig. 8) suggested that Fe(II) edge complexes were not significant reductants (e.g., Figs. 6 and 7). The large residual Mössbauer Fe(II) signal remaining after weak acid extraction (Fig. 5b) was, therefore, associated with phyllosilicate phases incapable of heterogeneous Tc(VII) reduction, such as silt-sized, Fe(II)-containing micas.

Fig. 6. Time-dependent behavior of two Fe^{2+} (aq) solutions (0.2 and 0.1 mmol L^{-1}) at pH 7 that were spiked with DCB-treated FRC phyllosilicate isolate (20 and 10 g L^{-1} at day -2) and Tc(VII) (10 $\mu\text{mol L}^{-1}$ at day 0): (a) Tc(VII) , (b) dissolved Fe(II) , and (c) total Fe(II) . Data represent means ($\pm\text{SD}$) of triplicate samples.

3.2.3. EXAFS spectroscopy of product Tc(IV)

Radial transforms of the Tc(IV) EXAFS data from FRC-dcb1 and FRC-dcb2 were nearly identical to one another (Fig. 9a) and quite different from heterogeneous Tc(IV) on goethite and hematite. The two FRC samples showed evidence for more Tc-Tc bonding in the second shell (e.g., 2.3 Å). The ferrihydrite model described above was changed to a combination of Tc-Fe monomers and Tc-Tc chains as in $\text{TcO}_2 \cdot n\text{H}_2\text{O}$. The contribution from the Tc-Fe bond was found to be small, and its parameters were consequently fixed at values from the Fe(III) oxide system. When optimized with the fixed values in Table 3; the model fitted the data well (Fig. 9b) while simultaneously

Fig. 7. Influence of pH on the reduction of Tc(VII) (10 $\mu\text{mol L}^{-1}$) spiked at day 0 by the DCB-treated FRC phyllosilicate isolate: (a) Tc(VII) and (b) total Fe(II) . No additional Fe^{2+} (aq) was added to the suspension beyond that associated with the mineral fraction. Data represent means ($\pm\text{SD}$) of triplicate samples.

refining to parameters for the Tc-Tc chains that were similar to $\text{TcO}_2 \cdot n\text{H}_2\text{O}$. Generally the Tc-Tc chain length in the precipitate was found to be consistently larger than a dimer (e.g., $N > 1$).

The high quality of our near edge data for samples and standards allowed us to test an alternative model for the FRC samples as a combination of Tc(IV) -ferrihydrite and $\text{TcO}_2 \cdot n\text{H}_2\text{O}$. This additive model yielded 35% Tc(IV) -ferrihydrite and 65% $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ for FRC-dcb1, and 30% Tc(IV) -ferrihydrite and 70% $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ for FRC-dcb2. These values were reasonably consistent with the EXAFS fitting in terms of the amount of Tc-Tc and Tc-Fe bonds. The values would be exactly consistent if the Tc(IV) -ferrihydrite contained all Tc(IV) as dimers.

3.3. Rate constants and comparative kinetic behavior

A kinetic analysis was performed on the heterogeneous Tc(VII) reduction data in Figs. 1, 2, 6, and 7 using the initial data points that showed a linear relationship between $\ln(C_t/C_0)$ vs. time. The reduction kinetics of Tc(VII) could be described with a first-order rate law, yielding the resulting pseudo-first-order rate constants, k_{obs} , summarized in Table 1.

The rate constants computed for hematite and goethite were similar to one another under comparable conditions,

Fig. 8. Influence of 0.5 mol L^{-1} HCl extraction of the DCB-treated FRC phyllosilicate isolate (spiked at day -2) on the reduction of Tc(VII) at pH 7 at two added $\text{Fe}^{2+}_{(\text{aq})}$ concentrations: (a) dissolved Tc(VII), (b) dissolved Fe(II), and (c) total Fe(II). Solid and Tc(VII) concentrations varied as noted. There was no Tc(VII) reduction. Data represent means ($\pm$ SD) of triplicate samples.

but these differed markedly from the FRC-dcb. Those for the Fe(III) oxides increased with sorbed Fe(II) concentration, with $k_{\text{obs}} = 15.14 \text{ h}^{-1}$ (pH 6.5) being the highest value that could be defensibly quantified by regression analysis. The heterogeneous reduction rate was so fast at pH 7 that it could not be established by wet chemical measurement (e.g., $k_{\text{obs}} > 16 \text{ h}^{-1}$). For those conditions where the rate was quantified (Fig. 10), k_{obs} demonstrated an exponential dependence on sorbed Fe(II) concentration indicating that other factors related to pH such as Fe(II) surface complex hydrolysis (e.g., $=\text{Fe}^{\text{III}}\text{OFe}^{\text{II}}\text{OH}^{\circ}$; Charlet et al., 1998; Silvester et al., 2005) were at play.

In contrast to the Fe(III) oxides, the heterogeneous reduction rate of Tc(VII) was univariant on FRC-dcb. The reduction rate of FRC-dcb was determined by its “intrinsic Fe(II) concentration”, and was not influenced by additional sorbed Fe(II), or by a one unit change in pH. The reduction rates on hematite and goethite [with $0.16\text{--}0.17 \text{ mmol L}^{-1}$ sorbed Fe(II)] were: (i) close to, but in excess of those observed for sorbed biogenic Fe(II) in Fe(III)-oxide containing sediment (Fredrickson et al., 2004) by factors of 2–3, (ii) over 100 times that of the FRC-dcb [with $0.09\text{--}0.18 \text{ mmol L}^{-1}$ intrinsic Fe(II)], and (iii) over 10^4 times the homogeneous reduction rate of Tc(VII) by $\text{Fe(II)}_{\text{aq}}$ reported by Zachara et al. (2007). The following qualitative affinity series for heterogeneous Tc(VII) reduction by Fe(II) was suggested by the experimental results: aqueous Fe(II) $\sim$ adsorbed Fe(II) in phyllosilicates [ion-exchangeable and some edge-complexed Fe(II)] $\ll$ structural Fe(II) in phyllosilicates $\ll$ Fe(II) adsorbed on Fe(III) oxides.

