

## An X-ray absorption study of the fate of technetium in reduced and reoxidised sediments and mineral phases

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### Abstract

Technetium is a long lived ( $2.13 \times 10^5$  a), beta emitting radionuclide which is a groundwater contaminant at a number of nuclear facilities throughout the world. Its environmental behaviour is primarily governed by its redox state. Under oxic conditions it forms the highly soluble pertechnetate ( $\text{TcO}_4^-$ ) ion; under reducing conditions it forms the poorly soluble, reduced forms of Tc, particularly the Tc(IV) ion which is expected to precipitate as hydrous  $\text{TcO}_2$  above its solubility limit ( $10^{-9} \text{ mol l}^{-1}$  at  $\sim \text{pH } 7$ ) or to be strongly sorbed to mineral surfaces at lower concentrations. Thus the redox cycling behaviour of Tc is predicted to be key to its environmental behaviour in the natural and engineered environment. Here the results of a series of X-ray absorption spectroscopy (XAS) experiments which examine the oxidation state and coordination environment of Tc in a range of estuarine, aquifer and freshwater sediment suspensions, and in an environmentally relevant amorphous Fe(II) phase under both reduced and reoxidised biogeochemical conditions are presented. In reduced sediments and the amorphous Fe(II) phase prior to reoxidation, XAS results show that Tc was retained as hydrous  $\text{TcO}_2$ -like phases across all samples. Under air reoxidation, experiments showed significant (up to 80%) remobilisation of Tc to solution as  $\text{TcO}_4^-$ . In pre-reduced freshwater sediments, aquifer sediments and the amorphous Fe(II) phase oxidised with air, XAS indicated that Tc remained associated with the solids as hydrous  $\text{TcO}_2$ -like phases. By contrast, in air reoxidised estuarine sediment XAS analysis suggested that both hydrous  $\text{TcO}_2$ -like phases and  $\text{TcO}_4^-$  were retained within the sediment. Finally, when microbially-mediated  $\text{NO}_3$  reoxidation occurred in estuarine and aquifer sediment slurries, experiments showed comparatively low (<8%) remobilisation of Tc from solids over similar timescales to air reoxidation experiments, whilst XAS again showed that both hydrous  $\text{TcO}_2$ -like phases and  $\text{TcO}_4^-$  were retained within the sediment. By contrast, in the amorphous Fe(II) phase, although  $\text{NO}_3$  reoxidation again led to low (<4%) remobilisation of Tc from

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solids, XAS analysis showed that Tc was retained as hydrous  $\text{TcO}_2$ -like phases alone. These results are discussed in the context of the redox cycling behaviour of Tc in the natural and engineered environment.

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## 1. Introduction

The redox active radionuclide Tc is found as a contaminant at a number of nuclear fuel cycle processing sites and its environmental behaviour is controlled primarily by its speciation. Under oxic conditions it forms the pertechnetate anion ( $\text{TcO}_4^-$ ) which is predicted to be one of the most mobile radionuclides in the environment. By contrast, under reducing conditions, poorly soluble  $\text{Tc(IV)}$  is predicted to form. In sediments, microbially-mediated reactions control the development of sediment anoxia and thus control Tc speciation and mobility (Burke et al., 2005; Begg et al., 2007; McBeth et al., 2007). In the sub-surface, microbes oxidise electron donors (e.g. acetate or hydrogen) and reduce a range of terminal electron acceptors. The utilisation of the different terminal electron acceptors depends on what is available and on the Gibbs free energy changes of the relevant reaction(s), and in sediments anoxia typically develops in the order  $\text{NO}_3^-$ , Mn-, Fe(III)-,  $\text{SO}_4$ -reduction and methanogenesis. It has been shown that, in pure culture,  $\text{Tc(VII)}$  can be directly (enzymatically) reduced by a hydrogenase enzyme using  $\text{H}_2$  as an electron donor (Lloyd et al., 1997; De Luca et al., 2001). However, this enzymatic pathway is thought to be adventitious, and is likely to be ineffectual at environmental concentrations of Tc and  $\text{H}_2$  (Lloyd et al., 1999). In the natural environment, it is thought that  $\text{Tc(VII)}$  reduction is dominated by competing abiotic reduction with products of microbial reduction, e.g. Fe(II) (Fredrickson et al., 2004; Abdelouas et al., 2005; Burke et al., 2005; McBeth et al., 2007; Begg et al., 2007; Zachara et al., 2007), although there is some evidence for enzymatic reduction in sediments at low Fe(II) concentrations (Wildung et al., 2004). As well as understanding the microbially-mediated reduction behaviour of Tc, recently work has examined the reoxidation behaviour of Tc (Standring et al., 2002; Burke et al., 2006; McBeth et al., 2007; Zachara et al., 2007). This is relevant where Tc that may have been reductively sorbed or precipitated on sediments may be disturbed or exposed to a fluctuating water table. Additionally, “biostimulation”,

