

## Redox interactions of technetium with iron-bearing minerals

J. M. MCBETH<sup>1,†</sup>, J. R. LLOYD<sup>1</sup>, G. T. W. LAW<sup>1</sup>, F. R. LIVENS<sup>1,2</sup>, I. T. BURKE<sup>3</sup> AND K. MORRIS<sup>1,\*</sup>

<sup>1</sup> Research Centre for Radwaste and Decommissioning and Williamson Research Centre for Molecular Environmental Science, School of Earth, Atmospheric and Environmental Sciences, The University of Manchester, Manchester M13 9PL, UK

<sup>2</sup> Centre for Radiochemistry Research, The University of Manchester, Manchester M13 9PL, UK

<sup>3</sup> Earth System Science Institute, School of Earth and Environment, University of Leeds, Leeds LS2 9JT, UK

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### ABSTRACT

Iron minerals influence the environmental redox behaviour and mobility of metals including the long-lived radionuclide technetium. Technetium is highly mobile in its oxidized form pertechnetate ( $\text{Tc(VII)O}_4^-$ ), however, when it is reduced to Tc(IV) it immobilizes readily via precipitation or sorption. In low concentration tracer experiments, and in higher concentration XAS experiments, pertechnetate was added to samples of biogenic and abiotically synthesized Fe(II)-bearing minerals (bio-magnetite, bio-vivianite, bio-siderite and an abiotically precipitated Fe(II) gel). Each mineral scavenged different quantities of Tc(VII) from solution with essentially complete removal in Fe(II)-gel and bio-magnetite systems and with  $84 \pm 4\%$  removal onto bio-siderite and  $68 \pm 5\%$  removal onto bio-vivianite over 45 days. In select, higher concentration, Tc XAS experiments, XANES spectra showed reductive precipitation to Tc(IV) in all samples. Furthermore, EXAFS spectra for bio-siderite, bio-vivianite and Fe(II)-gel showed that Tc(IV) was present as short range ordered hydrous Tc(IV) $\text{O}_2$ -like phases in the minerals and for some systems suggested possible incorporation in an octahedral coordination environment. Low concentration reoxidation experiments with air-, and in the case of the Fe(II) gel, nitrate-oxidation of the Tc(IV)-labelled samples resulted in only partial remobilization of Tc. Upon exposure to air, the Tc bound to the Fe-minerals was resistant to oxidative remobilization with a maximum of  $\sim 15\%$  Tc remobilized in the bio-vivianite system after 45 days of air exposure. Nitrate mediated oxidation of Fe(II)-gel inoculated with a stable consortium of nitrate-reducing, Fe(II)-oxidizing bacteria showed only  $3.8 \pm 0.4\%$  remobilization of reduced Tc(IV), again highlighting the recalcitrance of Tc(IV) to oxidative remobilization in Fe-bearing systems. The resultant XANES spectra of the reoxidized minerals showed Tc(IV)-like spectra in the reoxidized Fe-phases. Overall, this study highlights the role that Fe-bearing biogenic mineral phases have in controlling reductive scavenging of Tc(VII) to hydrous  $\text{TcO}_2$ -like phases onto a range of Fe(II)-bearing minerals. In addition, it suggests that on reoxidation of these phases, Fe-bound Tc(IV) may be octahedrally coordinated and is largely recalcitrant to reoxidation over medium-term timescales. This has implications when considering remediation approaches and in predictions of the long-term fate of Tc in the nuclear legacy.

**KEYWORDS:** technetium, redox cycling, iron minerals, remediation.

### Introduction

THE biogeochemistry of the long-lived radioactive element technetium ( $^{99}\text{Tc}$ ,  $t_{1/2} = 2.13 \times 10^5$  y) is an important factor governing its long term behaviour in natural and engineered environments. In its oxidized form, Tc is present as pertechnetate ( $\text{Tc(VII)O}_4^-$ ), a highly mobile anion that is a

\* E-mail: katherine.morris@manchester.ac.uk

† current address: Bigelow Laboratory for Ocean Sciences, 180 McKown Point Road, West Boothbay Harbor, Maine, 04575, USA

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contaminant at nuclear sites (Fredrickson *et al.*, 2004; Morris *et al.*, 2000; Skomurski *et al.*, 2010; Standring *et al.*, 2002). By contrast, under reducing conditions, poorly soluble Tc(IV) species dominate, with hydrous TcO<sub>2</sub>-like precipitates forming at concentrations greater than  $\sim 5 \times 10^{-9}$  mol l<sup>-1</sup> (Meyer *et al.*, 1991), Tc(IV) sorption and retention to sediments observed at very low concentrations ( $< 10^{-12}$  mol l<sup>-1</sup>; Burke *et al.*, 2010; Lear *et al.*, 2010) and with Tc(IV) colloids, Tc(IV)-carbonate complexes and Tc(IV)-organic complexes all reported to enhance the solubility of Tc(IV) above  $10^{-8}$  mol l<sup>-1</sup> under certain conditions (Alloit *et al.*, 2009; Gu *et al.*, 2011; Plymale *et al.*, 2011). Further, bioreduction (where indigenous sediment microorganisms are stimulated to produce reducing conditions by the addition of an electron donor) has been shown to be an effective means of removing Tc(VII) from solution in microcosm (Burke *et al.*, 2005; Begg *et al.*, 2007; Law *et al.*, 2010a), column (Michalsen *et al.*, 2006; Lear *et al.*, 2010) and field studies (Istok *et al.*, 2004) over a wide range of conditions. A typical feature in these bioreduction experiments is that the removal of Tc(VII) is associated with the development of microbially-mediated Fe(III) reduction in the sediments (Burke *et al.*, 2005; Fredrickson *et al.*, 2004; Li and Krumholz, 2008; Michalsen *et al.*, 2006; Wildung *et al.*, 2004). Furthermore, removal is thought to be dominated by abiotic electron transfer from sediment associated biogenic Fe(II) to Tc(VII) in all but Fe-poor environments (Lloyd *et al.*, 2000; Begg *et al.*, 2007; Fredrickson *et al.*, 2004; Plymale *et al.*, 2011; Law *et al.*, 2010a; Zachara *et al.*, 2007). Indeed, in experiments using different sediment types, Tc has been found to be associated primarily with Fe-rich (Lear *et al.*, 2010; Fredrickson *et al.*, 2004) or Fe(II)-rich (Burke *et al.*, 2010) nano particles. However, the details of which Fe(II)-bearing minerals mediate Tc(VII)-reduction in heterogeneous sediments are poorly constrained. In addition, when considering Tc behaviour in the environment, it is also necessary to explore the potential for oxidative remobilization of Tc(IV). Reoxidation of immobilized radionuclides in contaminated aquifers could occur via transport of oxygenated waters through the sediments, water table fluctuations, or disturbance of the geosphere by construction or erosion (Burke *et al.*, 2006; Wu *et al.*, 2007). Furthermore, reoxidation caused by nitrate, a common pollutant found at nuclear facilities, is