4. DISCUSSION

4.1. Tc-redox thermodynamics

As described recently by Zachara et al. (2007), the redox behavior of the Tc(IV)/Tc(VII) couple bears similarity to that of Cr(III)/Cr(VI), in terms of an overall three-electron transfer reaction that links a soluble oxidized anion, to a stable insoluble oxyhydroxide precipitate of lower valence. The Tc(IV)/Tc(VII) couple is more reducing than the Cr(III)/Cr(VI) couple (Rard et al., 1999):

At circumneutral pH, the homogeneous reduction reaction of Tc(VII) with ferrous iron is thermodynamically favorable over a fairly wide range of $\text{Fe}^{2+}_{(\text{aq})}$ and environmentally relevant Tc(VII) concentrations (e.g., $10^{-4}\text{--}10^{-9} \text{ mol L}^{-1}$):

Unlike the comparable reaction for Cr(VI), reaction (2) proceeds very slowly in the circumneutral pH range (Zachara et al., 2007). The “real” reaction (2) yields a complex Tc(IV):Fe(II/III) solid phase redox product that is intermediate in character between ferrihydrite and magnetite (Zachara et al., 2007). The redox product significantly accelerates further Tc(VII) reduction through Fe(II) sorption and heterogeneous reaction.

The slow rate of homogeneous reduction under favorable conditions has been speculated to result from the slow kinetic reactivity of the hydrated $\text{Fe}^{2+}_{(\text{aq})}$ ion and the existence of intermediate valence forms [Tc(VI), Tc(V)] with significantly lower redox potentials than the final, stable Tc(IV) valence state (Cui and Eriksen, 1996a; Rard et al., 1999; Zachara et al., 2007). A schematic of the three electron transfer process is shown in Fig. 11, based on Cui and Eriksen (1996a), Rard et al. (1999). In this

Fig. 9. (a) Tc-EXAFS spectra (Fourier-transform radial distribution function) for TcO₂·nH₂O, and heterogeneously precipitated Tc(IV) (10 μmol L⁻¹) on the DCB-treated FRC phyllosilicate isolates at pH 6.0 (FRC-dcb1, 10 g L⁻¹) and pH 6.5 (FRC-dcb2, 10 g L⁻¹) in the absence of additional Fe(II)_{aq}, (b) a comparison of data and EXAFS model calculations as described in the text with model parameters summarized in Table 3.

Table 3
EXAFS fit parameters for heterogeneous Tc(IV) on DCB-treated, FRC phyllosilicate mixtures

Shell	N	R (Å)	σ ² (Å ²)
<i>FRC-dcb1, pH 6</i>			
1st O	6*	2.01 (0.01)	0.0062 (0.001)
Fe short	0.17 (0.2)	2.58* (0.02)	0.008* (0.002)
Tc	1.7 (0.3)	2.57*	0.0058 (0.002)
2nd O short	4*	3.24 (0.04)	0.017 (0.003)
Fe long	0.4	3.49 (0.03)	0.0012 (0.002)
<i>FRC-dcb2, pH 6.5</i>			
1st O	6*	2.01 (0.01)	0.0062 (0.001)
Fe short	0.13 (0.2)	2.58* (0.02)	0.008* (0.002)
Tc	1.7 (0.3)	2.57*	0.0072 (0.002)
2nd O short	4*	3.19 (0.04)	0.0034 (0.002)
Fe long	0.4	3.48 (0.03)	0.0030 (0.002)

Parameters noted by * were fixed in the data fitting.

reaction series, pertechnetate engages in a one electron transfer reaction with low half-cell potential to yield a

structurally comparable, but energetic tetrahedral oxyanion, TcO₄²⁻:

Technetium(VI), in turn, rapidly disproportionates to Tc(V) and Tc(VII), and Tc(V) very rapidly disproportionates to Tc(IV) and Tc(VI). Continued cycles of one electron transfer combined with disproportionation lead to reaction completion.

The reaction series in Fig. 11 is driven by an electron donor with sufficiently low redox potential to move reaction (3) to the right, as facilitated by rapid rates of disproportionation that maintain low concentrations of the intermediate valence states. The rate of reaction (3) is likely to be rate-controlling in the transformation of Tc(VII) to Tc(IV). At circumneutral pH and the [Fe(II)]_{TOT} and [Tc(VII)]_{TOT} concentrations used in our experiments, various iron couples exhibit sufficient free energy to generate TcO₄²⁻. These couples include the following listed in their order of redox potential (lowest to highest) under our specific experimental

Fig. 10. A comparison of first order apparent rate constants for Tc(VII) heterogeneous reduction (from Table 1) as a function of solid-associated Fe(II). The marked differences in rate between the Fe(III) oxide and FRC phyllosilicate systems are evident. Heterogeneous reduction rates above pH 6.5 for both hematite and goethite were too rapid to quantify (e.g., k_{obs}) from regression analysis.

conditions: $\text{Fe}^{2+}_{(\text{aq})}/\text{Fe}_2\text{O}_{3(\text{s})} < \text{Fe}^{2+}_{(\text{aq})}/\text{FeOOH}_{(\text{s})} \leq \text{Fe}^{\text{III}}\text{OFe}^{\text{II}}\text{OH}^{\circ} = \text{Fe}^{\text{III}}\text{OH}$, $\text{FeOOH}_{(\text{s})}$ or $\text{Fe}_2\text{O}_{3(\text{s})}$ [where $=\text{Fe}^{\text{III}}\text{OH}$ is a surface site and $=\text{Fe}^{\text{III}}\text{OFe}^{\text{II}}\text{OH}^{\circ}$ is the hydrolyzed ferrous iron surface complex; (Silvester et al., 2005)] $< \text{Fe}^{2+}_{(\text{aq})}/\text{Fe}(\text{OH})_{3(\text{s})}$ [standard state half-cell potentials taken from: Cornell and Schwertmann (2000) for the Fe(III) oxides, Rard et al. (1999) for the Tc(VII)/Tc(VI) couple, and (Silvester et al., 2005) for the Fe(II) surface complexes; experimental redox potentials calculated with the Nernst equation].

