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Tc(VII) reduction kinetics by titanomagnetite (Fe_{3-x}Ti_xO₄) nanoparticles

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Abstract

Technetium contamination remains a major environmental problem at nuclear reprocessing sites, such as at the Hanford nuclear reservation, Washington, USA. Here we investigate the heterogeneous reduction of the highly soluble pertechnetate anion [Tc(VII)O₄⁻] to sparingly soluble Tc(IV)-bearing solids by a novel and well-characterized set of mixed-valent titanium-doped magnetite nanoparticles, structurally and chemically analogous to titanomagnetites naturally present in Hanford sediments. Titanomagnetite (Fe_{3-x}Ti_xO₄) nanoparticles (10–12 nm) with varying Ti content (0 ≤ x ≤ 0.53) were synthesized in aqueous suspension. Reaction with 10 and 30 μM Tc(VII) solution yielded fast exponentially decaying reduction kinetics with rates that increased with increasing solid-state Fe(II)/Fe(III) ratio in the nanoparticles, a characteristic systematically controlled by the Ti-content. Nanoparticles before and after reduction experiments and surface-associated products of Tc(VII) reduction were characterized using transmission electron microscopy (TEM), X-ray absorption near-edge spectroscopy (XANES), extended X-ray absorption fine structure spectroscopy (EXAFS), micro X-ray diffraction (μ-XRD), X-ray absorption (XA) and X-ray magnetic circular dichroism (XMCD). A mechanistic reaction model was developed involving reduction of Tc(VII) to form Tc(IV)/Fe(III) solids by structural Fe(II) enriched at the nanoparticle surface, a reactive Fe(II) pool that during reaction is resupplied and sustained by outward migration of Fe(II) from the particle interior with concurrent inward migration of charge-balancing cationic vacancies in a ratio of 3:1. The reaction process was quantitatively linked to mass and electron balanced changes in the Fe_{3-x}Ti_xO₄ nanoparticles, and the accessibility of structural Fe(II) from these phases was determined.

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1. INTRODUCTION

⁹⁹Tc is a radioactive fission product of uranium and plutonium generated by nuclear reactors. Its presence in the subsurface is largely a result of past disposal practices at nuclear reprocessing facilities, including the Hanford site in Washington State, USA, and elsewhere (Gee et al., 2007; Khaleel et al., 2007). The risk of unmitigated ⁹⁹Tc contamination is substantial because of its long half-life

(2.1 × 10⁵ yr), relatively high fission yield, and high potential mobility in surface and groundwater. Tc mobility is strongly dependent on its oxidation state. Under oxidizing conditions, it exists predominantly as Tc(VII) in the form of the highly soluble pertechnetate anion [TcO₄⁻], a species that is generally resistant to adsorption on mineral surfaces over common pH values (Cui and Eriksen, 1996b). Under reducing conditions, it exists predominantly as Tc(IV) in the form of sparingly soluble solid phases, nominally TcO₂·nH₂O. Immobilizing subsurface TcO₄⁻ by reduction to its less soluble counterpart has therefore been widely regarded as a promising remediation strategy component (e.g., Fredrickson et al., 2004; Darab et al., 2007; Jaisi et al., 2009).

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Ferrous iron in its various chemical forms is an important possible Tc(VII) reductant because of its reduction potential range and ubiquity in reducing environments. While thermodynamically favorable, Tc(VII) reduction to Tc(IV) by dissolved Fe(II) in homogeneous aqueous solution is known to be slow (Cui and Eriksen, 1996a; Zachara et al., 2007). However, when Fe(II) is sorbed onto mineral surfaces or comprises an intrinsic structural component of minerals, Tc(VII) reduction kinetics are strongly and disproportionately enhanced. Examples include Fe(II) sorbed on (oxy)(hydr)oxides of Fe(III), e.g., hematite and goethite (Peretyazhko et al., 2008a; Jaisi et al., 2009), Mn(III/IV), e.g., manganite and birnessite (Jaisi et al., 2009), Al (Peretyazhko et al., 2008b), as well as silicates (Peretyazhko et al., 2008a). Tc(VII) is also efficiently reduced by structural Fe(II), including that in magnetite (Cui and Eriksen, 1996b; Farrell et al., 1999), green rust (Pepper et al., 2003), pyrite (Maes et al., 2004), and clay minerals (Jaisi et al., 2008, 2009). Hence, there is substantial interest and potential strategic value in gaining a fundamental understanding of chemical mechanisms, the nature of the rate enhancement, and factors that control the extent of reaction in Fe(II)-based heterogeneous Tc(VII) reduction systems.

A host of issues influence this process. The thermodynamic reduction potential for the reactive Fe(II) pool at a mineral surface is poorly definable and difficult to probe, both for initial conditions and more comprehensively as a function of reaction time (Liger et al., 1999; Williams and Scherer, 2004; Silvester et al., 2005). Although for some pure phases a Fe(II)/Fe(III) reduction potential in the solid-state can be defined (Amonette, 2002), at the mineral-solution interface the reducing potential and therefore extent of reaction cannot at present be predicted a priori because it is sensitive to structure, composition, and physical accessibility of electron equivalents. For example, surface armoring by an initially present or concomitantly built-up Fe(III)-dominated passive oxidized layer or co-precipitated Fe(III)–Tc(IV) products layer (Zachara et al., 2007) can limit access to otherwise available bulk Fe(II) (White and Peterson, 1996; Peterson et al., 1997). Conversely, Fe(II) reducing equivalents stored wholly or in part in solid phases based on continuous iron polyhedra, both crystalline and amorphous, are in principle more widely accessible to adsorbed reactants than just that at the mineral surface because of relatively high ionic and/or electronic conductivity in the solid-state, even at ambient temperature (Shuey, 1975; Tronc et al., 1992). This higher accessibility can arise from sufficiently facile solid-state diffusivity of iron cations through lattice channels and defects (e.g., Jolivet and Tronc, 1988) or via solution pathways by dissolution/reprecipitation (White and Peterson, 1996), or from a sufficiently high solid-state electron mobility via Fe(II)–Fe(III) electron hopping (i.e., semiconduction) (Rosso et al., 2010; Skomurski et al., 2011), or a combination. These aspects are intrinsic to heterogeneous Tc(VII) reduction by sorbed or structural Fe(II) on iron (oxy)(hydr)oxides, and represent some of the key challenges for experimental interrogation towards predictive-level understanding.

In this study, we examine heterogeneous Tc(VII) reduction by a novel and well-characterized set of $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ titanomagnetite nanoparticles (Pearce et al., 2012). This mineral system and format were selected for several reasons. Magnetite (Fe_3O_4) is a proven Tc(VII) reductant (e.g., Cui and Eriksen, 1996b; Farrell et al., 1999) and a common Fe(II)-bearing mineral. It also features a naturally “tunable” solid-state Fe(II)/Fe(III) ratio, which in principle controls the thermodynamic reduction potential of the mineral phase. Specifically, magnetite has the inverse spinel structure, $A(\text{Fe}^{3+})^B(\text{Fe}^{2+}\text{Fe}^{3+})\text{O}_4$, where A and B refer to tetrahedral and octahedral sites, respectively. Natural magnetites are invariably impure, with Ti(IV) a major structural substituent (Cornell and Schwertmann, 2003; Pearce et al., 2006), particularly in sediments derived from basalt such as at the Hanford site (Baer et al., 2010). Replacement of Fe(III) by Ti(IV) in the lattice yields titanomagnetites ($\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$), phase intermediates along the binary join with ulvöspinel (Fe_2TiO_4). This substitution is accompanied by reduction of lattice Fe(III) to Fe(II) for charge balance, therefore a proportional increase in the Fe(II)/Fe(III) ratio to values greater than that in magnetite (1:2) is expected. Hence Ti-doping is both relevant to natural magnetite and, from an experimental strategy perspective, is ideal for systematically examining the relationship between built-in redox potential and Tc(VII) reduction rate. Related strategies have been used elsewhere, including studies of methylene blue reduction by $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ ($0 \leq x \leq 0.78$) in the presence of H_2O_2 (Yang et al., 2009), and nitrobenzene reduction using partially oxidized magnetite (ratios $\leq 1:2$) (Gorski et al., 2010). Furthermore, titanomagnetite nanoparticles are relatively easy to produce with precisely controlled composition and structure by room temperature synthesis (Millot et al., 1998; Perriat et al., 1999; Guigue-Millot et al., 2001, 2003; Pearce et al., 2012) and, because of their high specific surface area, experimental sensitivity to Tc(VII) reduction and accompanying changes to the solid surface is greatly improved. Finally, the selected system has unique advantages in terms of spectroscopic discrimination and tracking of concentration and oxidation state changes in various possible reactive pools of solid-associated Fe(II), including that structurally ordered within the bulk structure and that near the solid surface.