also a potential route to radionuclide reoxidation via, for example, biologically mediated Fe(II)-oxidation coupled to NO<sub>3</sub><sup>-</sup> reduction (Burke *et al.*, 2006; Geissler *et al.*, 2011; Morris *et al.*, 2008; Senko *et al.*, 2005; Wu *et al.*, 2010; Law *et al.*, 2010b; Law *et al.*, 2011). Recent experimental work on sediments suggests that Tc associated with Fe(II)-bearing sediments is recalcitrant to reoxidation even though significant reoxidation of Fe(II) to Fe(III) occurs during both air and nitrate reoxidation (Burke *et al.*, 2006; Fredrickson *et al.*, 2009; Geissler *et al.*, in press; Jaisi *et al.*, 2009). Thus, in an attempt to clarify the mineralogical constraints on the redox cycling behaviour of Tc, we incubated Tc(VII) in the presence of a range of environmentally relevant Fe(II)-bearing biogenically precipitated minerals: bio-magnetite (Fe<sub>3</sub>O<sub>4</sub>); bio-siderite (FeCO<sub>3</sub>); and bio-vivianite (Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·8H<sub>2</sub>O) as well as with an abiotically precipitated Fe(II)-gel that has previously been used as a growth medium for a stable Fe(II) oxidizing, nitrate reducing consortium (Morris *et al.*, 2008). The resulting, Tc(IV)-labelled, reduced mineral phases were then subject to oxidation with air, and for the Fe(II)-gel via microbially mediated oxidation with nitrate. Throughout, for selected samples, X-ray absorption spectroscopy (XAS) was coupled to stable elemental analysis techniques to characterize Tc solid state interactions.

## Methods

### Fe(II)-bearing mineral preparation

Several Fe(II)-bearing mineral phases were prepared: (1) biogenic magnetite, (2) biogenic vivianite, (3) biogenic siderite and (4) abiotically precipitated Fe(II) gel. The biogenic minerals were prepared using cultures of Fe-reducing bacteria that enzymatically reduced Fe(III) sources. For bio-magnetite, a pure culture of *Geobacter sulfurreducens* was grown at 30°C in a medium containing 15 mM acetate as electron donor and 50 mM fumarate as electron acceptor, under an anaerobic atmosphere (Lovley and Phillips, 1986). When cells reached late log phase growth they were harvested by centrifugation at 4000 g for 10 mins and rinsed twice (30 mM bicarbonate buffer, pH 6.8) under anaerobic conditions. To produce magnetite, aliquots of the washed cell suspension (~1 ml, final OD<sub>600</sub> of ~0.2) were added to 30 mM carbonate buffer solutions containing 50 mM Fe(III)-gel as the electron acceptor and 20 mM

acetate as the electron donor (Lovley and Phillips, 1986). The cultures were incubated for 2 weeks at 20°C until magnetite formed through dissimilatory Fe(III) reduction (Lovley *et al.*, 1987). Bio-vivianite was prepared by adding a 200 ml inoculum of growing *G. sulfurreducens* cell suspension to 800 ml of anaerobic freshwater medium with 56 mM Fe(III)-citrate as the only electron acceptor and 20 mM acetate as the electron donor (Islam *et al.*, 2005). The culture was incubated at 20°C until a white precipitate (vivianite) formed. Bio-siderite was prepared by adding 2 ml of a stable, Fe(III)-reducing consortium to 10 ml of anaerobic media containing 56 mM Fe(III)-citrate as the sole electron acceptor and 20 mM glycerol as the sole electron donor (Adams, 2004). The cultures were incubated at 20°C for three weeks until siderite formed. The abiotic Fe(II) gel was prepared anaerobically with 10 mM KNO<sub>3</sub> as electron donor and 20 mM FeSO<sub>4</sub>·7H<sub>2</sub>O as electron acceptor (Morris *et al.*, 2008). The medium contained 6.66 g l<sup>-1</sup> NaCl and 1 g l<sup>-1</sup> MgCl<sub>2</sub> to provide brackish conditions for the stable, nitrate-reducing Fe(II)-oxidizing microbial consortium used in later experiments. All Fe(II)-bearing mineral phases were analysed by X-ray diffraction (XRD) and electron microscopy.