whereby microbial anoxia is stimulated by addition of electron donors/nutrients to the subsurface has been proposed as a treatment for mobile  $\text{Tc(VII)}$  contamination in the sub-surface (Istok et al., 2004; Lloyd and Renshaw, 2005). Understanding the reoxidation behaviour of Tc in this situation is pertinent when active bio-stimulation has ceased, and reduced aquifer sediments may be exposed to oxidants such as  $\text{NO}_3^-$ -rich groundwaters flushing the anoxic treatment area (Burke et al., 2006; McBeth et al., 2007).

To assess the speciation of radionuclides in sediments, different approaches can be used. For example, in all but near field highly “contaminated” environments, Tc concentrations are low ( $<10^{-10}$  g Tc/g sediment; (Morris et al., 2000)) and here, indirect speciation techniques have been successfully used to provide information on the associations of the radionuclide in sediments (Standring et al., 2002; Keith-Roach et al., 2003; Abdelouas et al., 2005). However, this approach is limited as sequential extraction associations are operationally defined and therefore assess the solubility of the contaminant in a particular chemical extractant, rather than define the direct speciation of the radionuclide. In some circumstances (e.g. at higher Tc concentrations), direct spectroscopic techniques can be used. X-ray absorption spectroscopy (XAS) is perhaps the most useful of these since it can provide information on the average oxidation state and coordination environment of the analyte of interest, and can be applied to amorphous, heterogeneous or microcrystalline solids, or to solutions. Here, samples are loaded with relatively high concentrations of the analyte so that direct spectroscopic detection is possible (e.g. for Tc several tens to hundreds of ppm). Briefly, the sample is scanned with an intense, monochromatic X-ray beam across a range of energies from about 100 eV below the absorption edge to about 1000 eV above it. In the pre-edge region, absorption decreases with increasing energy. The absorption edge is specific to a particular element, and corresponds to an X-ray energy which will stimulate ejection of a core electron from the target element; at this point the absorption increases significantly.

The edge structure or “X-ray absorption near edge structure” (XANES) carries useful information on the valence state of the element of interest. At energies higher than the edge, the absorption gradually decreases and the structure of this “post-edge” region or the “extended X-ray absorption fine structure” (EXAFS) depends on the speciation and local coordination environment of the element of interest. Indeed, the EXAFS spectrum can be modelled quantitatively to give information on coordination environment. Thus XAS can directly probe key aspects of trace element/radionuclide speciation. However, XAS is an averaged technique, so that, in a sample containing a mixture of species, the spectrum will be a concentration-weighted average of the different spectra for the individual component species (Koningsberger and Prins, 1988; Livens et al., 2004). Finally, XAS cannot distinguish between backscattering atoms of similar atomic number that are at the same distance from the studied atom, and EXAFS analysis only gives interatomic distances that are accurate to ca.  $\pm 0.02$  Å in the first shell and ca.  $\pm 0.05$  Å in second and third shells, and coordination numbers which are only accurate to ca.  $\pm 20\%$  (Koningsberger and Prins, 1988; Livens et al., 2004; Maes et al., 2004).

In order to investigate the biogeochemistry and speciation of Tc using XAS techniques, a range of sediments from estuarine and freshwater environments were manipulated to understand the environmental behaviour of Tc by subjecting them to microbially-mediated reduction in the presence of  $^{99}\text{Tc}$ , then re-oxidising them both with air and via microbially-mediated oxidation by  $\text{NO}_3^-$ . Additionally, the redox cycling behaviour of Tc is closely linked to Fe biogeochemistry (Burke et al., 2006; McBeth et al., 2007; Zachara et al., 2007) so, as well as using sediments in reoxidation studies, an amorphous Fe(II) phase that has been used to examine microbially-mediated oxidation of Fe(II) by  $\text{NO}_3^-$  (Weber et al., 2001) was also studied. The experiments were radiolabelled with Tc at high enough levels (i.e. several hundred ppm) to allow direct speciation of the Tc in the sediment samples using XAS.

## 2. Methods

### 2.1. Safety

$^{99}\text{Tc}$  is a radioactive beta emitter (half life  $2.13 \times 10^5$  a;  $E_{\text{max}} = 294$  keV) and should be han-

dled in a properly equipped radiochemistry laboratory. The possession and use of radioactive materials is subject to statutory controls.

### 2.2. Sample preparation

The experiments focused on examining Tc-biogeochemistry in estuarine, aquifer and freshwater sediments and in an amorphous Fe(II) phase and a summary of all sample codes, origins and experimental conditions is given in Table 1.