The rapid reduction rates of Tc(VII) in our experimental systems with sorbed Fe(II) on crystalline Fe(III) oxides, and the exponential increase in rate constants with increasing sorbed Fe(II) and pH (Fig. 10) implicated the $=\text{Fe}^{\text{III}}\text{OFe}^{\text{II}}\text{OH}^{\circ}/=\text{Fe}^{\text{III}}\text{OH}$, $\text{FeOOH}_{(\text{s})}$ or $\text{Fe}_2\text{O}_{3(\text{s})}$ couples, as rapid kinetic reductants for Tc(VII). This unique reactant as described by Charlet et al. (1998), Silvester et al. (2005) forms through enhanced or heterogeneous hydrolysis at the oxide–water interface. The reactivity of this surface species for Tc(VII) is remarkably rapid, as virtually instantaneous reduction occurs at pH 6.5 and above, even in the absence of measurable Tc(VII) adsorption. The molecular nature of this surface entity is under debate [e.g., Williams and Scherer, 2004], as will be discussed in the next section. Our results suggest that the reaction series in Fig. 11 is kinetically expedited at the solid–water interface of Fe(III) oxides.

The redox potential of structural $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ sites in the phyllosilicate octahedral layer, the presumed dominant

reductant in our phyllosilicate experiments, have not been formally measured but are believed to be lower than those of aqueous $\text{Fe}(\text{II})/\text{Fe}(\text{III})$ couples and higher than those of sorbed Fe(II) on Fe(III) oxides (Amonette et al., 2000). The redox chemistry of Fe(II) in the octahedral layer is complex, and in high Fe-smectites can involve intra-solid migration to form reactive Fe(II) clusters involving $\text{Fe}^{\text{II}}\text{--O--Fe}^{\text{II}}$ and $\text{Fe}^{\text{II}}\text{--O--Fe}^{\text{III}}$ redox centers (Lear and Stucki, 1987; Komadel et al., 1990).

4.2. Reduction mechanisms and implications of product speciation

4.2.1. Fe(III) oxides

Tc-EXAFS measurements of the product of heterogeneous reduction were virtually identical on both hematite and goethite, and these in-turn, were like the Tc(IV)-ferrihydrite standard (Fig. 4a) and ferrihydrite-like redox products resulting from the homogeneous reaction of Tc(VII) and $\text{Fe}^{2+}_{(\text{aq})}$ (Zachara et al., 2007). While the contribution of second shell Fe to all of the Tc spectra was unmistakable, the precise nature of Fe(III) in, or associated with, the redox products was indeterminate as shown by the similarity in the Tc(IV)-ferrihydrite, -goethite, and -hematite reference spectra (Fig. 4a). It is possible that Fe(III) was solubilized at low pH during Tc(IV)-goethite and Tc(IV)-hematite standard synthesis (Jang et al., 2007) which precipitated as ferrihydrite in association with Tc(IV) at higher pH. These ambiguities and close similarities between the EXAFS spectra of samples and the Tc(IV)-ferrihydrite standard led us to apply the EXAFS model of Zachara et al. (2007) that involved either the substitution within, or direct surface complexation of Tc(IV) octahedral monomers and dimers to a defected, ferrihydrite-like structure. This model yielded excellent fits of the EXAFS spectra (Fig. 4b), with reasonable structural parameters (Table 2). The identity of the heterogeneous Tc(IV) product as a surface complex to ferrihydrite, goethite, or hematite, or as a co-precipitate was indeterminate because of large, outer shell disorder, and minor apparent influence of Fe(III) structure on Tc-EXAFS results. Any of these end states could result from the direct redox reaction of Tc(VII) with surface Fe(II) complexes (e.g., $=\text{Fe}^{\text{III}}\text{OFe}^{\text{II}+}$ or $=\text{Fe}^{\text{III}}\text{OFe}^{\text{II}}\text{OH}^{\circ}$; Charlet et al., 1998); or reactive surface $=\text{Fe}(\text{III})\text{--OH}_2^{2+}$ sites that serve as conduits for transfer of internal, delocalized electron density.

Recent ^{57}Fe Mössbauer measurements at sub-mono-layer concentrations suggest that sorbed Fe(II) on Fe(III) oxides is oxidized by the bulk solid, and does not retain the molecular configuration of a classic surface Fe(II) complex (Williams and Scherer, 2004, 2005). Mössbauer mea-

Fig. 11. General reaction mechanism and intermediate states for the 3-electron redox transformation of Tc(VII) to Tc(IV) involving disproportionation as described by Cui and Eriksen (1996a) and Rard et al. (1999).

measurements indicate that the oxidized Fe(II) at the interface adopts magnetic ordering and hence, structural configuration comparable to the bulk Fe(III) oxide (Williams and Scherer, 2004, 2005). Silvester et al. (2005) hypothesized that the initial adsorption and subsequent redox reaction of sorbed Fe(II) occurs on crystal growth sites. Molecular calculations imply the plausibility of such redox reaction, suggesting that it is driven by the greater thermodynamic stability of Fe(III) as compared to Fe(II) surface species. The phenomena results in delocalization of negative charge density (from sorbed Fe(II)) to the bulk solid several atomic layers from the interface (Kerisit and Rosso, 2006).