#### Low concentration tracer experiments

Batch experiments were prepared to study Tc(VII) interactions with the Fe(II)-bearing mineral phases. The abiotic Fe(II) gel was prepared as described above. Preparations of bio-magnetite, -vivianite and -siderite were washed three times in anoxic bicarbonate buffer, sonicated to break up large particles, and re-suspended in 30 mM anoxic bicarbonate buffered brackish medium at pH ~7 and under anoxic conditions (N<sub>2</sub>:CO<sub>2</sub>; 80:20). The final total Fe(II) concentrations were approximately: 2 mmol l<sup>-1</sup> in the vivianite samples, 7 mmol l<sup>-1</sup> in magnetite samples, 16 mmol l<sup>-1</sup> in siderite samples and 20 mmol l<sup>-1</sup> in abiotic Fe(II) gel samples. Technetium (as ammonium pertechnetate) was then added to triplicates of bio-magnetite, -siderite, -vivianite and amorphous Fe(II) gel to give a final concentration between 1–5 μM TcO<sub>4</sub><sup>-</sup>. Samples were stored at 20°C in the dark. Bottles were periodically shaken and sampled for Fe(II), soluble Tc, pH and Eh.

To study air reoxidation, samples containing Tc associated with the mineral phases were trans-

ferred to sterile conical flasks capped with sterile vented bungs (Whatman Bugstopper; Maidstone, UK), and shaken on an orbital shaker at 200 rpm at 20°C in the dark. The flasks were monitored for evaporation and any losses were replaced with sterile deionized water before sampling for Fe(II), soluble Tc, pH, and Eh. To study nitrate-mediated reoxidation, samples containing Tc associated with the mineral phases were amended with 10% (vol:vol) of a stable consortium of nitrate-reducing Fe(II)-oxidizing bacteria enriched from an estuarine sediment (Morris *et al.*, 2008; Law *et al.*, 2011). Samples were incubated at 20°C and sampled for pH, Eh, Fe(II) and soluble Tc, with any changes in colour or increases in headspace pressure noted.

#### Geochemical methods

Periodically, samples were taken and centrifuged for 4 min at 15,000 g. To estimate total bioavailable Fe and bioavailable Fe(II), a 0.5 N HCl extraction, with and without hydroxylamine addition and followed by ferrozine assay on a sample of the mineral slurry was used (Lovley and Phillips, 1987). Technetium activity in solution was measured by liquid scintillation counting of 0.5 ml of supernatant solution added to 15 ml liquid scintillant (Tri-Carb 1900 TR Scintillation Counter, Packard; Optiphase HiSafe3 Liquid Scintillant, Perkin Elmer) for 10 min. The liquid scintillation counter (LSC) had a detection limit of ~30 cpm (~0.6 Bq per sample). Triplicate data are shown as error bars, representing 1 standard error from the three replicates.

#### X-ray absorption spectroscopy (XAS)

Higher Tc activity XAS samples were prepared in parallel to tracer experiments. Pertechnetate was added to bottles of Fe(II)-bearing minerals under reducing conditions to achieve ~500–5000 ppm Tc sorption on the solids. Bottles were incubated until removal of Tc from solution had stabilized (~14 days for bio-magnetite and Fe(II)-gel samples, ~1 month for bio-vivianite samples and ~3 months for bio-siderite samples) and these samples were frozen at -80°C prior to XAS analysis. Parallel samples were then reoxidized with air or nitrate. Air reoxidation samples for bio-magnetite, bio-siderite, bio-vivianite and Fe(II)-gel were prepared as above and aerated by gentle agitation daily. In addition, initial tests

with the stable, nitrate-reducing Fe(II)-oxidizing culture showed that microbially mediated nitrate reoxidation was only significant for the Fe(II)-gel. Nitrate reoxidation was therefore only performed on the Fe(II)-gel system with 10 mM nitrate and a 10% inoculum of the nitrate reducing, Fe(II)-oxidizing consortium. In all cases, after ~14 days reoxidation, samples were retained frozen at  $-80^{\circ}\text{C}$  prior to XAS analysis. Sample mounting was performed under anaerobic conditions as described previously (Morris *et al.*, 2008). Technetium K-edge X-ray absorption spectra were collected in fluorescence mode on station 16.5 of the Daresbury SRS (Morris *et al.*, 2008). Multiple scans (typically 4–12 scans) were summed and calibrated using *EXCALIB* and XANES and EXAFS spectra were extracted using *EXBACK* and *EXSPLINE* respectively. The XANES spectra (21000–21200 eV) revealed a dominant Tc(IV)-like structure. As a result, EXAFS modelling was constrained to Tc(IV)-like coordination environments. Here, background subtracted EXAFS spectra were modelled in *DLEXCURV* using full curved wave theory (Gurman *et al.*, 1984). Phaseshifts were derived from *ab initio* calculations using Hedin-Lundqvist potentials and von-Barth ground states (Binsted, 1998). Extracted EXAFS spectra were used to determine an approximate radial distribution function around the central, absorbing Tc atom; the extracted EXAFS spectra can be related to ‘shells’ of surrounding backscattering ions characterized by atom type, number of atoms, absorber-scatterer distance and the Debye–Waller factor ( $2\sigma^2$ ). The data were fitted in  $k^3$ -space by defining a theoretical model that was informed by previously determined values for absorber-scatterer interatomic distances and numbers of atoms to define model starting points (Morris *et al.*, 2008). Shells of backscatterers were added around the central atom and by refining an energy correction  $E_f$  (Fermi Energy), the absorber-scatterer distance and the Debye–Waller Factor ( $2\sigma^2$ ) for each shell, the least squares residual (the *R*-factor) was minimized and the values of absorber scatter distance and Debye–Waller factor were recorded. Initially, the number of scatterers was fixed at 6 O atoms at 2.00 Å, the first shell, octahedral coordination environment for hydrous Tc(IV) oxide and then refined. Beyond the inner coordination sphere, the number of atoms in the shell was fixed at 1. Coordination environments that were considered were: 1 Tc at  $\sim 2.5$  Å or 1 Fe at  $\sim 2.7$  Å (Morris *et*

*al.*, 2008). Within this framework, additional shells were deemed significant if the least squares residual (*R* value) was reduced by  $>5\%$  and they gave realistic values for absorber-scatterer distance and the Debye–Waller factor ( $2\sigma^2$ ) was in the range  $\sim 0.005$ – $0.025$ .