Titanomagnetite oxidation produces titanomaghemite through a topotactic reaction which maintains the inverse spinel structure. The generalized formula for these phases may be written (Worm and Banerjee, 1984):

where y is the oxidation parameter that varies from $0 \leq y \leq 1$, where $y = 0$ equates to unoxidized and $y = 1$ equates to oxidized, with a limit of one electron removed per formula unit. The symbol $\square$ represents cationic vacancies that accumulate in the structure due to diffusive migration of iron cations out of the octahedral sublattice concurrent with oxidation at a rate of one vacancy per three electrons removed from the solid. The relevant one-electron oxidation reactions and end-member phases over the full compositional range of x and y are:

The oxidation process can be driven to the right either by proton-promoted dissolution that releases Fe(II) (Jolivet and Tronc, 1988; Tronc et al., 1989), for example at low pH by:

or by consumption of electrons by an oxidant at the particle surface (Worm and Banerjee, 1984), or both as in Eq. (5). In the present study, we investigate the kinetics of heterogeneous Tc(VII) reduction by $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ nanoparticles with x ranging from magnetite to titanomagnetite, nominally 0.00–0.53 (0.00, 0.15, 0.25, 0.38 and 0.53), in slightly alkaline pH aqueous solution under controlled anoxic conditions. Reaction products in the few Fe(II)-based Tc(VII) reduction studies reported to date suggest formation of relatively insoluble Tc(IV)–Fe(III) precipitates under similar conditions, with some evidence for magnetite-like and ferrihydrite-like Tc(IV)-containing phases (Lukens et al., 2002; Zachara et al., 2007), but remain poorly understood.

In our system, in accordance with the above the reactive electron donating component will be described in terms of Fe(II)-based reducing equivalents released from the nanoparticle structure and consumed in reaction with pertechnetate at particle surfaces. A mass and charge-balanced oxidation model for our system that encompasses both the pH-dependence of possible proton-promoted Fe(II) release coupled with heterogeneous reduction of Tc(VII), assuming complete reduction to Tc(IV), is therefore:

where the Tc(IV)–Fe(III) product as written, a structurally unspecified mixture of TcO_2 hydrate and ferrihydrite, is hypothetical but nonetheless stoichiometric and consistent with previous work, in our case possessing an expected 1:1 ratio of Tc(IV)/Fe(III) due to the transfer of three electrons to Tc and concomitant release and incorporation of one Fe(III) from the octahedral sublattice of the titanomagnetite structure.

Nanoparticle properties such as size, morphology, specific surface area and crystallinity have been characterized by transmission electron microscopy (TEM), BET specific surface area analysis, and micro-X-ray diffraction (μ -XRD) (Pearce et al., 2012). In particular, μ -XRD was performed *in situ* on anoxic nanoparticle suspensions before and after reaction to assess changes in the structurally

ordered bulk Fe(II) concentration via changes in the titanomagnetite cell parameter. A combination of chemical analysis, μ -XRD, X-ray absorption (XA) and X-ray magnetic circular dichroism (XMCD) were used to distinguish Fe(II)(aq) released from nanoparticles, surface-associated Fe(II), and structurally ordered Fe(II) in the nanoparticles. XMCD was used to track the structurally ordered Fe(II) pool in site-specific detail by distinguishing tetrahedral and octahedral Fe(II) and Fe(III) in the lattice (Pearce et al., 2010). Macroscopic time dependent aqueous [Tc(VII)] changes were measured using liquid scintillation counting (LSC). The reaction process can be quantitatively linked to mass and electron balanced changes in the $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ nanoparticles. Surface-associated products of Tc(VII) reduction were characterized using TEM and X-ray absorption spectroscopy.

2. MATERIALS AND METHODS

2.1. Nanoparticle synthesis

The synthesis protocol has been reported in detail in Pearce et al. (2012); essential details are briefly reviewed here. $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ nanoparticles were synthesized under ambient conditions and in aqueous suspension by co-precipitating a stoichiometric mixture of FeCl_2 , FeCl_3 and TiCl_4 in 0.3 M HCl ($\text{pH} < 1$) with ammonium (NH_4OH) solution in an anoxic glovebox (N_2 atmosphere from LN_2 boil-off; lower than 1 ppm residual O_2 ; hereafter referred to as the glovebox). The nanoparticles were precipitated instantaneously according to the equation:

The nanoparticles were magnetically separated from the aqueous phase and washed twice with degassed and deionized milli-Q ($>18 \text{ M}\Omega \text{ cm}$ resistivity) water (DDW) to remove possible impurities such as residual metal chlorides. After washing, the nanoparticles were resuspended in water prepared equivalently and stored inside the glovebox. The suspensions naturally equilibrated to a solution pH of ~ 8.5 , consistent with Reaction (4) as described below.

2.2. Nanoparticle characterization

The suspension density was determined and the chemical composition of the $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ nanoparticles, in terms of Fe(II), and total Fe and Ti was characterized by dissolving in N_2 -sparged 5 M HCl inside the glovebox overnight with shaking. Fe(II) was then determined using the ferrozine method (Stookey, 1970) and total Fe and Ti were determined using ICP-MS. The specific surface area (multipoint BET SSA) of the titanomagnetite nanoparticles was measured with a Quantachrome Autosorb automated gas sorption system (Quantachrome Co.) using nitrogen gas at 77 K. The samples were dried by degassing at $\sim 423 \text{ K}$ under vacuum for 24 h before measurements. Zeta-potential measurements were carried out using a ZetaPALS Zeta Potential Analyzer (Brookhaven Instruments Corporation).

In the glovebox, nanoparticle suspensions ($x = 0.00$ and 0.25) were added to 10 mL 0.002 M NaCl solution to reach a solid/solution ratio of 0.1 mg/mL. Sample pH was adjusted to a range of values between 3 and 10 using 0.001, 0.01, and 0.1 M HCl or NaOH solutions. After pH adjustment, samples were shaken in the glovebox overnight to reach equilibrium. Samples were taken out of the chamber and sonicated for 5 min directly before zeta potential measurement in the zeta cell.