Our RT and 77 K Mössbauer measurements of $^{57}\text{Fe(II)}$ on ^{56}Fe -goethite both before and after reaction with Tc(VII) (Fig. 3) were similar to $^{57}\text{Fe(II)}$ on ^{56}Fe -goethite/natural goethite reported by Silvester et al. (2005), Williams and Scherer (2004), implying oxidation of surface $^{57}\text{Fe(II)}$ by electron transfer to the bulk oxide, and its conversion to a goethite-like layer. Broadening of our Mössbauer spectra implied the possible presence of multiple Fe(III) environments with slightly different Mössbauer parameters, that were empirically fit with three sites (A, B, and C). While these findings were expected for the unreacted, Fe(II)-sorbed goethite; they were not expected for the Tc(VII)-reacted goethite that had experienced heterogeneous surface Tc(IV) precipitation, heterogeneous Fe(II) oxidation (at the interface or in bulk), and a second, coincident phase of Fe(II) sorption that renewed the initial Fe(II) sorption density (e.g., Figs. 1 and 2). Additional ^{57}Fe -Mössbauer measurements are needed on the products of this heterogeneous reaction with both hematite and goethite to clearly identify the structural state of Fe(III) associated with Tc(IV). Technetium(IV) EXAFS appears to be relatively insensitive to the nature of the heterogeneous Fe(III) product, and may be an inadequate structural probe for co-associated Fe(III). Moreover, the Tc(IV)-goethite and -hematite EXAFS standards may have been compromised by the acid synthesis procedure. An alternative synthesis procedure for the reference phases is needed that does not subject the Fe(III) oxide sorbents to extremes in pH.

Uncertainty exists on whether dissolved Fe(II) is an essential partner in heterogeneous redox reactions of the type studied here as suggested by Williams and Scherer (2004), Park and Dempsey (2005), and others. Williams and Scherer (2004) found that the sorbed Fe(II) on goethite (that displayed a Mössbauer spectra like that in Fig. 3a) was unreactive to nitroaromatic compounds (NAC) in the absence of $\text{Fe}^{2+}_{(\text{aq})}$. Park and Dempsey (2005) proposed an anode/cathode model for the heterogeneous oxidation of sorbed Fe(II) on goethite where the reduction of dissolved oxygen at electron-rich, interfacial regions of sorbed Fe(II) is coupled to the oxidation of aqueous Fe(II) at electron poor regions with consequent structural incorporation of product Fe(III). Implicit in this conceptual model is (i) the presence of multiple sites or faces that may exhibit different adsorption affinities for $\text{Fe}^{2+}_{(\text{aq})}$ and different intrinsic crystal growth rates as has been measured experimentally (Weidler et al., 1998; Chun et al., 2006), and (ii) the plausibility of significant bulk electron diffusion

in both goethite and hematite as suggested by molecular modeling (Kerisit and Rosso, 2006). Our results (Figs. 1 and 2) showed clearly that Tc(VII) reduction was coincident with a stoichiometric event of $\text{Fe}^{2+}_{(\text{aq})}$ adsorption at all pH values studied, consistent with the model of Park and Dempsey (2005).

4.2.2. Phyllosilicates

The heterogeneous reduction behavior of Tc(VII) in FRC-phyllsilicate mixture was similar to recent observations of the reactivity of NAC with DCB-reduced, Fe-containing phyllosilicates. Hofstetter et al. (2003, 2006) found that ion-exchangeable Fe(II) on reduced phyllosilicates was not reactive toward NAC. Moreover, NAC reduction showed little pH dependence, as did Tc(VII) reduction with the FRC-dcb, leading to the conclusion (Hofstetter et al., 2006) that edge-complexed Fe(II) made minor contribution to the heterogeneous reduction reaction, as the reactivity of Fe(II) edge complexes typically show strong pH dependency through hydrolysis (Klausen et al., 1995). Hofstetter et al. (2003, 2006) concluded that electron transfer occurred primarily from structural Fe(II) in the octahedral layer and that the Fe content, distribution and arrangement of Fe(II) and Fe(III) in the octahedral layer controlled heterogeneous redox reactivity for NAC. Structural Fe(II) in the octahedral layer of the fine-grained phyllosilicates was probably the primary Fe(II) species responsible for Tc(VII) reduction given our preparation procedure (CaCl_2 /PIPES washing).

As compared to Tc(IV) associated with hematite and goethite, the redox product on the FRC-dcb showed more Tc–Tc bonding (Fig. 9), and less Fe(III) in the second coordination shell. The presence of a large amount of Tc–Tc bonding could be explained in two ways: (1) the coexistence of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ and Tc(IV)–Fe(III) complexes similar to those observed on goethite and hematite, and (2) short (several octahedral units) lengths of TcO_2 chains bound to Fe(III) associated with the phyllosilicate substrate. The presence of identifiable Fe scatterers in the Tc(IV) precipitate, may support our posit of electron transfer from submicron sized-phyllsilicates where a significant fraction of reaction sites exist along crystallite edges where structural, octahedral Fe is exposed. Alternatively, it may indicate that a portion of the heterogeneous reaction centers were edge-complexed Fe(II) (e.g., to aluminol sites) where the reaction product was free to coprecipitate with Tc after electron transfer and disproportionation. Whether the greater amount of Tc–Tc bonding in the Tc(IV) precipitate in the FRC-dcb as compared to the Fe(III) oxide sorbents was a result of Fe(II) location, or kinetic factors such as a slower reduction rate was not ascertained.

4.3. Comparisons of reduction/precipitation mechanisms with NAC

Analogies have been drawn herein between the behavior of Tc(VII) and NAC because of similarities in certain experimental results. NACs are highly suited as redox probe compounds because they exhibit a range in reactivities and redox potentials (Rugge et al., 1998; Hofstetter

et al., 2003, 2006; Elsner et al., 2004; Williams and Scherer, 2004). The reduced product is generally weakly adsorbed by the mineral substrate, allowing for study of how electron transfer influences the morphology and growth of the heterogeneous substrate in the absence of potentially inhibitory, strongly sorbing redox products (e.g., Chun et al., 2006).