#### XRD, TEM and ESEM analyses

Samples for XRD, TEM and environmental scanning electron microscopy (ESEM) analysis were washed twice with anaerobic deionized water. XRD samples were transferred to glass slides and dried under an anaerobic atmosphere prior to analysis with a Phillips PW 1730 X-ray generator and diffractometer (Eindhoven, The Netherlands). TEM imaging of the bio-magnetite sample was performed on a Philips CM20 microscope equipped with a tungsten filament, operating at 120 kV. The washed sample was re-suspended in ethanol, dropped onto a carbon-coated copper grid and left to dry in an anaerobic atmosphere prior to insertion into the TEM. ESEM samples (bio-siderite, bio-vivianite and amorphous Fe(II)-gel) were mounted on stubs and analysed at 0.4–0.6 torr and 15–20 keV on a Philips XL30 ESEM-FEG.

## Results and discussion

### Mineral characterization

The electron microscopy images (Fig. 1) coupled with the XRD traces for bio-magnetite, bio-vivianite, and bio-siderite confirmed their predominant ( $>95\%$ ) mineral identities. The abiotic Fe(II) gel was amorphous, with the XRD trace showing no distinct Fe-mineral Bragg peaks. The electron microscopy images allowed morphological characterization with black nano-magnetite grains ( $\sim 30$  nm in diameter, Fig. 1a) forming aggregates from 40–200 nm diameter; white vivianite crystals (Fig. 1b) forming radiating rosettes with thin blades 20–40  $\mu\text{m}$  in length and 5–10  $\mu\text{m}$  width; white siderite crystals (Fig. 1c) forming thin plates of  $\sim 200$   $\mu\text{m}$  square and coated with amorphous material, and the Fe(II)-gel forming a green-grey precipitate with amorphous character (Fig. 1d).

### Low-concentration tracer experiments

Low-concentration tracer experiments examining the removal of Tc(VII) to the Fe(II)-bearing mineral phases were performed. Briefly, different

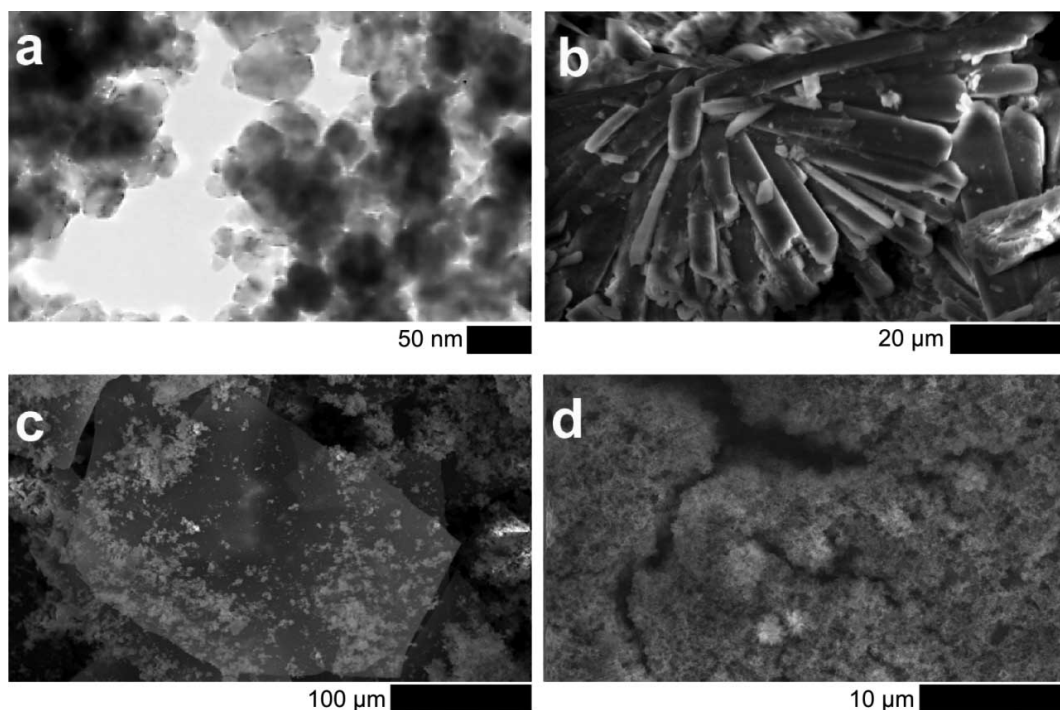


FIG. 1. Mineral appearance and grain size. (a) TEM image of bio-magnetite; ESEM images of (b) bio-vivianite, (c) bio-siderite and (d) Fe(II)-gel. Scale bars are indicated under each image.

minerals showed different Tc sorption with essentially complete removal of Tc from solution observed within two weeks to the abiotic Fe(II)-gel and magnetite, and with  $85\pm 4\%$  retained by siderite and  $68\pm 5\%$  retained by vivianite after 45 days (Fig. 2a–d). Recent work has shown that Tc(IV)-carbonate complexes may form in systems with high levels of carbonate, enhancing Tc(IV) solubility (Alliot *et al.*, 2009). In our microbially active, carbonate buffered experimental systems this warrants further investigation.