2.2.1. Micro X-ray diffraction (μ -XRD)

Nanoparticle suspensions, before and after reaction with Tc(VII), were characterized *in situ* by μ -XRD using a Rigaku D/Max Rapid II instrument with a 2D image plate detector. X-rays were generated with a MicroMax 007HF generator fitted with a rotating Cr anode ($\lambda = 2.2897 \text{ \AA}$), and focused on the specimen through a 30 μm diameter collimator. The suspensions were loaded into boron-rich 0.5 mm O.D. capillary tubes (Charles Supper Company) in the glovebox and the capillaries were sealed with capillary wax (Charles Supper Company). The capillaries were maintained under anoxic conditions until immediately prior to measurement. 2DP, Rigaku 2D Data Processing Software (Ver. 1.0, Rigaku 2007) was used to integrate the diffraction rings captured by the 2-D image plate detector. The analysis of diffraction data was done using JADE 8.5 from Materials Data Inc., and the PDF4+ database from ICSD. The background was fitted by a cubic spline function, and the diffraction peaks were fitted using the pseudo-Voigt profile shape function. Cell refinement was also carried out in JADE using a cubic magnetite (Fe_3O_4) structure (PDF No. 00-019-0629) as the starting model. The correct sample-to-detector distance was verified by measuring the lattice constant of a Si standard (Silicon powder, NIST 640c). The observed lattice parameter deviated from the standard by 0.002 $\text{\AA}$.

2.2.2. Transmission electron microscopy (TEM)

Particle size and morphology were measured by a Jeol JEM 2010 transmission electron microscope (TEM) equipped with a LaB_6 filament and postcolumn attached with a Gatan Image Filter (GIF2000). The acceleration voltage on the microscope is 200 kV, and the point-to-point resolution of the microscope is 0.19 nm. All images were recorded by a slow-scan charge-coupled device (CCD) camera and processed using Digital Micrograph (Gatan, USA). TEM samples were prepared by dipping a 400 mesh copper grid coated with lacey carbon film into diluted nanoparticle suspension and then drying it inside the glovebox. Samples were taken out of the glovebox directly before measurements.

2.2.3. Synchrotron X-ray spectroscopies (XA, XMCD, XANES, EXAFS)

Nanoparticles were characterized before and after reaction by XA spectroscopy and XMCD, a XA difference spectrum technique based on circularly polarized light absorption in alternating opposing static applied magnetic fields that is sensitive to the oxidation state and local structure of magnetically ordered iron cations at solid surfaces

(van der Laan et al., 1986; van der Laan and Thole, 1991; Chen et al., 1995; Stohr, 1995). XA spectra at the Fe $L_{2,3}$ edges were obtained on beamline 4.0.2 at the Advanced Light Source (ALS), Berkeley, CA, using the eight-pole resistive magnet endstation (Arenholz and Prestemon, 2005). Samples were prepared by drying aliquots of the nanoparticle suspension onto carbon tape attached to the sample manipulator in a glovebox. XA was monitored in total-electron yield (TEY) mode, which has an effective probing depth of 50 $\text{\AA}$ (Gota et al., 2000). At each energy point, XA spectra were measured for two opposite magnetization directions by reversing the applied field of 0.6 T. After normalization to the incident beam intensity, the XMCD spectrum is obtained as the difference between the two XA spectra (Patrick et al., 2002). To obtain the cation distribution over the two structural Fe site types, the experimental XMCD was fit by means of a nonlinear least-squares analysis, using the calculated spectra for each site. In these calculations, described in van der Laan and Kirkman (1992) and van der Laan and Thole (1991), the 10 Dq crystal field parameters were taken as 1.2 and 0.6 eV for Fe B and A sites. The results were convoluted by a Lorentzian of $\Gamma = 0.3$ (0.5) eV for the L_3 (L_2) edge to account for intrinsic core-hole lifetime broadening and by a Gaussian of $\sigma = 0.2$ eV to account for instrumental broadening.

Tc K-edge XANES and EXAFS measurements on the nanoparticles after reaction were made at 20-BM at the Advanced Photon Source (APS), Argonne, IL. A Si (111) monochromator was used with a 1-mm entrance slit located approximately 50 m from the source. The monochromator allowed an energy resolution of about 4 eV at the Tc edge. The sample cells were sealed in Teflon holders with two layers of Kapton in the glovebox. The measurements were made in fluorescence mode using a 13-element Ge fluorescence detector. A Mo foil sample was used for energy calibration. The EXAFS and XANES data were analyzed using the Athena and Artemis interfaces to the IFEFFIT program package (Ravel and Newville, 2005).

2.3. Wet chemical experiments

All glassware and plastic bottles for wet chemical experiments were soaked in 1% HNO_3 overnight and then rinsed several times with distilled and deionized water before use. All chemicals, plastic syringes, tubes, vials, pipette tips, and syringe filters were deoxygenated for at least 24 h inside the glovebox prior to use. All dissolution and reduction experiments were conducted inside the glovebox. Degassed and deionized water (DDW) was stored in an anoxic chamber for preparation of all solutions and suspensions. All chemicals were reagent grade or better.

2.3.1. Fe(II)(aq) release kinetics

The time- and pH-dependence of Fe(II)(aq) release from the pure magnetite nanoparticles ($x = 0.00$) was measured at pH values buffered to 6, 7, and 8, to determine the optimum pH for the Tc(VII) reduction experiments, providing the lowest dissolved Fe(II)(aq) concentrations so that measured Tc(VII) reduction rates would correspond to Fe(II)

associated with the titanomagnetite nanoparticles. The buffer solution for pH 6 and 7 was 30 mM PIPES (Na-1,4-piperazine-*N,N'*-bis(2-ethanesulfonic acid)) solution, and for pH 8 it was 30 mM HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) solution. Fe(II)(aq) release experiments were conducted by spiking 7 mL of nanoparticle suspension into 100 mL of buffer solution, to give a concentration of $0.65 \text{ g L}^{-1} \text{ Fe}_{3-x}\text{Ti}_x\text{O}_4$, in 100 mL glass serum reaction bottles capped with rubber stoppers and crimp sealed. Sample aliquots were taken over time and filtered using $0.2 \mu\text{m}$ syringe filters. 0.2 mL of the filtrate was added to 1.8 mL ferrozine reagent (1 g L^{-1} ferrozine in 50 mM HEPES buffer, pH 7.0). Aqueous Fe(II) concentration was determined by measuring the absorbance at 562 nm using a Shimadzu UV-2501 PC spectrophotometer. Systematically increasing amounts of Fe(II) were released from the magnetite nanoparticles as pH values decreased, up to $\sim 8 \text{ mg L}^{-1}$ at equilibrium for pH 6 (Fig. 1); at pH 8 the equilibrated [Fe(II)(aq)] was near estimated methodological detection limits ($\sim 0.004 \text{ mM}$). Therefore, pH 8 HEPES solution (30 mM) was used for all Tc(VII) reduction experiments for all nanoparticle compositions. This pH is 1–2 pH units above the measured PZC for all $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ nanoparticle samples (pH 6–7), thus the influence of aggregation phenomena on measured kinetics are expected to be minimal.

Dissolution experiments were carried out to determine the rate of Fe(II) release from all nanoparticle compositions $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ ($x = 0.00\text{--}0.53$) at pH 8. Known volumes of nanoparticle suspensions were added to glass serum bottles containing 20 mL pH 8 HEPES solution (30 mM) to give a concentration of $0.5 \text{ g L}^{-1} \text{ Fe}_{3-x}\text{Ti}_x\text{O}_4$. The bottles were continuously shaken at 150 rpm for the duration of the experiment. For sampling, aliquots of suspension (1.5 mL) were transferred into Eppendorf centrifuge tubes and centrifuged for 5 min at 30,000 rpm. The concentration of Fe(II) in the supernatant was analyzed by ferrozine assay, and total Fe and Ti concentrations were measured using an ICP-MS Agilent 7500. A solution of known Fe(II) concentration was prepared as an internal standard and ana-

lyzed using the same procedure as for the nanoparticle suspensions, in order to detect any oxidation or adsorption of aqueous Fe(II) during the experiment. All experiments were performed in triplicate.