#### 2.2.1. Microbially-mediated reduction of sediments

Oxic surface sediments were prepared for XAS studies from: (a) a clay rich fine grained intertidal estuarine sediment from the Paull mudflat on the Humber Estuary, UK (Burke et al., 2005, 2006); (b) an unconsolidated, clay rich saprolite from an aquifer in the USA (areas of which are contaminated with radioactivity) collected from the USDoE Field Research Center (FRC) site in Oak Ridge Tennessee (McBeth et al., 2007); and (c) a sandy loam from a freshwater sampling area representative of the Dounreay site, UK (Begg et al., 2007). Work in the authors' laboratories showed that, for a range of oxic sediments, when Tc was present at the high concentrations needed for XAS (ca. 50–500 ppm Tc on sediment) typically it retarded the development of microbial anoxia (data not shown). Thus, to prepare XAS samples sediments were incubated in sealed 10 mL serum bottles in the absence of Tc until they were reduced and then “spiked” with a known quantity of  $\text{TcO}_4^-$  to allow abiotic reduction of soluble Tc(VII) to poorly soluble reduced Tc(IV) species by reaction with reduced phases in the sediments. The biogeochemical condition of the microcosms was monitored prior to spiking with Tc so that systems with predominantly Fe(III)-reducing (containing ca. 50% Fe(II) in solids by 0.5 N HCl extraction) and  $\text{SO}_4^{2-}$ -reducing (where the  $\text{SO}_4^{2-}/\text{Cl}^-$  ratio in porewaters was decreasing significantly and where microcosms were black) conditions could be identified. Overall, this scenario equates to a situation where mobile  $\text{TcO}_4^-$  carried in groundwater passes through a reducing zone in sediments. Typically, sediment microcosms contained ca. 2 g wet sediment and for Humber sediments 10 mL river water, or for FRC and Dounreay sediments 10 mL synthetic groundwater and samples were spiked with ca. 200–300 kBq  $^{99}\text{Tc}$  (as ammonium pertechnetate) to give a final concentration of ca. 200–500 ppm

Table 1

Table showing sample code, origin and experimental conditions for sediment and mineral phases used in XAS experiments

Sample code	Sample origin	Experimental conditions
(1) Humber Fe-R	Humber <i>estuary</i> sediment (Burke et al., 2005)	Fe(III)-reducing
(2) Humber S-R	Humber <i>estuary</i> sediment (Burke et al., 2005)	Sulfate-reducing
(3) FRC Fe-R	USDoE Field Research Centre <i>aquifer</i> material, Oak Ridge (McBeth et al., 2007)	Fe(III)-reducing
(4) Dounreay R	Dounreay, <i>freshwater</i> sediment (Begg et al., 2007)	Fe(III)-reducing; possibly sulfate-reducing
(5) Humber Bio-R	Humber <i>estuary</i> sediment (Burke et al., 2005)	Progressively anoxic sediment
(6) Fe(II) media-R	Amorphous iron (II) phase (Weber et al., 2001)	Abiotic reduction to Fe(II) mineral phases
(7) Reoxidised solution	Solution from Humber <i>estuary</i> sediment	Air reoxidation
(8) Humber Fe-R air	Humber <i>estuary</i> sediment (Burke et al., 2006)	Air reoxidation
(9) Humber S-R air	Humber <i>estuary</i> sediment (Burke et al., 2006)	Air reoxidation
(10) FRC Fe-R air	USDoE Field Research Centre, <i>aquifer</i> material, Oak Ridge (McBeth et al., 2007)	Air reoxidation
(11) Dounreay Fe-R air	Dounreay, <i>freshwater</i> sediment (Begg et al., 2007)	Air reoxidation
(12) Humber Fe-R NO <sub>3</sub> <sup>-</sup>	Humber <i>estuary</i> sediment (Burke et al., 2006)	Nitrate reoxidation 100 mM NO <sub>3</sub> <sup>-</sup>
(13) Humber S-R NO <sub>3</sub> <sup>-</sup>	Humber <i>estuary</i> sediment (Burke et al., 2006)	Nitrate reoxidation 100 mM NO <sub>3</sub> <sup>-</sup>
(14) FRC Fe-R low NO <sub>3</sub> <sup>-</sup>	USDoE Field Research Centre, <i>aquifer</i> material, Oak Ridge (McBeth et al., 2007)	Nitrate reoxidation 25 mM NO <sub>3</sub> <sup>-</sup>
(15) FRC Fe-R high NO <sub>3</sub> <sup>-</sup>	USDoE Field Research Centre, <i>aquifer</i> material, Oak Ridge (McBeth et al., 2007)	Nitrate reoxidation 100 mM NO <sub>3</sub> <sup>-</sup>
(16) Fe(II) media air	Amorphous Fe(II) phase (Weber et al., 2001)	Air reoxidation
(17) Fe(II) media NO <sub>3</sub> <sup>-</sup>	Amorphous Fe(II) phase (Weber et al., 2001)	Nitrate reoxidation 14 mM NO <sub>3</sub> <sup>-</sup>