A critical difference between NAC and Tc, however is that the reduced Tc(IV) product is quite insoluble ($<10^{-8}$ mol L $^{-1}$ depending on its molecular speciation), strongly associates with the solid surface as a surface precipitate or complex, and likely displays limited diffusional mobility after reaching the Tc(IV) state and hydrolyzing. Consequently, Tc(IV), which has a similar ionic radii (0.645 Å) to Fe(III) (0.640 Å), is available at the interface to complex with or cover crystal nucleation sites; inhibit redox-initiated, face-specific growth (Chun et al., 2006); and/or coprecipitate within new Fe(III) oxide phases formed by heterogeneous Fe(II) oxidation as limited by structural and charge balance constraints. These reactions influence the speciation of the Tc(IV)/Fe(III) redox product investigated herein, and distinguish Tc behavior and the resulting Fe(III) redox products from those generated by reaction with NAC.

4.4. Geochemical implications

New results presented herein demonstrate that mineral associated Fe(II) can be an effective heterogeneous reductant of Tc(VII) under anoxic conditions, yielding insoluble Tc(IV) precipitates, coprecipitates, and/or surface complexes that may significantly retard Tc migration. The heterogeneous process is orders of magnitude more rapid than the homogeneous reduction of Tc(VII) by Fe $^{2+}_{(aq)}$. Sorbed Fe(II) on Fe(III) oxides is a more rapid heterogeneous reductant of Tc(VII) than is structural/edge-complexed Fe(II) within or on layer silicates. The more rapid reduction rate promoted by the Fe(III) oxide system is attributed to more favorable thermodynamics of sorbed Fe(II) resulting from its hydroxylation, and the unique, but still poorly understood redox chemistry of Fe(II) at and within the near surface region of crystalline Fe(III) oxides. The large noted difference in heterogeneous reduction rates for the Fe(III) oxide versus phyllosilicate systems, were equivalent to differences noted in whole sediment dominated by these phases where Fe(II) was of biotic origin (Fredrickson et al., 2004). Vandergraaf et al. (1984) noted that Tc accumulated along grain boundaries of Fe(III) oxides in anoxic granitic and gabbro rock thin sections and not on mineral surfaces containing significant structural Fe(II) (such as biotite, pyroxene, or hornblende), an observation consistent with the importance the heterogeneous reaction on Fe(III)-oxide surfaces. Ferrous iron associated with ferric oxides was also the dominant reductant for NAC in anaerobic aquifer sediments (Rugge et al., 1998).

Given that ^{99}Tc concentrations as an environmental contaminant are generally low (e.g., $<10^{-5}$ mol L $^{-1}$), our results suggest that heterogeneous Tc(VII) reduction should occur rapidly in anoxic subsurface sediments at pH >6 that contain even small amounts of goethite or hematite, and Fe $^{2+}_{(aq)}$ of either abiotic or biotic origin.

The slower, but still significant heterogeneous reduction rates of Tc(VII) on reduced phyllosilicates of “average” total Fe(II) content as studied here, suggest that this process should also be important in subsurface sediments where layer silicates are typically ubiquitous, and often reduced. Moreover, ferrous containing phyllosilicates may contain effectively large structural repositories of electron equivalents (Amonette, 2002) allowing their function as long-term, flux-capturing reductive sinks of ^{99}Tc (e.g., Istok et al., 2004). The different molecular speciation of heterogeneous reduction products on Fe(III) oxides and layer silicates is expected to strongly influence their oxidation rates (e.g., Zachara et al., 2007) if and when molecular oxygen concentrations increase in bathing subsurface or sediment pore waters.

ACKNOWLEDGMENTS

We would like to thank Paul Gassman for ^{56}Fe -goethite synthesis; Steven Smith and Andrew Plymale for preparation and characterization of FRC-dcb sediments and for performing preliminary Tc(VII) reduction experiments by Fe(II) adsorbed on Fe(III) oxides. The research was supported by the Environmental Remediation Sciences Program (ERSP), Office of Biological and Environmental Research (OBER), Environmental Remediation Sciences Division (ERSD), U.S. Department of Energy (DOE). Mössbauer spectroscopy measurements were performed in the Environmental Molecular Sciences Laboratory (EMSL) that is managed and supported by OBER-ERSD. PNNL is operated for the DOE by Battelle. PNC/XOR facilities at the Advanced Photon Source, and research at these facilities, are supported by the U.S. Department of Energy Basic Energy Sciences, a major facilities access grant from NSERC, the University of Washington, Simon Fraser University, the Pacific Northwest National Laboratory and the Advanced Photon Source. Use of the Advanced Photon Source is also supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract DE-AC02-06CH11357.

REFERENCES

- Amonette J. E. (2002) Iron redox chemistry of clays and oxides: environmental applications. In: *Electrochemical Properties of Clays, CMS Workshop Lectures* (ed. A. Fitch). The Clay Mineral Society, Aurora, CO.
- Amonette J. E., Workman D. J., Kennedy D. W., Fruchter J. S. and Gorby Y. A. (2000) Dechlorination of carbon tetrachloride by Fe(II) associated with goethite. *Environ. Sci. Technol.* **34**, 4606–4613.
- Anschutz A. J. and Penn R. L. (2005) Reduction of crystalline iron(III) oxyhydroxides using hydroquinone: influence of phase and particle size. *Geochem. Trans.* **6**, 60–66.
- Bain D. C. and Smith B. F. (1994) Spectroscopic and chemical determinative methods. In *Clay Mineralogy* (ed. M. J. Wilson). Chapman and Hall, London.
- Behrends T. and Van Cappellen P. (2005) Competition between enzymatic and abiotic reduction of uranium(VI) under iron reducing conditions. *Chem. Geol.* **220**, 315–327.
- Bennett R. and Willey N. (2003) Soil availability, plant uptake and soil to plant transfer of Tc-99—a review. *J. Environ. Radiol.* **65**, 215–231.
- Bondietti E. A. and Francis C. W. (1979) Geologic migration potentials of Tc-99 and Np-237. *Science* **203**, 1337–1340.