2.3.2. Tc(VII) reduction kinetics

Tc(VII) reduction experiments were conducted in 30 mL glass serum bottles with rubber stoppers and crimp seals. A known volume of nanoparticle suspension was added to HEPES buffer solution to give a solid to solution ratio of 1.3 mg:30 mL. The bottles were then sealed and continuously shaken for at least 20 h to allow Fe(II) release from nanoparticles to reach equilibrium. A $^{99}\text{Tc(VII)}$ stock solution (5 mM) was prepared by diluting NH_4TcO_4 (Perkin-Elmer Life Science Inc., Boston, MA) in DDW. The reaction was spiked with Tc(VII) solution to give a concentration of $10 \mu\text{M}$ or $30 \mu\text{M}$ after the 20 h equilibration period. The Tc-spiked solutions were continuously shaken and sampled over time. For sampling, aliquots of suspension (3 mL) were filtered using a $0.1 \mu\text{m}$ syringe filter. The filtrate (1 mL) was mixed with anoxic scintillation cocktail (9 mL) in the glovebox. The sample was then counted on a Packard 2500TR liquid scintillation counter (Packard Instrument Co., Meriden, CT) for 10 min. Background counts were collected by measuring HEPES buffer solution without Tc(VII). The concentration of Tc(VII) in solution was calculated from the background subtracted counts for the samples in dpm/mL. All experiments were performed in triplicate.

Control experiments were conducted to test for potential Tc(VII) adsorption onto the glass bottles and the syringe filters. Tc(VII) solution ($1 \mu\text{M}$) was spiked into HEPES solution (50 mL) in a glass bottle and shaken for five days. The final Tc(VII) concentration decreased less than 3%. Tc(VII) solution ($1 \mu\text{M}$) was also filtered through the $0.1 \mu\text{m}$ syringe filters used in the reduction experiments. The Tc(VII) concentration decreased $\sim 3.3\%$ after filtration. Thus, the effect of Tc(VII) adsorption by the glass serum bottles and the syringe filters was minimal.

3. RESULTS AND DISCUSSION

3.1. Starting materials

The characteristics of the initial titanomagnetite nanoparticles used here are summarized in Table 1, and are consistent with the properties reported in Pearce et al. (2012). TEM analysis showed that the particles are nearly spherical with a diameter of 9.4–13 nm ($\pm 2 \text{ nm}$), in good agreement with the size expected from the BET specific surface area analysis. The total Fe(II)/Fe(III) ratio of the samples, as determined by chemical analysis, were expectedly somewhat lower than the theoretical Fe(II)/Fe(III) ratio, calculated from the ratio of $\text{FeCl}_2/\text{FeCl}_3$ used in the synthesis, as a result of the washing step employed to remove any unreacted metal chlorides after synthesis. This washing step resulted in slight oxidation of the otherwise stoichiometric titanomagnetite nanoparticles due to partial Fe(II) dissolution akin to Reaction (4), producing samples that were on the titanomagnetite–titanomaghemite join. Similar Fe(II)

Fig. 1. pH-dependent dissolution of magnetite ($x = 0.00$) nanoparticles.

Table 1

Summary of characteristics of synthetic magnetite and titanomagnetite nanoparticles (Pearce et al., 2012).

x	Size (nm)	SSA ^a (m ² g ⁻¹)	a^b (Å)	Total Fe(II)/Fe(III) ^c	Structural Fe(II)/Fe(III) ^d	Surface Fe(II)/Fe(III) ^e	Dissolved Fe(II) ^f (μmol)
0	11.8	98.2	8.4062	0.559	0.556	0.604	0.0315
0.15	9.4	121.3	8.4155	0.701	0.656	0.667	0.1203
0.25	9.8	129.6	8.4217	0.783	0.730	0.745	0.1889
0.38	10.6	117.3	8.4292	0.948	0.829	0.878	0.2255
0.53	13.0	109.9	8.4337	1.208	0.893	1.130	0.3293

^a BET specific surface area (SSA).^b Unit-cell parameters calculated from XRD patterns.^c Total Fe(II)/Fe(III) ratio measured using acid digestion method.^d Fe(II)/Fe(III) ratio in structure measured by XRD.^e Fe(II)/Fe(III) ratio at surface measured by XMCD.^f Dissolved Fe(II) from 1.3 mg Fe_{3-x}Ti_xO₄ at 24 h (at equilibrium) in 30 mL buffer solution.

dissolution upon washing was also found for magnetite nanoparticles by Gorski and Scherer (2010). μ -XRD patterns were obtained for all samples under anoxic conditions in aqueous suspension and the only peaks present corresponded to a single titanomagnetite phase. The cubic unit cell edge parameter (space group Fd-3m) increased with increasing Ti content (x) (Table 1). This trend is well documented for bulk titanomagnetites due to the structural substitution of Ti(IV) for Fe(III) within the octahedral cationic sublattice and the corresponding reduction of Fe(III) to Fe(II) to maintain charge balance (Wechsler et al., 1984; Bosi et al., 2009; Pearce et al., 2010). However, with increasing x , the structural Fe(II)/Fe(III) ratio, calculated from the unit cell edge as described in Pearce et al. (2012) deviates from that predicted by chemical analysis of digested nanoparticles. The discrepancy between the chemical analysis and structural Fe(II)/Fe(III) ratio suggests the presence of a non-structural non-crystalline Fe(II)/Ti(IV)-containing phase that becomes significant at $x = 0.53$. This is a result of the ambient conditions employed to synthesize the nanoparticles. At room temperature, there is insufficient energy to continually replace lattice Fe(III) with the larger Fe(II) cation that charge balances Ti(IV) along the compositional solid solution series toward ulvöspinel. Recent work on bulk phases has verified the existence of a miscibility gap in this series, in principle for a similar reason, and predicts phase separation at low temperature, with a critical solvus temperature of 823 K and critical composition $x = 0.54$ (Lilova et al., 2012). Thus, although stoichiometric amounts of FeCl₂, FeCl₃ and TiCl₄ were used in the synthesis, at $x = 0.53$ not all of the Ti was incorporated into the structure and the excess Ti, along with the excess charge-balancing Fe(II), are present at $x = 0.53$ nanoparticle surfaces as a non-structural phase. For $x = 0.53$ this phase persists even after the washing step, and TEM analysis shows evidence of an amorphous phase (Pearce et al., 2012). Possible procedures to synthesize homogeneous titanomagnetite for higher Ti-contents (Guigue-Millot et al., 2001) are not conducive to the formation of nano-scale material and were not pursued in this study.

The nanoparticles were also analyzed using XA and XMCD to provide surface sensitive information. For these techniques signal strength decreases exponentially with depth to a maximum information depth of 50 Å (Gota

et al., 2000). Quantitative iron site occupations and oxidation states can be obtained by fitting the Fe XMCD spectra using the weighted sum of the theoretically calculated spectra for each Fe site to obtain an Fe(II)/Fe(III) ratio for the nanoparticle surface (Table 1). The surface Fe(II)/Fe(III) ratio is slightly higher than that for the bulk, particularly for the higher x samples, suggesting partial redistribution of Fe(II) from the interior to the surface as an intrinsic characteristic of the nanoparticles. This characteristic was also observed for microparticle samples in the same x range as the nanoparticles, synthesized at high temperatures, which required exposure to oxidizing buffers to re-equilibrate the surface composition to match that of the bulk (Pearce et al., 2010). This re-equilibration is not possible for the nanoparticles, as heating results in sintering and the potential concurrent reduction in surface area would be detrimental for reactivity studies.