Tc(IV) on sediments. For the Humber estuarine sediment, Tc-labelled, pre-reduced samples with predominantly Fe(III)-reducing (*Sample 1*. Humber Fe-R) and predominantly SO<sub>4</sub>-reducing conditions (*Sample 2*. Humber S-R) were made up. For FRC *aquifer* and Dounreay *freshwater* sediments pre-reduced, spiked samples undergoing predominantly Fe(III)-reducing conditions (*Sample 3*. FRC Fe-R) and with significant Fe(II) ingrown to sediments (>95%) (*Sample 4*. Dounreay R) were prepared. In the case of pre-reduced sediments, samples were left for up to 30 days after spiking and typically, >97% removal of Tc from solution occurred within the first week of incubation.

Additionally, oxic FRC and Humber sediments with <sup>99</sup>Tc were incubated under the conditions described above to see if indigenous microbes could reduce the high levels of TcO<sub>4</sub><sup>-</sup> in the system. Here, only the Humber sediment showed development of progressive anoxia, giving a sample where the indigenous microbial community had facilitated the removal of Tc(VII) (*Sample 5*. Humber Bio-R). In this case, anoxia took over 6 months to develop, very much slower than in parallel experiments undertaken at lower (μmol L<sup>-1</sup>) <sup>99</sup>Tc concentrations where reductive removal was complete within 20–30 days (Burke et al., 2005).

Table 2

Composition of the Fe(II) medium used for amorphous Fe(II) phase reoxidation experiments

Component	Quantity (g L <sup>-1</sup> )
NaHCO <sub>3</sub>	2.50
NH <sub>4</sub> Cl	0.25
NaH <sub>2</sub> PO <sub>4</sub> · H <sub>2</sub> O	0.60
KCl	0.10
KNO <sub>3</sub>	1.42
FeSO <sub>4</sub> · 7H <sub>2</sub> O	5.56
NaCl	6.66
MgCl <sub>2</sub> · 6H <sub>2</sub> O	1.00
pH	7–8

### 2.2.2. The reduced amorphous Fe(II) phase

In order to investigate the effect of microbially-mediated anoxic oxidation of Fe(II) on the speciation of Tc, a sterile *freshwater* medium was prepared with the addition of NaCl and MgCl to simulate brackish conditions and containing 14 mM NO<sub>3</sub><sup>-</sup> and 20 mM Fe(II) (Table 2). The resultant Fe(II) containing slurry was grey/green and was largely X-ray amorphous. To prepare reduced samples for XAS, the sterile amorphous Fe(II) phase (ca. 2 g wet, blue–green mineral paste to 30 ml of solution) was spiked with ca. 300 kBq <sup>99</sup>Tc as ammonium pertechnetate. After 2 weeks, >99% of the spike

was removed from solution via abiotic reaction with Fe(II) to give a final  $^{99}\text{Tc}$  on the mineral paste of ca. 200–500 ppm (*Sample 6. Fe(II) media-R*). For reoxidation systems, enrichment cultures of Fe(II)-oxidising,  $\text{NO}_3^-$ -reducing microorganisms were prepared by incubation of the sterile amorphous Fe(II) phase with  $\text{NO}_3^-$ -enriched Humber sediments in the dark at 21 °C and stocks were maintained by transferring a 10% inoculum of this enrichment culture to fresh medium on a fortnightly basis. This inoculum was sub-cultured for at least 8 weeks before experimental work began and was shown to contain a stable microbial consortium over 12 months (unpublished data).

### 2.2.3. Oxidised sediments

The reduced Humber estuarine, FRC aquifer and Dounreay freshwater sediments were then reoxidised in air and Humber and FRC sediments were successfully reoxidised via microbially-mediated  $\text{NO}_3^-$  oxidation. For air reoxidation, Tc-labelled Fe(III)- and  $\text{SO}_4^-$ -reducing Humber sediments and Fe(III)-reducing FRC and Dounreay sediments were pumped with air injected via a needle typically on a daily basis for at least 3 weeks prior to sampling (Burke et al., 2006; McBeth et al., 2007). This approach was used to minimize the risk of exposure to the significant amounts of radioactive Tc used in these experiments. Typically, a substantial fraction (up to 80%) of the sediment-bound Tc had been remobilised to solution and between ca. 50 and 200 ppm Tc was left on the solid samples (Burke et al., 2006; McBeth et al., 2007). A sample of the supernatant solution from the air-oxidised Humber  $\text{SO}_4^-$ -reducing sediment was collected (*Sample 7. Reoxidised solution*) as well as four air-reoxidised sediment samples (*Sample 8. Humber Fe-R air; Sample 9. Humber S-R air; Sample 10. FRC Fe-R air; and Sample 11. Dounreay R air*).