Air reoxidation experiments were performed over 45 days and generally, Tc-remobilization was low during reoxidation ( $< 4\%$  for bio-magnetite and Fe(II)-gel,  $6.2\pm 0.8\%$  for bio-siderite, and  $18.7\pm 1.9\%$  for bio-vivianite). An attempt to assess the extent of iron reoxidation was also made in these systems by monitoring 0.5 N HCl extractable  $Fe_{Total}$  and Fe(II). However, in the case of the more crystalline phases (bio-magnetite, bio-siderite and bio-vivianite) this extraction proved problematic as 0.5 N HCl was ineffectual for mineral dissolution which is consistent with other work from our laboratory

(Law *et al.*, 2011). In the amorphous Fe(II)-gel system, the mild acid extraction produced reproducible trends and provided some insight into reoxidation progress. Here, on exposure to air, 0.5 N HCl extractable Fe(II) decreased steadily from  $93\pm 1\%$  to  $8\pm 1\%$  of total iron by 32 days, suggesting significant reoxidation over  $\sim 1$  month and consistent with an observed mineral colour change from grey-green to rust-orange during the course of reoxidation. For the bio-magnetite, bio-siderite and bio-vivianite there was visual evidence for partial reoxidation of the mineral phases with bio-magnetite changing from black to dark brown; bio-vivianite changing from white to blue/green and bio-siderite changing from white to beige, yet there was little ( $< 20\%$ ) oxidative remobilization of Tc in all of these systems during 45 days contact with air. Overall, this suggests that mineral-bound Tc is recalcitrant to oxidative remobilization with air in these systems.

Further reoxidation experiments with 10 mM nitrate and a 10% inoculum of the enrichment culture with bio-magnetite, -vivianite, -siderite,

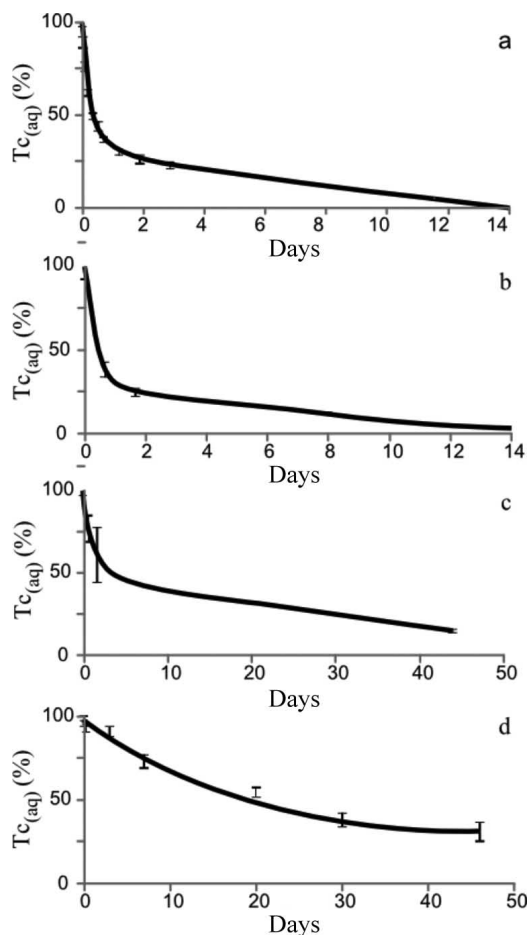


FIG. 2. Tracer Tc sorption to reduced biominerals (0–14 days for Fe(II)-gel and bio-magnetite; 0–50 days for bio-siderite and bio-vivianite). From top to bottom: (a) amorphous Fe(II) gel, (b) bio-magnetite, (c) bio-siderite and (d) bio-vivianite. The y axis represents the percentage of Tc remaining in solution with time. Error bars represent  $1\sigma$  experimental uncertainty from triplicate experiments (where not visible, error bars are within the symbol size).

and Fe(II)-gel at tracer Tc concentrations were performed. After 80 days, there was little visible evidence for significant Fe(II) oxidation in bio-magnetite, -siderite and -vivianite but the Fe(II)-gel had clearly changed from a grey-green to an orange brown colour on reoxidation. Nitrate mediated oxidative remobilization of technetium was negligible in the case of bio-magnetite and -vivianite (<3%) although the highest increased

concentration of Tc in solution after reoxidation ( $\sim 15\pm 4\%$ ) was in the bio-siderite system. As expected, the amorphous Fe(II) phase showed significant Fe(II)-reoxidation, with 0.5 N HCl extractable Fe(II) decreasing from  $87\pm 2\%$  of total iron to  $26\pm 2\%$  after 80 days but only  $3.8\pm 0.4\%$  of the Tc on the solid phase was remobilized to solution. Overall, only the Fe(II)-gel showed clear evidence for microbially mediated nitrate reoxidation of Fe(II) with a clear colour change, a measurable decrease in the 0.5 N HCl extractable Fe(II), and generation of gas pressure as bio-oxidation, presumably via reduction to  $N_2$ , progressed. Oxidative Tc remobilization to solution was negligible in bio-magnetite and bio-vivianite and was very low (<3%) in the case of the Fe(II)-gel, even though the majority of the Fe was reoxidized to Fe(III). Intriguingly, in the case of the bio-siderite  $\sim 15\%$  of the sorbed Tc was remobilized to solution even though no clear evidence for nitrate mediated iron oxidation was observed in the experiments; this perhaps reflects soluble Tc(IV)-carbonate complex formation (Alliot *et al.*, 2009).