The dissolution study of Fe_{3-x}Ti_xO₄ ($x = 0.00$ – 0.53) nanoparticles showed that the amount of dissolved Fe(II) at pH 8 (cf., Reaction (4)) was strongly and systematically dependent on the Ti content (x). Negligible amounts of Fe(II) were released from Fe₃O₄ nanoparticles. For Fe_{3-x}Ti_xO₄ nanoparticles, the amount of Fe(II) in solution increased until it reached equilibrium after ~24 h, and the nanoparticles with higher x released more Fe(II) into solution at equilibrium, as shown in Table 1 (Pearce et al., 2012).

3.2. Kinetic behavior

To probe the effect of tuning the Fe(II)/Fe(III) ratio in the solid, using the Ti content, on Tc(VII) reduction, the rates of reduction of 10 μM Tc(VII) by 1.3 mg of Fe_{3-x}Ti_xO₄ nanoparticles ($x = 0.00$ – 0.53), with comparable surface area, at pH 8 were measured. Fig. 2a shows the change in Tc(VII) concentrations with time for titanomagnetite nanoparticles with different Fe(II)/Fe(III) ratios. During these four hour experiments, magnetite nanoparticles ($x = 0.00$) reduced 30% of the Tc(VII) in solution, but titanomagnetite nanoparticles ($x > 0.00$) reduced 72–100% of the Tc(VII). Thus, increasing the Fe(II)/Fe(III) ratio in the solid phase by substitution of Ti(IV) into the cationic sublattice significantly increased the activity of the Fe_{3-x}Ti_xO₄ nanoparticles with respect to Tc(VII)

Fig. 2. Reduction of 10 μM Tc(VII) solution at pH 8 by 1.3 mg $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ nanoparticles. (a) Tc(VII) concentration as a function of time for $x = 0.00$ (■), 0.15 (●), 0.25 (▲), 0.38 (□) and 0.53 (*). (b) First order rate constants for the initial linear stage of Tc(VII) reduction as a function of Fe(II)/Fe(III) ratio in the titanomagnetite nanoparticles.

reduction. The removal of Tc(VII) from solution by magnetite is reported to follow first-order kinetics (Cui and Eriksen, 1996b). However, the reaction kinetics for the four hour time course of Tc(VII) reduction by $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ nanoparticles measured here (Fig. 2a) could not be described by a single exponential function, suggesting a more complex, multi-stage reaction (discussed below). To investigate the effect of the Fe(II)/Fe(III) ratio in the solid on Tc(VII) reduction, rate constants were calculated by linear regression of $\ln([\text{Tc}]/[\text{Tc}]_0)$ versus time plots for the initial stages of reduction (30 min) (Fig. 2b). Tc(VII) reduction rates increased linearly with Fe(II)/Fe(III) ratio for $x \leq 0.38$ indicating that the redox reactivity of $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ nanoparticles is systematically related to the stoichiometry up to this value of x .

As described previously, for the $x = 0.53$ sample not all of the Ti is incorporated into the spinel structure and the remaining Ti(IV), along with the excess charge-balancing Fe(II), is localized in a separate amorphous phase on the nanoparticle surface (Pearce et al., 2012). This sample displays an initial Tc(VII) reduction rate higher than the linear trend (Fig. 2b), suggesting that this surface Fe(II)-bearing

phase accounts for higher observed initial reactivity. This distinction emphasizes the importance of the form and accessibility of Fe(II)-based reducing equivalents with respect to reactivity and, when combined with the remaining observed systematic rate behavior, attests to the compositional and structural homogeneity of the lower x nanoparticles.

Attribution of faster observed Tc(VII) reduction rates to an increase in structural Fe(II)/Fe(III) ratio is similar to that reported in previous contaminant reduction studies (Peterson et al., 1996; Neumann et al., 2008, 2009; Gorski and Scherer, 2010), and in electrochemical parlance can be likened to decreasing the open circuit potential (E_{OCP}) built into the solid. For example, a systematic relationship between redox reactivity and stoichiometry was established for the magnetite–maghemite solid solution series (Peterson et al., 1996; Neumann et al., 2008, 2009; Gorski and Scherer, 2010). In addition to increasing relative amounts of Fe(II) and decreasing E_{OCP} , localization of reducing equivalents to the surface of $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ nanoparticles increases their accessibility. Cui and Eriksen (1996a) proposed that the removal of Tc from solution involves sorption of TcO_4^- on Fe(II)-bearing minerals followed by a surface-mediated three-electron reduction of TcO_4^- to $\text{TcO}_2 \cdot n\text{H}_2\text{O}$, a situation tacitly implied and consistent with our proposed Reaction (5). Therefore, higher concentrations of Fe(II) at the mineral surface, as with the $x = 0.53$ sample, accelerates the electron transfer from Fe(II) to Tc(VII).

The reaction kinetics for 10 μM Tc(VII) were rapid, with most of the Tc(VII) reduced in less than one hour (Fig. 2a). To probe the reaction kinetics in more detail, the initial Tc(VII) concentration was increased to 30 μM and the mass of nanoparticles used in the experiment was maintained at 1.3 mg (Fig. 3a). Akin to the solid-state redox potential argument above, this experiment can be viewed as making the E_{OCP} of the solution more electropositive relative to that in the solid. The initial (30 min) reaction kinetics for the experiments with the higher initial concentration of Tc(VII) displayed systematic behavior similar to that for the 10 μM Tc(VII) solution (Fig. 3b), with a linear relationship between initial rate constant and Fe(II)/Fe(III) ratio for the $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ nanoparticles with $x \leq 0.38$ and a less systematic higher rate constant for $x = 0.53$ (Fig. 3b).

To determine the effect of oxidant concentration on the rate of reduction, the amount of Fe(II) oxidized (cf., Reaction (5), defined as three times the concentration of Tc(VII) reduced assuming reduction to Tc(IV)) in the initial 30 min linear stage of the reaction was calculated for the reduction experiments with 10 and 30 μM Tc(VII), and compared with the amount of Fe(II) released in the absence of an oxidant during the dissolution experiments, for $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ nanoparticles with different Fe(II)/Fe(III) ratios (Fig. 4). For the same x , the amount of Fe(II) oxidized in the first 30 min of the reaction, increased with increasing Tc(VII) concentration. The reactions during this time are complex, involving simultaneous dissolution of Fe(II), absorption of Tc(VII), and reduction/oxidation processes at the interface that expectedly deposits insoluble forms of Tc(IV) and Fe(III) (Reaction (5)). Exposing the $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ nanoparticles to HEPES buffer

Fig. 3. Reduction of 30 μM Tc(VII) solution at pH 8 by 1.3 mg $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ nanoparticles. (a) Tc(VII) concentration as a function of time for $x = 0.15$ (●), 0.25 (▲), 0.38 (□) and 0.53 (*). (b) First order rate constants for the initial linear stage of Tc(VII) reduction as a function of Fe(II)/Fe(III) ratio in the titanomagnetite nanoparticles.