For  $\text{NO}_3^-$  reoxidation experiments, pre-reduced Tc-labelled Humber sediments (replicates of samples 1 and 2) were injected with an anaerobic solution of  $\text{KNO}_3$  to a final concentration of 100 mM and reoxidised for 30 days (*Sample 12. Humber Fe-R  $\text{NO}_3^-$ ; Sample 13. Humber S-R  $\text{NO}_3^-$* ). Two FRC Fe-R sediments (replicates of sample 3) were also injected with 25 mM and 100 mM  $\text{KNO}_3$ , respectively (*Sample 14. FRC Fe-R Low  $\text{NO}_3^-$ ; Sample 15. FRC Fe-R High  $\text{NO}_3^-$* ). At the point of sampling (between 30 and 60 days), less than 8% of sediment bound Tc had been remobilised to solution in all  $\text{NO}_3^-$ -reoxidised

samples and Tc concentrations on solids ranged from 50 to 200 ppm.

### 2.2.4. The oxidised amorphous Fe(II) phase

The Tc-labelled amorphous Fe(II) phase was reoxidised with air by transferring the reduced mineral slurry (ca. 2 g slurry in 30 mL) into a 250 mL conical flask, capping with a porous bung and shaking the slurry in the dark at 10 °C at 150 rpm for 1 week (*Sample 16. Fe(II) media air*). At that point, ca. 13% of the mineral bound Tc had been remobilised to solution and ca. 67% of the extractable Fe was present as Fe(III). For  $\text{NO}_3^-$  reoxidation, the sterile Tc-labelled medium was amended with 14 mmol  $\text{L}^{-1}$   $\text{NO}_3^-$  and inoculated with 10% of the stable Fe(II)-oxidising,  $\text{NO}_3^-$ -reducing enrichment culture and the mineral slurry was left to reoxidise for 57 days with gentle shaking once a fortnight (*Sample 17. Fe(II) media  $\text{NO}_3^-$* ). At that point, ca. 4% of the mineral bound Tc had been remobilised to solution and ca. 61% of the extractable Fe was present as Fe(III). For both samples, the Tc concentration on solids remained at several hundred ppm after reoxidation.

## 2.3. X-ray absorption spectroscopy

### 2.3.1. XAS sample preparation and data acquisition

Sediment slurries were spun down (10 min, 1000 g) and an approximately 300  $\mu\text{L}$  pellet of the solid sediment or mineral paste with less than 50% moisture content was mounted for XAS analysis. Samples were mounted in air tight Perspex sample cells with Kapton windows, triple contained in heat sealed plastic bags and stored at  $-80$  °C prior to analysis. During the preparation of air sensitive phases, samples were handled and mounted under anaerobic conditions. Technetium K-edge X-ray absorption spectra were collected in fluorescence mode on station 16.5 of the Daresbury SRS (see Burke et al., 2005, 2006; McBeth et al., 2007, for details of beamline setup and conditions). Multiple scans (typically 4–12 scans) were collected and summed and background subtracted spectra were analysed as detailed in Sections 2.3.2, 2.3.3, and 2.3.4.

### 2.3.2. EXAFS modelling approach – reduced samples

Background subtracted EXAFS spectra were analysed in EXCURV98 using full curved wave theory (Gurman et al., 1984). Phase shifts were derived from *ab initio* calculations using Hedin–Lundqvist