#### *Fate of technetium in reduced and reoxidized mineral phases.*

To assess the oxidation state and coordination environment of Tc associated with the Fe(II)-bearing minerals, Tc-loaded samples were prepared at the higher concentrations required to produce good signal to noise ratios during XAS analysis (500–5000 ppm).

It should be noted that these concentrations are elevated compared to typical anthropogenic environmental concentrations of technetium (Morris *et al.*, 2000; Keith-Roach *et al.*, 2003). However, in severely contaminated engineered environments, concentrations of Tc will be comparable to those required for XAS experiments (Lukens *et al.*, 2002). Furthermore, microcosm experiments suggest that Tc is likely to occur in concentrated ‘hotspots’ associated with Fe rich particles in reduced environmental media (Burke *et al.*, 2010; Fredrickson *et al.*, 2009; Lear *et al.*, 2010). It is therefore important to understand technetium speciation in environmentally relevant Fe(II)-containing minerals. Normalized Tc X-ray absorption near edge structure (XANES) spectra for the mineral phases are shown in Fig. 3. Comparison of these data with the  $TcO_4^-$  standard and the literature indicate that for all the reduced minerals, there

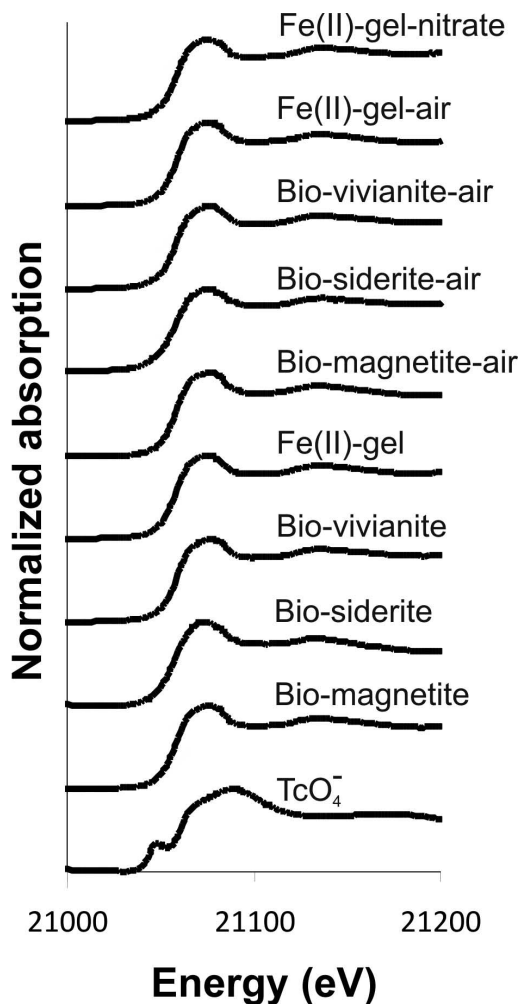


FIG. 3.  $^{99}\text{Tc}$  K-edge XANES for the reduced and reoxidized mineral samples.

was no evidence for the pre-edge feature that is characteristic of the forbidden  $1s \rightarrow 4d$  transition seen in  $\text{TcO}_4^-$  species (Maes *et al.*, 2004); indeed all the spectra were typical of a Tc(IV)-like valence (Fredrickson *et al.*, 2004; Plymale *et al.*, 2011; Morris *et al.*, 2008). Thus, low concentration tracer experiments coupled with higher concentration XANES experiments show that the different Fe(II)-bearing mineral phases have different reactivity to Tc(VII) but that abiotically mediated reductive scavenging of  $\text{TcO}_4^-$  to Tc(IV) is the dominant retention mechanism for Tc in these systems. Background subtracted, normalized and  $k^3$ -weighted EXAFS spectra and Fourier

transform results with corresponding best fit models are presented in Fig. 4 and Table 1. In all cases, the EXAFS for these samples were best modelled with six oxygen atoms at 1.98–2.01 Å, an octahedral Tc(IV)-like coordination environment. Further significant improvements to the modelling of all reduced samples were made by the addition of an outer shell of backscatters of either 1 Tc at  $\sim 2.5$  Å or 1 Fe at  $\sim 2.6$ – $2.7$  Å, which is consistent with the presence of hydrous  $\text{TcO}_2$ -like phases with short range order (Table 1; Morris *et al.*, 2008) and is typical of spectra for Tc(IV) in a hydrous  $\text{TcO}_2$ -like environment in bioreduced sediments and Fe(II)-bearing minerals (Morris *et al.*, 2008; Law *et al.*, 2010a; Plymale *et al.*, 2011). For the reduced minerals, the bio-siderite, bio-vivianite and Fe(II)-gel all showed significantly better fits with a backscatterer in the second shell, and with marginally better fits apparent with a Tc-backscatterer. This is similar to past work on sediments and indicates a short range environment for Tc in these systems (Morris *et al.*, 2008; Law *et al.*, 2010a; Plymale *et al.*, 2011). The bio-magnetite sample showed a poor fit to the model with a Tc-backscatterer in the second shell; here the Tc-backscatterer model required an unrealistically short bond length (2.46 Å) or showed a high Debye–Waller factor. Instead, within our fitting procedure we noted an improved fit with an Fe backscatterer at  $\sim 2.6$  Å perhaps suggesting Tc(IV) may be present within the mineralogical structure of bio-magnetite. Clearly, further refinements were possible in the EXAFS modelling, however, it is apparent from Fig. 4 that the experimentally derived EXAFS spectra for the different bio-minerals have subtly different coordination environments and that without appropriate model spectra, which are very difficult to prepare for these environmental media, over interpretation was possible.