- Buerge I. J. and Hug S. J. (1999) Influence of mineral surfaces on chromium(VI) reduction by iron(II). *Environ. Sci. Technol.* **33**, 4285–4291.
- Burke I. T., Boothman C., Lloyd J. R., Mortimer R. J. G., Livens F. R. and Morris K. (2005) Effects of progressive anoxia on the solubility of technetium in sediments. *Environ. Sci. Technol.* **39**, 4109–4116.
- Charlet L. and Tournassat C. (2005) Fe(II)–Na(I)–Ca(II) cation exchange on montmorillonite in chloride medium: evidence for preferential clay adsorption of chloride–metal ion pairs in seawater. *Aquat. Geochem.* **11**, 115–137.
- Charlet L., Silvester E. and Liger E. (1998) N-compound reduction and actinide immobilization in surficial fluids by Fe(II): the surface Fe(III)OFe(II)OH degrees species, as major reductant. *Chem. Geol.* **151**, 85–93.
- Chun C. L., Penn R. L. and Arnold W. A. (2006) Kinetic and microscopic studies of reductive transformations of organic contaminants on goethite. *Environ. Sci. Technol.* **40**, 3299–3304.
- Coby A. J. and Picardal F. W. (2005) Inhibition of NO_3^- and NO_2^- reduction by microbial Fe(III) reduction: Evidence of a reaction between NO_2^- and cell surface-bound Fe^{2+} . *Appl. Environ. Microbiol.* **71**, 5267–5274.
- Colon D., Weber E. J. and Anderson J. L. (2006) QSAR study of the reduction of nitroaromatics by Fe(II) species. *Environ. Sci. Technol.* **40**, 4976–4982.
- Cornell R. M. and Schwertmann U. (2000) *The Iron Oxides: Structure, Properties, Reactions, Occurrences, and Uses*. Wiley-VCH, New York.
- Cui D. Q. and Eriksen T. E. (1996a) Reduction of pertechnetate by ferrous iron in solution: influence of sorbed and precipitated Fe(II). *Environ. Sci. Technol.* **30**, 2259–2262.
- Cui D. Q. and Eriksen T. E. (1996b) Reduction of pertechnetate in solution by heterogeneous electron transfer from Fe(II)-containing geological material. *Environ. Sci. Technol.* **30**, 2263–2269.
- Elsner M., Schwarzenbach R. P. and Haderlein S. B. (2004) Reactivity of Fe(II)-bearing minerals toward reductive transformation of organic contaminants. *Environ. Sci. Technol.* **38**, 799–807.
- Fredrickson J. K., Zachara J. M., Kennedy D. W., Dong H. L., Onstott T. C., Hinman N. W. and Li S. M. (1998) Biogenic iron mineralization accompanying the dissimilatory reduction of hydrous ferric oxide by a groundwater bacterium. *Geochim. Cosmochim. Acta* **62**, 3239–3257.
- Fredrickson J. K., Zachara J. M., Kennedy D. W., Kukkadapu R. K., McKinley J. P., Heald S. M., Liu C. X. and Plymale A. E. (2004) Reduction of TcO_4^- by sediment-associated biogenic Fe(II). *Geochim. Cosmochim. Acta* **68**, 3171–3187.
- Gregory K. B., Larese-Casanova P., Parkin G. F. and Scherer M. M. (2004) Abiotic transformation of hexahydro-1,3,5-trinitro-1,3,5-triazine by Fe(II) bound to magnetite. *Environ. Sci. Technol.* **38**, 1408–1414.
- Haderlein S. B. and Pecher K. (1999) Pollutant reduction in heterogeneous Fe(II)/Fe(III)-systems. In *Kinetics and Mechanisms of Reactions at the Mineral/Water Interface* (eds. D. L. Sparks and T. J. Grundl). American Chemical Society.
- Hansen H. C. B., Koch C. B., Nancke-Krogh H., Borggaard O. K. and Sorensen J. (1996) Abiotic nitrate reduction to ammonium: key role of green rust. *Environ. Sci. Technol.* **30**, 2053–2056.
- Hess N. J., Yuanxian X., Rai D. and Conradson S. D. (2004) Thermodynamic model for the solubility of $\text{TcO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ in the aqueous $\text{Tc(IV)}-\text{Na}^+-\text{Cl}^--\text{H}^+-\text{OH}^--\text{H}_2\text{O}$ system. *J. Solution Chem.* **33**, 199–226.
- Hofstetter T. B., Schwarzenbach R. P. and Haderlein S. B. (2003) Reactivity of Fe(II) species associated with clay minerals. *Environ. Sci. Technol.* **37**, 519–528.