potentials and von-Barth ground states (Binsted, 1998). Fourier transforms of the EXAFS spectra were used to obtain an approximate radial distribution function around the central Tc atom (the absorber atom); the peaks of the Fourier transform can be related to “shells” of surrounding backscattering ions characterised by atom type, number of atoms, absorber–scatterer distance, and the Debye–Waller factor,  $2\sigma^2$ . For reduced samples, the data were fitted in  $k^3$  space by defining a theoretical model which was informed by the relevant literature (Wharton et al., 2000; Lukens et al., 2002; Maes et al., 2004) and used whole integer values for the shells of backscatterers around the central atom. Shells of backscatterers were added around the central atom and, by refining an energy correction, Ef (the Fermi energy which for final fits typically varied between  $-10$  and  $0$ ), the absorber–scatterer distance, and the Debye–Waller factor for each shell, the least squares residual (the  $R$ -factor) was minimized and the values of absorber scatterer distance and Debye–Waller factor were recorded. Initially, for reduced samples the number of scatterers was fixed at 6 O atoms at distance ca. 2.0 Å, corresponding to the first shell coordination environment for hydrous Tc(IV) oxide (Lukens et al., 2002; Maes et al., 2004) and then refined. For shells of scatterers beyond the inner coordination sphere around Tc, the number of atoms in the shell was fixed at 1 and not further refined. For Fe(III)-reducing sediments and for the amorphous Fe(II) phase the second shells of backscatterers that were considered were 1 Tc at ca. 2.5 Å (Almahamid et al., 1995; Maes et al., 2004) and 1 Fe at ca. 2.7 Å. The Tc–Fe interatomic distance of 2.7 Å is within error of the geometrically calculated distance for Tc–Fe in the system based on experimental distances of Tc(IV)–O of 1.94–2.08 Å (Almahamid et al., 1995) and Fe–O bond distances in model compounds of goethite and Fe(II) chloride of 1.94–2.20 Å (Apted et al., 1995; O’Day et al., 2004). The different backscatterers were only considered to be significant if the overall fit ( $R$ -factor) was reduced by  $>5\%$  and all results for Fe and Tc were recorded (Tables 3a, 3b).

### 2.3.3. EXAFS modelling approach – reoxidised samples

For selected air and  $\text{NO}_3$  reoxidised sediment samples, EXAFS spectra suggested that both hydrous  $\text{TcO}_2$ -like phases and  $\text{TcO}_4^-$  were present in the sediment components (see below). To model

Table 3a

Summary of EXAFS modelling results for reduced sediments and reduced mineral phases

Sample	Shell	O.T.	$r$ (Å)	$2\sigma^2$ (Å <sup>2</sup> )	$R$
(1) Humber Fe-R	1	6 O	2.01	0.014	51.9
	1	6 O	2.01	0.013	45.9
	2	1 Fe	2.72	0.007	
	1	6 O	2.01	0.013	40.9
	2	1 Tc	2.54	0.012	
(2) Humber S-R	1	6 O	2.00	0.013	38.0
	1	6 O	2.00	0.013	33.5
	2	1 Fe	2.68	0.021	
	1	6 O	2.00	0.013	33.1
	2	1 Tc	2.52	0.017	
(3) FRC Fe-R	1	6 O	2.02	0.011	66.0
	1	6 O	2.02	0.012	57.6
	2	1 Fe	2.69	0.004	
	1	6 O	2.02	0.013	46.1
	2	1 Tc	2.52	0.004	
(4) Dounreay R	1	6 O	2.01	0.010	42.7
	1	6 O	2.01	0.011	37.6
	2	1 Fe	2.67	0.012	
	1	6 O	2.01	0.010	37.1
	2	1 Tc	2.49	0.013	
(5) Humber progressively anoxic	1	6 O	2.01	0.014	45.6
	1	6 O	2.00	0.014	33.5
	2	1 Fe	2.65	0.006	
	1	6 O	2.00	0.015	32.5
	2	1 Tc	2.50	0.010	
(6) Fe(II) media-R	1	6 O	1.98	0.012	39.4
	1	6 O	1.98	0.013	33.0
	2	1 Fe	2.67	0.010	
	1	6 O	1.99	0.014	30.8
	2	1 Tc	2.50	0.014	

O.T. is the modeled occupancy ( $\pm 25\%$ ) and type;  $r$  (Å) is the interatomic distance ( $\pm 0.02$  Å for the first shell,  $\pm 0.05$  Å for outer shells);  $2\sigma^2$  is the Debye–Waller factor ( $\pm 25\%$ ); and  $R$  is the normalized least squares residual (%).

the relevant samples, it was assumed that all the Tc was either Tc(VII) bound to four oxygens at 1.7 Å (shell 1) or Tc(IV) bound to six oxygens at 2.0 Å (shell 2). If the proportion of Tc(VII) was  $P$ , then  $N1 = 4 \times P$  and  $N2 = 6(1 - P)$ , which can be expressed as  $6 - (1.5 \times N1)$ . Thus, the proportion of Tc(VII) was refined by refining  $N1$  and varying  $N2$  from this expression rather than fitting  $N2$  as an independent variable (Burke et al., 2006). For the FRC FeR sediment and Dounreay R sediment reoxidised with air, and the amorphous Fe(II) phase reoxidised with air and  $\text{NO}_3$ , EXAFS modeling suggested hydrous  $\text{TcO}_2$ -like coordination environ-

Table 3b  
Summary of EXAFS modelling results for reoxidised solution, sediments and reoxidised mineral phases