Fig. 4. Effect of oxidant concentration on Fe(II) release and oxidation for $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ nanoparticles at pH 8. Amount of Fe(II) released after 24 h dissolution (■), amount of Fe(II) oxidized by 10 μM Tc(VII) solution (●) and by 30 μM Tc(VII) solution (▲) during the first 30 min of reaction.

solution at pH 8 without Tc(VII) in the dissolution experiments produces a driving force for the movement of Fe(II) from the bulk spinel structure towards the surface, with concomitant formation of vacancies to maintain charge balance (Pearce et al., 2012) (Reaction (4)). After 24 h, an equilibrium is reached between the Fe(II) in the solid phase and the aqueous Fe(II), resulting in small concentrations of Fe(II) in solution (Table 1). In the presence of Tc(VII), this equilibrium is perturbed by the oxidation of Fe(II) to Fe(III) at the nanoparticle surface, concurrent with reduction of sorbed Tc(VII) to precipitate a Tc(IV)–Fe(III) phase (Reaction (5)). A higher concentration of Tc(VII) in solution results in the oxidation of more Fe(II) to Fe(III). The oxidized Fe(II) is subsequently resupplied by the re-adsorption of Fe(II) from solution and by the movement of more Fe(II) from the solid interior to the $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ nanoparticle surface. The results in Fig. 4 indicate that the amount of highly reactive Fe(II) at the surface of the titanomagnetite nanoparticles is greatly influenced by the presence of redox active species in solution. Enhanced Fe(II) release from magnetite has also been observed during U(VI) reduction (Singer et al., 2012).

To explore the potential for long-term reduction reactions, the reaction time for 1.3 mg $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ nanoparticles with 30 μM Tc(VII) solution was increased from four hours to 20 days. Fig. 5 shows the change in Tc(VII) concentration as a function of time. While the x -dependence remained consistent with the above, the measured behavior here demonstrates that pertechnetate reduction continues unabated over this longer time interval, particularly for higher x nanoparticles, so long as Tc(VII) is present. These experiments also more clearly display an overall rate behavior that is generally at least biphasic, with a fast initial reduction process transitioning to a slow decay at about 30 h. Tronc and co-workers made similar observations of biphasic kinetics in their studies of the time dependence of Fe(II) release from magnetite at low pH (Jolivet and Tronc, 1988; Tronc et al., 1989). At pH 2.0–2.5, an initial

Fig. 5. Long-term reduction of 30 μM Tc(VII) solution at pH 8 by 1.3 mg $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ nanoparticles in pH 8 HEPES buffer solution. Tc(VII) concentration as a function of time for $x = 0.00$ (■), 0.15 (●), 0.25 (▲), 0.38 (□) and 0.53 (*).

stage of nearly instantaneous Fe(II) release (~40% of the Fe(II) content) was followed by slow but persistent release of the remaining Fe(II) content over a month-long time period. The observed break in the kinetics was attributed to a transition to rate-limiting iron cation diffusion out of the solid through a fully oxidized maghemite surface layer ~4 Å thick, arising from the initial fast release process.

Our long-term experiments were also taken as an opportunity to compare with previous measurements of the Tc(VII) reduction rate by powdered natural magnetite in artificial groundwater at nearly the same pH (8.2) (Cui and Eriksen, 1996b). When differences in experimental conditions, specifically the particle surface area to solution volume ratio, are taken into consideration as described in Cui and Eriksen (1996b), our measured reduction rate for magnetite ($x = 0.00$) is within an order of magnitude, $0.820 \pm 0.18 \text{ day}^{-1}$ in this study versus $0.0639 \pm 0.0041 \text{ day}^{-1}$ in Cui and Eriksen (1996b), with the difference in reactivity possibly resulting from the higher energy of the nanoparticle surface. The apparent consistency supports the potential scalability of the nanoparticle format used here to encompass bulk synthetic and natural titanomagnetite samples in future work.

Despite the fact that the concentration of Fe(II) provided in the form of the nanoparticles was much more than three times that of Tc(VII) (Table 2), not all of the Tc(VII) was reduced at the end of the experiment, except for the $x = 0.53$ sample (Table 2). This demonstrates that the amount of Fe(II) is not the limiting factor for Tc(VII) reduction in this system, but rather over the long-term accessibility to structural Fe(II) in the solid becomes rate controlling, generally consistent with concepts speculated in the dissolution studies of Tronc et al. (1989). In spinels, electron diffusivity remains high at ambient conditions relative to cationic diffusivity because of facile electron hopping along the iron cationic sublattice (Tsuda et al., 2000). However, diffusion of these two species must be coupled to maintain charge balance in the solid (cf., Reactions (2) and (3)), thus accessibility to structural Fe(II) can be limited by comparatively slow cationic migration out of the solid (Jolivet and Tronc, 1988). Another possible effect is progressive armoring of the particles by build-up of Tc(IV)–Fe(III) reaction products at the surface (Reaction

(5)). These products could in principle block active sites on the nanoparticle surface for continued iron release and inhibit subsequent electron transfer between Tc(IV) and structural Fe(II) (e.g., Peterson et al., 1996; White and Peterson, 1996). To determine the extent of the prospective armoring effect, we estimated the percent coverage of the nanoparticle surface by progressive deposition of Tc(IV)–Fe(III) reaction products to the surface according to Reaction (5), assuming a minimum thickness of 4 Å (about half a magnetite unit cell edge) and a molar volume consistent with that of the underlying nanoparticle. For a given sample x , measured changes in the Fe(II)/Fe(III) ratio (r) after reaction were used in conjunction with the following expression derived from the generalized titanomagnetite formula (Eq. (1)) to estimate the associated changes in oxidation parameter y as:

$$y = \frac{1 + x - 2r + 2xr}{1 + \frac{2}{3}r}, \quad (7)$$

a relation that was then used to estimate the number of electron equivalents extracted from the nanoparticle and the extent of Tc(IV)–Fe(III) deposition. Results in Table 2 show that even when all of the Tc(VII) is reduced by the $x = 0.53$ sample, only 29.4% of the nanoparticle surface is covered by a Tc(IV)–Fe(III) reaction product, with a large proportion of active sites at the surface therefore still available. Thus, this ‘armoring’ effect cannot be solely responsible for limiting Tc(VII) reduction by $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ nanoparticles. To further investigate this, the $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ nanoparticles after reaction with Tc(VII) were analyzed using TEM, EXAFS, μ -XRD and XA/XMCD.

3.3. Reduction products

Titanomagnetite nanoparticles after long-term reaction with Tc(VII) for 20 days were separated from solution for characterization. The concentration of Fe(II) in the solution after the reduction reaction was less than 0.6 μM , and thus below the detection limit of the ferrozine method (Sarradin et al., 2005). It was not possible to use the ferrozine assay and ICP-MS to measure the Fe(II)/Fe(III) ratios of the $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ nanoparticles after reaction with Tc(VII) due to adverse redox reactions between Fe(III) and Tc(IV)

Table 2
Properties of $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ nanoparticles before and after 20 day reduction experiments.

x	Total Fe(II) ^a (μmol)	Reduced Tc(VII) ^b (μmol)	Surface coating ^c (%)	XRD Fe(II)/Fe(III) ^d		XMCD Fe(II)/Fe(III) ^e		XAS Ti/Fe ^f	
				Before	After	Before	After	Before	After
0.15	5.740	0.524	12.2	0.658	0.423	0.667	0.549	0.0526	0.0442
0.25	6.014	0.673	13.7	0.733	0.435	0.745	0.584	0.0856	0.0672
0.38	6.193	0.752	20.1	0.833	0.468	0.878	0.701	0.0120	0.0112
0.53	6.893	0.882	29.4	0.896	0.403	1.130	0.960	0.190	0.103

^a Total amount of Fe(II) in 1.3 mg $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ nanoparticles according to acid digestion results.

^b Total amount of Tc(VII) reduced at the end of long-term experiments (starting concentration = 0.9 μmol).

^c Calculated percent thickness of Tc(IV)/Fe(III) coating from total Fe(II)/Fe(III) and unit cell parameter after reduction.

^d Fe(II)/Fe(III) calculated from unit cell parameters and the ‘master curve’.

^e Calculated from fit of XMCD spectra using theoretical spectra.