For air reoxidized Fe-minerals, the XANES spectra were again dominated by Tc(IV)-like features (Fig. 3), suggesting that mineral associated Tc was retained as Tc(IV) in these reoxidized systems. EXAFS modelling was also consistent with this interpretation, with the air reoxidized samples showing hydrous  $\text{TcO}_2$ -like coordination environments (6 O at 2.00 Å and this time with either Tc or Fe suitable as backscatterers at either  $\sim 2.5$  Å or  $\sim 2.6$ – $2.7$  Å, respectively (Fig. 4; Table 1)). Again, the bio-magnetite-air and interestingly, the bio-vivianite-air samples were best modelled with a second shell Fe-backscatterer (Table 1) indicating that

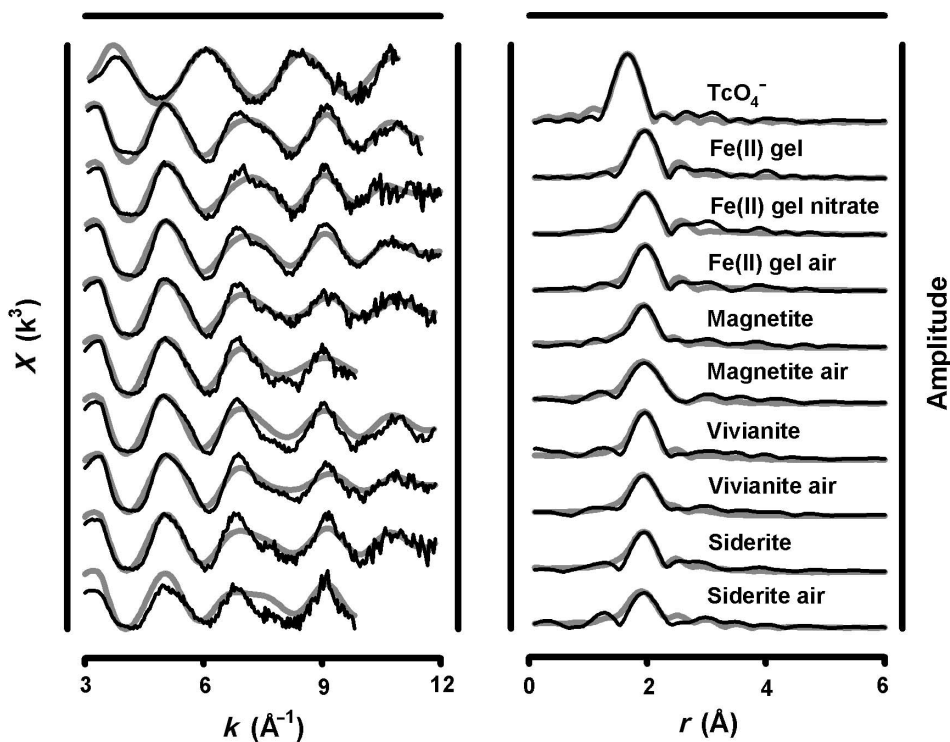


FIG. 4. Background-subtracted, normalized, and  $k^3$ -weighted  $^{99}\text{Tc}$  K-edge EXAFS spectra (left) and corresponding Fourier transform (right) obtained for reduced and reoxidized mineral samples and for the best modelled fit obtained in Table 1. Fourier transforms are phase shifted for Tc–O and were performed over the  $k$  range shown. Black lines are the experimental data, grey lines are the best fit.

octahedrally coordinated Tc(IV) may be incorporated into the reoxidized mineral product. Interestingly, in sediment microcosm experiments where Tc(IV)-labelled sediments have been reoxidized, some samples have been shown to contain both Tc(VII) and Tc(IV) using XAS techniques (Burke *et al.*, 2006; Morris *et al.*, 2008; Fredrickson *et al.*, 2009). In a study using sediments from the Oak Ridge Field Research Center (Fredrickson *et al.*, 2009), both Tc(IV) and Tc(VII) were observed on the wet sediment paste using XANES and repeated washing with water removed the sediment associated Tc(VII). The authors suggested that ingress of oxygen was limited in the compact aggregates present in the sediments implying that any reoxidized Tc(VII) was unable to diffuse readily from the sediment. They also suggested that there was a fraction of the Tc that remained sediment bound as Tc(IV) after extensive washing with water and that this Tc was probably speciated as a stable or

‘armoured’ hydrous Tc(IV)-like phase associated with Fe reoxidation products (Fredrickson *et al.*, 2009). The data presented here suggest that in pure Fe-mineral systems (even those that display nano-particulate characteristics) the small amount of Tc(VII) that seems to form on air reoxidation is quickly removed from the wet mineral paste and is readily released to solution. Furthermore, in these experiments the presence of refractory, octahedrally coordinated Tc(IV)-bearing Fe mineral phase(s) with short range order is confirmed. Indeed, recent modelling work on Tc(IV) associations into the Fe(III)-bearing mineral hematite suggests that incorporation of a few weight percent of Tc(IV) is energetically feasible (Skomurski *et al.*, 2010). This is broadly consistent with our observation that upon exposure to air, Tc(IV) is recalcitrant to reoxidation in Fe-bearing minerals. Finally, the nitrate reoxidized Fe(II)-gel also displayed both XANES and EXAFS consistent with a short range



TABLE 1. Summary of EXAFS modelling results.