Sample	Shell	O.T.	Distance (Å)	$2\sigma^2$	$R$
(7) Reoxidised solution	1	4 O	1.72	0.004	31.0
(8) Humber Fe-R air	1	1.8 O	1.71	0.007	50.3
	2	3.3 O	1.99	0.012	
	1	1.8 O	1.71	0.008	48.9
	2	3.3 O	1.99	0.012	
	3	1 Fe	2.73	0.025	
	1	1.8 O	1.71	0.008	46.7
	2	3.3 O	1.99	0.011	
	3	1 Tc	2.58	0.032	
(9) Humber SR air	1	1 O	1.67	0.004	35.5
	2	4.5 O	1.98	0.011	
	1	1 O	1.67	0.004	31.5
	2	4.5 O	1.97	0.012	
	3	1 Fe	2.66	0.020	
	1	1 O	1.68	0.005	31.3
	2	4.5 O	1.98	0.011	
	3	1 Tc	2.48	0.024	
(10) FRC Fe-R air	1	6 O	2.01	0.010	50.6
	1	6 O	2.01	0.010	40.0
	2	1 Fe	2.73	0.004	
	1	6 O	2.02	0.014	31.5
	2	1 Tc	2.55	0.004	
(11) Dounreay R air	1	6 O	1.99	0.012	40.6
	1	6 O	2.00	0.012	33.6
	2	1 Fe	2.66	0.007	
	1	6 O	2.00	0.012	33.2
	2	1 Tc	2.49	0.012	
(12) Humber Fe-R NO <sub>3</sub> <sup>-</sup>	1	2.0 O	1.73	0.010	52.7
	2	2.8 O	2.01	0.009	
	1	2.1 O	1.73	0.012	51.3
	2	2.8 O	2.02	0.009	
	3	1 Fe	2.70	0.020	
	1	2.1 O	1.73	0.012	49.0
	2	2.8 O	2.01	0.009	
	3	1 Tc	2.52	0.024	
(13) Humber SR NO <sub>3</sub> <sup>-</sup>	1	1.3 O	1.69	0.007	45.9

Table 3b (continued)

Sample	Shell	O.T.	Distance (Å)	$2\sigma^2$	$R$
	2	4.1 O	1.97	0.014	
	1	1.3 O	1.69	0.007	42.9
	2	4.1 O	1.98	0.014	
	3	1 Fe	2.71	0.021	
	1	1.3 O	1.70	0.007	42.0
	2	4.1 O	1.99	0.011	
	3	1 Tc	2.60	0.020	
(14) FRC Fe-R, low NO <sub>3</sub> <sup>-</sup>	1	2.0 O	1.72	0.014	65.4
	2	3.0 O	2.02	0.008	
	1	2.0 O	1.72	0.014	58.4
	2	3.0 O	2.02	0.008	
	3	1 Fe	2.70	0.010	
	1	2.0 O	1.72	0.012	49.6
	2	3.0 O	2.02	0.010	
	3	1 Tc	2.54	0.010	
(16) Fe(II)-media, air	1	6 O	1.99	0.015	41.6
	1	6 O	1.99	0.014	38.2
	2	1 Fe	2.67	0.016	
	1	6 O	1.99	0.015	35.2
	2	1 Tc	2.50	0.017	
(17) Fe(II)-media, NO <sub>3</sub> <sup>-</sup>	1	6 O	1.98	0.017	50.7
	1	6 O	1.98	0.017	47.5
	2	1 Fe	2.69	0.014	
	1	6 O	1.98	0.017	44.7
	2	1 Tc	2.52	0.015	

O.T. is the modeled occupancy ( $\pm 25\%$ ) and type;  $r$  (Å) is the interatomic distance ( $\pm 0.02$  Å for the first shell,  $\pm 0.05$  Å for outer shells);  $2\sigma^2$  is the Debye–Waller factor ( $\pm 25\%$ ); and  $R$  is the normalized least squares residual (%).

ments (see below) and spectra were modeled as for reduced samples above.

#### 2.3.4. XANES analysis – reoxidised samples

XANES spectra for reduced samples (21 000–21 200 eV) were compiled. After identification of Tc(IV) and Tc(VII) as constituents of some of the reoxidised sediment samples using the diagnostic Tc–O bond distances from EXAFS analyses and assessment of the fraction of Tc(VII) in the sample from consideration of the occupancy of different

shells (Section 3.2), XANES data for these samples were also modeled. The approach was to use least squares fitting of the XANES spectra of representative hydrous  $\text{TcO}_2$ -like sediments (i.e. the most reduced, Humber SR sediment) and  $\text{TcO}_4^-$  (i.e. an ammonium pertechnetate standard) end members (Cotter-Howells et al., 2005; Burke et al., 2006). Finally, for reoxidised samples that EXAFS modeling indicated were dominated by hydrous  $\text{TcO}_2$ -like phases, XANES spectra were again compiled to allow comparison between samples.