- Hofstetter T. B., Neumann A. and Schwarzenbach R. P. (2006) Reduction of nitroaromatic compounds by Fe(II) species associated with iron-rich smectites. *Environ. Sci. Technol.* **40**, 235–242.
- Holta P., Hautojarvi A. and Hakanen M. (1992) Transport and retardation of non-sorbing radionuclides in crystalline rock fractures. *Radiochim. Acta* **58/59**, 285–290.
- Hyacinthe C., Bonneville S. and Van Cappellen P. (2006) Reactive iron(III) in sediments: chemical versus microbial extractions. *Geochim. Cosmochim. Acta* **70**, 4166–4180.
- Istok J. D., Senko J. M., Krumholz L. R., Watson D., Bogle M. A., Peacock A., Chang J.-Y. and White D. C. (2004) In situ bioreduction of technetium and uranium in a nitrate-contaminated aquifer. *Environ. Sci. Technol.* **38**, 468–475.
- Jang J. H., Dempsey B. A. and Burgos W. D. (2007) Solubility of hematite revisited: effects of hydration. *Environ. Sci. Technol.* **41**, 7303–7308.
- Jeon B. H., Dempsey B. A., Burgos W. D. and Royer R. A. (2001) Reactions of ferrous iron with hematite. *Colloids Surf. A: Physicochem. Eng. Aspects* **191**, 41–55.
- Jeon B. H., Dempsey B. A. and Burgos W. D. (2003) Kinetics and mechanisms for reactions of Fe(II) with iron(III) oxides. *Environ. Sci. Technol.* **37**, 3309–3315.
- Jeon B. H., Dempsey B. A., Royer R. A. and Burgos W. D. (2004) Low-temperature oxygen trap for maintaining strict anoxic conditions. *J. Environ. Eng. ASCE* **130**, 1407–1410.
- Jeon B. H., Dempsey B. A., Burgos W. D., Barnett M. O. and Roden E. E. (2005) Chemical reduction of U(VI) by Fe(II) at the solid–water interface using natural and synthetic Fe(III) oxides. *Environ. Sci. Technol.* **39**, 5642–5649.
- Jolivet J. P., Tronc E., Barbe C. and Livage J. (1990) Interfacial electron-transfer in colloidal spinel iron-oxide silver ion reduction in aqueous-medium. *J. Colloid Interf. Sci.* **138**, 465–472.
- Kerisit S. and Rosso K. (2006) Computer simulation of electron transfer at hematite surfaces. *Geochim. Cosmochim. Acta* **70**, 1888–1903.
- Kim S. and Picardal F. W. (1999) Enhanced anaerobic biotransformation of carbon tetrachloride in the presence of reduced iron oxides. *Environ. Toxicol. Chem.* **18**, 2142–2150.
- Klausen J., Trober S. P., Haderlein S. B. and Schwarzenbach R. P. (1995) Reduction of substituted nitrobenzenes by Fe(II) in aqueous mineral suspensions. *Environ. Sci. Technol.* **29**, 2396–2404.
- Komadel P., Lear P. R. and Stucki J. W. (1990) Reduction and reoxidation of nontronite: extent of reduction and reaction rates. *Clays Clay Miner.* **38**, 203–208.
- Komlos J., Kukkadapu R. K., Zachara J. M. and Jaffe P. R. (2007) Biostimulation of iron reduction and subsequent oxidation of sediment containing Fe-silicates and Fe-oxides: effect of redox cycling on Fe(III) bioreduction. *Water Res.* **41**(13), 2996–3007.
- Kukkadapu R. K., Zachara J. M., Smith S. C., Fredrickson J. K. and Liu C. X. (2001) Dissimilatory bacterial reduction of Al-substituted goethite in subsurface sediments. *Geochim. Cosmochim. Acta* **65**, 2913–2924.
- Kukkadapu R. K., Zachara J. M., Fredrickson J. K., McKinley J. P., Kennedy D. W., Smith S. C. and Dong H. L. (2006) Reductive biotransformation of Fe in shale–limestone saprolite containing Fe(III) oxides and Fe(II)/Fe(III) phyllosilicates. *Geochim. Cosmochim. Acta* **70**, 3662–3676.
- Larsen O., Postma D. and Jakobsen R. (2006) The reactivity of iron oxides towards reductive dissolution with ascorbic acid in a shallow sandy aquifer (Romo, Denmark). *Geochim. Cosmochim. Acta* **70**, 4827–4835.
- Lear P. R. and Stucki J. W. (1987) Intervalence electron transfer and magnetic exchange in reduced nontronite. *Clays Clay Miner.* **35**, 373–378.