^f Calculated from integrated area of the XA spectra for the Fe and Ti $L_{2,3}$ -edges.

at acid pH during HCl digestion (Peretyazhko et al., 2008b). Therefore, alternative analytical techniques were employed to obtain information on the stoichiometry of the reaction between Fe(II) in the solid phase and Tc(VII).

Samples $x = 0.15$ and $x = 0.38$ after reduction experiments were analyzed by high-resolution TEM. There was no change in the size of the particles after reduction and the lattice fringes were continuous across particles, with some distortion at the surface, as illustrated in Fig. 6 for the $x = 0.38$ sample. However, it is not possible to distinguish between delocalization of contrast as a result of aberrations of the imaging system, distortion as a result of electron beam damage, and the presence of Fe/Tc precipitates on the surface. As implied in the analysis of the armoring effect above, even in the 20 day experiments for high x nanoparticles where the extent of reduction was largest, very little deposition of a Tc(IV)–Fe(III) product phase is predicted (Table 2). For simplicity, assuming that this extent of reduction/deposition was coupled to inward growth of a fully oxidized titanomaghemite layer, with an unoxidized residual core, the inward penetration of the oxidized front would only be ~ 2 Å thick from the initial surface. Hence, reaction fronts of these dimensions remain too small and too labile under a focused electron beam to be conclusively imaged with presently available TEM capabilities.

Reaction products were, however, easily detected and characterized spectroscopically. To determine the Tc oxidation state and bonding environment, reacted titanomaghemite nanoparticles bearing Fe/Tc precipitates at the surface were analyzed using *K*-edge XA spectroscopy (Fig. 7). The line shape of the XANES spectra for all of the samples was consistent with a Tc oxidation state of 4+ as shown in Fig. 7A for $x = 0.53$, compared with a TcO_2 reference spectrum (Hess et al., 2004). The XANES spectra for all of the samples showed no evidence of a mixed Tc(IV)/Tc(VII) phase, confirming that the loss of Tc(VII) from the supernatant was due to reduction to Tc(IV) and not adsorption of Tc(VII) by the solid. The radial transforms of the Tc-EXAFS data for Tc(IV) on $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ for all reacted samples ($x = 0, 0.15, 0.25, 0.38$ and 0.53) were quite similar. The EXAFS data for heterogeneous Tc(IV) precipitates on the $x = 0.53$ sample (Fig. 7B) were satisfactorily modeled with a $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ linear chain developed by Lukens et al. (2002), which was extended to include edge sharing octahedral interactions with an Fe–O surface in Zachara et al. (2007) and there applied to a synthetic Tc(IV)–ferrihydrite reference phase. It consists of variable length edge-sharing chains of Tc–O octahedra at $R = 1.99$ Å bonded in an edge-sharing fashion to Fe–O octahedra located on the surface of the host Fe(III) oxide substrate. The inset in Fig. 7B

Fig. 6. TEM of $\text{Fe}_{2.62}\text{Ti}_{0.38}\text{O}_4$ nanoparticles before (a) and after (b) reaction with $30 \mu\text{M}$ Tc(VII) solution for 20 days.

Fig. 7. Tc *K*-edge XANES, including a TcO_2 reference spectrum (Hess et al., 2004) (A), k^2 -weighted Tc-EXAFS spectrum and inset showing the model used for fitting with Fe (brown spheres), O (red spheres) and Tc (blue spheres) (B) and radial transform (C) of $\text{Fe}_{2.47}\text{Ti}_{0.53}\text{O}_4$ nanoparticles after reaction with $30 \mu\text{M}$ Tc(VII) solution (solid line) and results of fitting with the model of TcO_2 chains attached to an Fe octahedron in an edge sharing configuration (dashed line). The transform is over the range $k = 2$ – $13 \text{ \AA}^{-1}$, and the fitting was over the range 1 – $3.4 \text{ \AA}$.

shows a visual representation of the model with the average length of the TcO_2 chains included as a variable in the fitting. The radial transform contrasts markedly with that for abiotically precipitated $\text{TcO}_2 \cdot n\text{H}_2\text{O}$, showing the presence of far less Tc–Tc bonding (average chain length is approximately 2) in the second shell at $R = 2.56 \text{ \AA}$ and the presence of Tc–Fe bonding at $R = 2.59 \text{ \AA}$. The good correspondence of the structural model applied here to that used in previous work (Zachara et al., 2007) suggests that the Fe/Tc reaction products observed here may be similar, and also lends additional support for the reaction stoichiometry incorporated in Reaction (5) above.

A fraction of the reaction products were also maintained in aqueous suspension, under anoxic conditions, and characterized *in situ* by μ -XRD. Fig. 8 shows the pattern for $x = 0.38$ before and after reaction with Tc(VII), which is representative of all the reacted $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ nanoparticle samples. Titanomagnetite was the only crystalline phase present with no new crystalline Tc-bearing phases produced during the reaction. A shift in the peak positions towards higher 2-theta values occurred after reaction with Tc(VII) (Fig. 8), indicating a transition towards a titanomaghemite-like phase consistent with Reaction (5). This shift corresponded to a decrease in the unit-cell parameters of $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ nanoparticles after reduction (Table 2). Given the comprehensive systematic relationship between titanomagnetite unit-cell parameter and stoichiometry (Fe(II)/Fe(III) ratio) reported by Pearce et al. (2012) in the ‘master curve’, here we used it to calculate the change in structural Fe(II)/Fe(III) ratio before and after Tc(VII) reduction (Table 2). The decrease in structural Fe(II)/Fe(III) ratio after reaction was larger for samples with higher x , implying that with higher x more structural Fe(II) was oxidized by the reduction of Tc(VII), in agreement with the higher concentration of Tc(VII) reduced at the end of the experiment. This is also the case for $x = 0.53$, indicating that the additional amorphous Ti(IV)/Fe(II)-bearing surface phase had a limited effect on the long-term reactivity of this sample, having likely been fully consumed during the early stage. Thus, the higher concentration of structural Fe(II) in the

$\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ nanoparticles is a significant factor in the increased reduction activity towards Tc(VII), consistent with Reaction (5), particularly over longer reaction timescales.

The titanomagnetite nanoparticles before and after reaction with Tc(VII) were also analyzed using XA and XMCD at the Fe $L_{2,3}$ -edge. XA is a measure of total Fe, and XMCD is a function of the magnetic component of the sample, sensitive with *A*- and *B*-site-specificity to structural Fe(II) and Fe(III) in the nanoparticles emphasizing that constituency residing within $50 \text{ \AA}$ of the surface (Gota et al., 2000). The XA and XMCD spectra for titanomagnetite nanoparticles ($x = 0.15, 0.25, 0.38$ and 0.53) before and after reaction with Tc(VII) are shown in Fig. 9. Measured XMCD spectra for the nanoparticles have three main peaks: *B*-site Fe(II) (negative peak at $\sim 708 \text{ eV}$), *A*-site Fe(III) (positive peak at $\sim 709.5 \text{ eV}$), and *B*-site Fe(III) (negative peak at $\sim 710.5 \text{ eV}$). According to calculated fundamental spectra for these three main components in magnetite, the experimental XMCD spectrum can be fit to produce occupancy ratios for the proportions of Fe(II) and Fe(III) in the *B*-site, and of Fe(III) in the *A*-site. The Fe(II)/Fe(III) ratios for titanomagnetite nanoparticles before and after reaction, calculated from the XMCD spectra, are shown in Table 2. In all cases, the ratio decreased after reduction experiments, indicating that structural Fe(II) was oxidized to Fe(III), concurrent with the reduction of Tc(VII) to Tc(IV). The decreasing amount of structural Fe(II) is observed as a decrease in the intensity of the Fe(II) *B*-site peak (Fig. 9), after normalization of the spectra to the Fe(III) *B*-site peak. The reduction in intensity of the Fe(II) peak is relatively small for $x = 0.53$ when compared to the other titanomagnetite samples ($x = 0.15, 0.25$, and 0.38), even though this sample reduced the highest concentration of Tc(VII). This small structural change does not correlate with the large decrease in the lower energy shoulder corresponding to total Fe(II) in the XA after reaction with Tc(VII) (Fig. 9), suggesting that a proportion of the Fe(II) reducing equivalents required for the reduction of Tc(VII) came from the non-structural excess Ti(IV)/Fe(II) phase on the $x = 0.53$ nanoparticle surface.