Sample	Shell	C.N, type	Distance (Å)	$2\sigma^2$	$R$
Reoxidized solution*	1	4 O	1.72	0.004	31.0
Bio-magnetite	1	6 O	1.99	0.017	37.5
	1	6 O	1.99	0.017	34.2
	2	1 Tc	2.46 <sup>†</sup>	0.022	
	1	6 O	1.99	0.017	35.8
	2	1 Tc	2.50	0.028 <sup>‡</sup>	
	1	6 O	1.99	0.018	34.3
Bio-siderite	2	1 Fe	2.61	0.019	
	1	6 O	1.99	0.019	49.3
	1	6 O	1.99	0.019	42.0
	2	1 Tc	2.49	0.015	
	1	6 O	1.99	0.019	43.3
Bio-vivianite	2	1 Fe	2.63	0.011	
	1	6 O	2.00	0.014	40.6
	1	6 O	2.00	0.014	37.1
	2	1 Tc	2.48	0.021	
	1	6 O	2.00	0.014	38.2
Abiotically precipitated Fe(II) gel*	2	1 Fe	2.63	0.019	
	1	6 O	1.98	0.012	39.4
	1	6 O	1.99	0.013	30.8
	2	1 Tc	2.50	0.014	
	1	6 O	1.99	0.013	33.0
Bio-magnetite AIR	2	1 Fe	2.67	0.010	
	1	6 O	2.00	0.018	37.0
	1	6 O	1.99	0.017	35.2
	2	1 Tc	2.43 <sup>†</sup>	0.032	
	1	6 O	2.00	0.017	36.4
	2	1 Tc	2.50	0.040 <sup>‡</sup>	
Bio-siderite AIR	1	6 O	2.00	0.018	34.3
	2	1 Fe	2.60	0.027	
	1	6 O	2.01	0.025	54.3
	1	6 O	2.01	0.022	50.0
	2	1 Tc	2.49	0.010	
	1	6 O	1.99	0.023	53.3
Bio-vivianite AIR	2	1 Fe	2.67	0.012	
	1	6 O	1.99	0.019	40.7
	1	6 O	1.99	0.018	37.4
	2	1 Tc	2.48	0.023	
	1	6 O	1.99	0.019	36.9
Fe(II)-gel AIR*	2	1 Fe	2.62	0.019	
	1	6 O	1.99	0.015	41.6
	1	6 O	1.99	0.015	35.2
	2	1 Tc	2.50	0.017	
Fe(II)-gel NITRATE*	1	6 O	2.00	0.014	38.2
	2	1 Fe	2.67	0.016	
	1	6 O	1.98	0.017	50.7
	1	6 O	1.98	0.017	44.7
	2	1 Tc	2.52	0.014	
	1	6 O	1.98	0.017	47.5
	2	1 Fe	2.69	0.015	

C.N, type is the modelled occupancy ( $\pm 25\%$ ) and type; Distance (Å) is the interatomic distance ( $\pm 0.02\text{Å}$  for the first shell,  $\pm 0.05\text{Å}$  for outer shells);  $2\sigma^2$  is the Debye–Waller factor ( $\pm 25\%$ ); and  $R$  is the normalized least squares residual (%).

\* Data from Morris *et al.*, 2008. <sup>†</sup> Short bond-distance. <sup>‡</sup> High Debye–Waller factor.

ordered, hydrous TcO<sub>2</sub>-like environment (Figs. 3 and 4; Table 1), once more highlighting the stability of Fe-Tc(IV) phases in a range of redox cycled systems.

## Summary

Tc(VII) was variably reductively precipitated as Tc(IV) by all the reduced iron phases in this study and when associated with the mineral was largely recalcitrant to reoxidation or remobilization, and was retained as Tc(IV). Our results from air reoxidation experiments using single, well defined Fe(II) phases are similar to typical results from microcosm experiments using natural sediments in that there is a significant fraction of Tc(IV) that is recalcitrant to remobilization (Burke *et al.*, 2006; McBeth *et al.*, 2007; Fredrickson *et al.*, 2009; Geissler *et al.*, 2011). However, on reoxidation of some natural sediments, both Tc(VII) and Tc(IV) have been observed in wet sediment pastes (Burke *et al.*, 2006; McBeth *et al.*, 2007; Fredrickson *et al.*, 2009). In the Fe-mineral systems described here, no mixed Tc(VII) and Tc(IV) was seen in the reoxidized samples suggesting that even in the nano-scale bio-magnetite system, oxygen and water ingress was not limited. This suggests that the Fe-mineral experiments are simplified models for some natural sediments where only Tc(IV) has been observed on reoxidation (Begg *et al.*, 2008; Fredrickson *et al.*, 2009; Geissler *et al.*, 2011) and do not capture the complexity of some environments where oxygen ingress is constrained by the nature of the sediment samples. The recalcitrance of Tc to reoxidation and thus remobilization in these minerals is similar to observations with sediment reoxidation, where typically, significant fractions of Tc are retained on sediments as short-range-ordered, hydrous Tc(IV)-like phases co-associated with Fe, and are stable over several months of reoxidation. Interestingly, the EXAFS spectra for the bio-magnetite and bio-magnetite air samples were clearly better fitted with an Fe-backscatterer in the second shell of the model rather than a Tc backscatterer and this is consistent with incorporation of octahedrally coordinated Tc into the reduced and reoxidized Fe-bearing minerals. Overall, this work highlights the potential for medium term Tc(IV)-retention in reduced, Fe(II)-rich environments even upon perturbation and reoxidation of those environments.

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