- Lieser K. H. and Bauscher C. (1987) Technetium in the hydrosphere and in the geosphere. 1. Chemistry of technetium and iron in natural waters and influence of the redox potential on the sorption of technetium. *Radiochim. Acta* **42**, 205–213.
- Liger E., Charlet L. and Van Cappellen P. (1999) Surface catalysis of uranium(VI) reduction by iron(II). *Geochim. Cosmochim. Acta* **63**, 2939–2955.
- Liu C., Zachara J. M., Foster-Mills N. S. and Strickland J. (2007) Kinetics of reductive dissolution of hematite by bio-reduced anthraquinone-2,6-disulfonate. *Environ. Sci. Technol.* **41**, 7730–7735.
- Lloyd J. R., Sole V. A., Van Praagh C. V. G. and Lovley D. R. (2000) Direct and Fe(II)-mediated reduction of technetium by Fe(III)-reducing bacteria. *Appl. Environ. Microbiol.* **66**, 3743–3749.
- Lukens, Jr., W. W., Bucher J. J., Edelstein N. M. and Shuh D. K. (2002) Products of pertechnetate radiolysis in highly alkaline solution: Structure of $\text{TcO}_2 \cdot x\text{H}_2\text{O}$. *Environ. Sci. Technol.* **36**, 1124–1129.
- Murad E. and Cashion J. (2004) *Mössbauer Spectroscopy of Environmental Materials and their Industrial Utilization*. Kluwer Academic Publishers, Dordrecht.
- Park B. and Dempsey B. A. (2005) Heterogeneous oxidation of Fe(II) on ferric oxide at neutral pH and a low partial pressure of O_2 . *Environ. Sci. Technol.* **39**, 5000–6494.
- Pecher K., Haderlein S. B. and Schwarzenbach R. P. (2002) Reduction of polyhalogenated methanes by surface-bound Fe(II) in aqueous suspensions of iron oxides. *Environ. Sci. Technol.* **36**, 1734–1741.
- Pepper S. E., Bunker D. J., Bryan N. D., Livens F. R., Charnock J. M., Patrick R. A. D. and Collison D. (2003) Treatment of radioactive wastes: an X-ray absorption spectroscopy study of the reaction of technetium with green rust. *J. Colloids Interf. Sci.* **268**, 408–412.
- Rancourt d. G. and Ping J. Y. (1991) Voigt-based methods for arbitrary-shape static hyperfine parameter distributions in Mossbauer spectroscopy. *Nucl. Instrum. Methods Phys. Rev.* **B58**, 85–87.
- Rard J. A., Rand M. H., Anderegg G. and Wanner H. (1999) *Chemical Thermodynamics of Technetium*. Elsevier, Amsterdam, The Netherlands.
- Ravel B. and Newville M. (2005) ATHENA, ARTEMIS, HEPHAESTUS; data analysis for X-ray absorption spectroscopy using IFEFFIT. *J. Synchrotron Radiat.* **12**, 537–541.
- Rehr J. J. and Albers R. C. (2000) Theoretical approaches to X-ray absorption fine structure. *Rev. Mod. Phys.* **72**, 621–654.
- Roden E. E. (2004) Analysis of long-term bacterial vs. chemical Fe(III) oxide reduction kinetics. *Geochim. Cosmochim. Acta* **68**, 3205–3216.
- Rugge K., Hofstetter T. B., Haderlein S. B., Bjerg P. L., Knudsen S., Zraunig C., Mosbaek H. and Christensen T. H. (1998) Characterization of predominant reductants in an anaerobic leachate-contaminated aquifer by nitroaromatic probe compounds. *Environ. Sci. Technol.* **32**, 23–31.
- Schroeder N. C., Morgan D., Rokop D. J. and Fabryka-Martin J. (1993) Migration of technetium-99 in the alluvial aquifer at the Nevada test site, Nevada. *Radiochim. Acta* **60**, 203–209.
- Schwertmann U. and Cornell R. M. (2000) *Iron Oxides in the Laboratory*. Wiley-VCH, Weinheim, Germany.
- Serne R. J. and Mann F. M. (2004) *Preliminary Data from 216-B-26 Borehole in BC Cribs Area*. RPP-20303, Rev. 0, CH2M Hill Hanford Group, Inc., Richland, WA.
- Silvester E., Charlet L., Tournassat C., Gehin A., Greneche J. M. and Liger E. (2005) Redox potential measurements and Mossbauer spectrometry of Fe(II) adsorbed onto Fe(III) (oxyhydr)oxides. *Geochim. Cosmochim. Acta* **69**, 4801–4815.
- Sorensen J. and Thorling L. (1991) Stimulation by lepidocrocite ($\gamma\text{-FeOOH}$) of Fe(II)-dependent nitrite reduction. *Geochim. Cosmochim. Acta* **55**, 1289–1294.
- Strathmann T. J. and Stone A. T. (2003) Mineral surface catalysis of reactions between Fe(II) and oxime carbamate pesticides. *Geochim. Cosmochim. Acta* **67**, 2775–2791.
- Stucki J. W., Golden D. C. and Roth C. B. (1984) Effects of reduction and reoxidation of structural iron on the surface charge and dissolution of dioctahedral smectites. *Clays Clay Miner.* **32**, 350–356.
- Stucki J. W., Lee K., Goodman B. A. and Kostka J. C. (2007) Effects of in-situ biostimulation on iron mineral speciation in a subsurface soil. *Geochim. Cosmochim. Acta* **72**(4), 834–843.
- Stumm W. and Sulzberger B. (1992) The cycling of iron in natural environments—considerations based on laboratory studies of heterogeneous redox processes. *Geochim. Cosmochim. Acta* **56**, 3233–3257.
- Szecsody J. E., Fruchter J. S., Williams M. D., Vermeul V. R. and Sklarew D. (2004) In situ chemical reduction of aquifer sediments: enhancement of reactive iron phases and TCE dechlorination. *Environ. Sci. Technol.* **38**, 4656–4663.
- Vandergraaf T. T., Ticknor K. V. and George I. M. (1984) Reactions between technetium in solution and iron-containing minerals under oxic and anoxic conditions. In *Geochemical Behavior of Disposed Radioactive Waste* (eds. G. S. Barney, J. D. Navratil and W. W. Schulz). American Chemical Society, Washington, DC.
- Ward A. L., Gee G. W., Zhang Z. F. and Keller J. M. (2004) *Vadose Zone Contaminant Fate and Transport Analysis for the 216-B-26 Trench*. PNNL-14907, Pacific Northwest National Laboratory, Richland, WA.
- Weidler P. G., Hug S. J., Wetche T. P. and Hiemstra T. (1998) Determination of growth rates of (100) and (110) faces of synthetic goethite by scanning force microscopy. *Geochim. Cosmochim. Acta* **62**, 3407–3412.
- Wharton M. J., Atkins B., Charnock J. M., Livens F. R., Patrick R. A. D. and Collison D. (2000) An X-ray adsorption spectroscopy study of the coprecipitation of Tc and Re with macinawite (FeS). *Appl. Geochem.* **15**, 347–354.
- Wildung R. E., Mcfadden K. M. and Garland T. R. (1979) Technetium sources and behavior in the environment. *J. Environ. Qual.* **8**, 156–161.
- Wildung R. E., Gorby Y. A., Krupka K. M., Hess N. J., Li S. W., Plymale A. E., McKinley J. P. and Fredrickson J. K. (2000) Effect of electron donor and solution chemistry on products of dissimilatory reduction of technetium by *Shewanella putrefaciens*. *Appl. Environ. Microbiol.* **66**, 2451–2460.
- Wildung R. E., Li S. W., Murray C. J., Krupka K. M., Xie Y., Hess N. J. and Roden E. E. (2004) Technetium reduction in sediments of a shallow aquifer exhibiting dissimilatory iron reduction potential. *FEMS Microbiol. Ecol.* **49**, 151–162.
- Williams A. G. B. and Scherer M. M. (2004) Spectroscopic evidence for Fe(II)–Fe(III) electron transfer at the iron oxide–water interface. *Environ. Sci. Technol.* **38**, 4782–4790.
- Zachara J. M., Fredrickson J. K., Li S. M., Kennedy D. W., Smith S. C. and Gassman P. L. (1998) Bacterial reduction of crystalline Fe^{3+} oxides in single phase suspensions and subsurface materials. *Am. Mineral.* **83**, 1426–1443.
- Zachara J. M., Heald S. M., Jeon B. H., Kukkadapu R. K., Liu C., McKinley J. P., Dohnalkova A. C. and Moore D. A. (2007) Reduction of pertechnetate [Tc(VII)] by aqueous Fe(II) and the nature of solid phase redox products. *Geochim. Cosmochim. Acta* **71**, 2137–2157.

Associate editor: Donald L. Sparks