Fig. 8. μ -XRD of $\text{Fe}_{2.62}\text{Ti}_{0.38}\text{O}_4$ nanoparticles before (black) and after (red) reaction with $30 \mu\text{M}$ Tc(VII) solution for 20 days, with magnetite ICDD PDF No. 00-019-0629.

Fig. 9. Comparison of XA and XMCD spectra of $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ ($x = 0.15, 0.25, 0.38$, and 0.53) nanoparticles before (grey line) and after (black line) reduction experiments with $30 \mu\text{M}$ Tc(VII) solution.

The Ti/Fe ratio at the surface of the $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ nanoparticles before and after reaction with Tc(VII) was calculated from the integrated area of the XA spectra for the Fe and Ti $L_{2,3}$ -edges taken at the same point on the sample, after background subtraction as described in Droubay (1999) (Table 2). The ratios decrease corresponding to the movement of Fe(II) reducing equivalents from the interior to the surface and subsequent oxidation by Tc(VII) to form the Tc(IV)/Fe(III) surface phase confirmed by EXAFS. The decrease in Ti/Fe ratio is anomalously large for $x = 0.53$ as a result of its higher reactivity attributed to the non-structural excess Ti(IV)/Fe(II) phase initially present on this sample.

For the purpose of discriminating different pools of reactive Fe(II) encompassed by our experiments, Fig. 10 combines the Fe(II)/Fe(III) ratios for the nanoparticles before and after reaction with Tc(VII) . The total Fe(II)/Fe(III) ratios before reaction were determined by digestion and chemical analysis. The Fe(II)/Fe(III) ratios in the structure of the nanoparticles before and after reaction were determined from the unit cell parameters measured using $\mu\text{-XRD}$ in combination with the ‘master curve’. The Fe(II)/Fe(III) ratios at the surface of the nanoparticles before and after reaction were determined from a nonlinear least-squares analysis fit of the experimental XMCD spectra. The final Fe(II)/Fe(III) ratio for the nanoparticles was also calculated by taking into account the amount of Fe(II) required to reduce the Tc(VII) that was removed

Fig. 10. Fe(II)/Fe(III) ratios before and after long-term reduction experiments of $30 \mu\text{M}$ Tc(VII) by 1.3 mg $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ nanoparticles in pH 8 HEPES buffer solution plotted against the total Fe(II)/Fe(III) before reduction as determined by chemical analysis. (♦) Total Fe(II)/Fe(III) from chemical analysis before reduction; (▲) surface Fe(II)/Fe(III) from XMCD before reduction; (□) structural Fe(II)/Fe(III) from XRD before reduction; (■) surface Fe(II)/Fe(III) from XMCD after reduction; (×) structural Fe(II)/Fe(III) from XRD after reduction; (●) Fe(II)/Fe(III) calculated from concentration of Fe(II) required to reduce Tc(VII) from LSC data.

from solution, as measured by LSC. The Fe(II)/Fe(III) ratio for the structural Fe component of the nanoparticles after reaction with Tc(VII) , calculated from $\mu\text{-XRD}$ data,

is in very good agreement with that predicted by the amount of Tc(VII) reduced, showing that there was a stoichiometric reaction between the Fe(II) in the structure of the nanoparticles and the Tc(VII). Remarkably, in all of the nanoparticle samples, the final Fe(II)/Fe(III) ratio is found to be approximately 0.4, suggesting that oxidation to this extent may be the limiting factor for the reduction of Tc(VII) under these conditions. This value may represent the minimum ratio in the solid that maintains its structural stability as the system approaches equilibrium in our experiments.

For the $x = 0.53$ sample, the μ -XRD Fe(II)/Fe(III) ratio is slightly lower than predicted by the concentration of Tc(VII) reduced (Fig. 10). Fig. 5 shows that all of the Tc(VII) was reduced after the 6th day of the 20 day experiment. Reduction of all of the available Tc(VII) (30 μ M) produced an effective Fe(II)/Fe(III) ratio of 0.5 (calculated by subtracting the amount of Fe(II) required to remove all of the Tc(VII) from solution from the initial Fe(II) concentration in the $x = 0.53$ nanoparticles) which is higher than the proposed equilibrium value for the system. Thus, there was still a net driving force for the removal of Fe(II) from the bulk to the surface with subsequent release of Fe(II) into solution to reach the near-equilibrium value of 0.4 for Fe(II)/Fe(III) in the structure, as measured by μ -XRD. This observation lends further support to the assertion that build-up of the Tc(IV)/Fe(III) product phase on the surface is not substantial enough to limit the reduction reaction in our experiments (cf., Table 2), because Fe(II) reducing equivalents can still move from the interior to the surface, even when all of the Tc(VII) has been reduced.

The change in Fe(II)/Fe(III) ratio as a result of Tc(VII) reduction measured by XMCD is significantly less than that calculated from the reduced Tc(VII) or measured by μ -XRD (Fig. 10). This can be explained by considering the reaction of the nanoparticles with Tc(VII) resulting in oxidation of Fe(II) at the surface and requiring resupply of Fe(II) from the nanoparticle interior. As described in Pearce et al. (2012) reducing the concentration of Fe(II) in the solution around the nanoparticles, either by dilution, as in the dissolution experiments, or by addition of an external oxidant such as Tc(VII) sustains the driving force for the movement of Fe(II) outward from the interior and results in the accumulation of Fe(II) at the surface, until equilibrium is reached between the Fe(II)/Fe(III) ratio in the nanoparticles and their surrounding environment. XMCD is more sensitive to the structural Fe at the surface of the nanoparticles, and it selectively samples this Fe(II)-enriched surface region resulting in an Fe(II)/Fe(III) ratio that is higher than that measured for the bulk $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ nanoparticle structure.

In addition to the mechanistic insights for heterogeneous Tc(VII) reduction enabled by the present system of $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ nanoparticles, this study shows that titanium substitution is an elegant way to adjust the solid-state Fe(II)/Fe(III) ratio in titanomagnetite and increase the redox reactivity towards key environmental contaminants. These materials, which can be synthesized in aqueous solution and under ambient conditions, are powerful reductants with 'tunable' reactivity, making them promising low-cost,

high-efficiency materials for environmental remediation applications. Here structural Fe(II) reactivity strongly depends on the properties of the solid, including local bonding environment and Fe(II)/Fe(III) ratio, as well as on the composition of the surrounding solution, including the concentration of redox active species.

Natural titanomagnetites exhibit a range of Ti contents and in sediments their structural Fe(II)/Fe(III) ratio can be modified by exposure to oxygen from atmospheric flux or oxygenated meteoric water. Conversely, we speculate that these materials will also display a degree of reversibility with respect to reincorporation of Fe(II) into the structure by exposure to reducing microenvironments, such as those that can arise from oxygen-scavenging mineral reactions or microbial activity. Continued study appears justified to assess such effects, and to provide a greater understanding of the effects of changing titanomagnetite stoichiometry on their redox reactivity with respect to contaminant reduction in the subsurface.

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