### 3. Results and discussion

#### 3.1. Tc fate in reducing sediments and the amorphous Fe(II) phase

For all reduced samples, a summary of the background subtracted, normalised and  $k^3$  weighted EXAFS spectra, together with the Fourier transforms corresponding to the best fit using the adapted fitting approach are given in Fig. 1 for experimental (black) and model (grey) data and

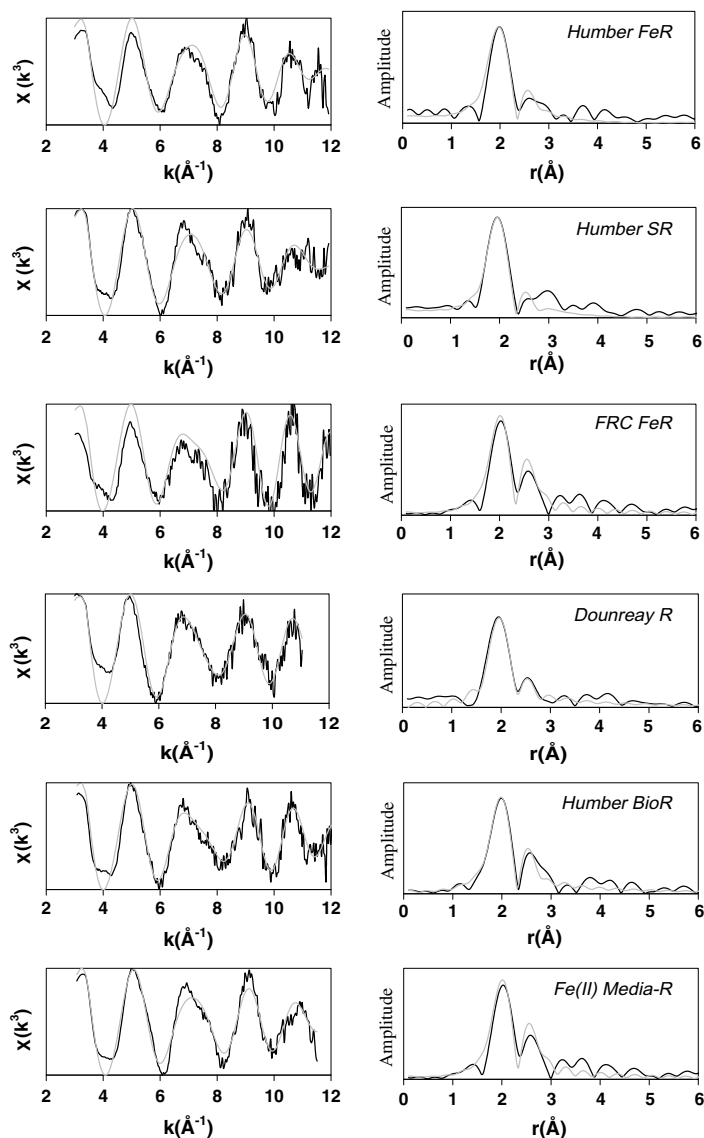


Fig. 1. Background-subtracted, normalized, and  $k^3$ -weighted  $^{99}\text{Tc}$  K-edge EXAFS spectra (left) and corresponding Fourier transform (right) obtained for reduced samples and for the best modeled fit obtained in Table 3a. Fourier transforms are phase shifted for Tc–O and were performed over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



details of the different fits showing the effect on the *R*-factor (goodness of fit) of changing the number of shells and type of scatterer in the fit are given in Table 3a. All of the samples give very similar spectra with a major peak at ca. 2.00 Å and smaller features between 2 and 3 Å. For all samples, modelling with a first shell coordination environment of 6 O atoms at ca. 2.00 Å gave the best initial fit (Table 3a). Additionally, for the Humber SR sediment there was no evidence for a TcS<sub>2</sub> like environment. The key differences between the Tc–O and Tc–S environments are the difference in bond lengths, the scattering amplitudes, and the *k*-dependence of the amplitudes. As discussed, for hydrous TcO<sub>2</sub>, the bond length is ca. 2.00 Å whilst for TcS<sub>2</sub>, Tc–S bond lengths are between 2.30 and 2.50 Å (Wharton et al., 2000) and clearly the TcS<sub>2</sub>-like environment did not model well for these samples. Further significant improvements to the modelling of all reduced samples were made by the addition of an outer shell of backscatterers of either 1 Fe at ca. 2.7 Å or 1 Tc at ca. 2.5 Å as informed for Tc by models of hydrous TcO<sub>2</sub> in the literature or for Fe by geometric considerations. In all cases, adding a shell of Tc scatterers at 2.50–2.54 Å gave the best fit for the model on the basis of the *R*-values, although it should be noted that Fe as a backscatterer also made a significant improvement to fits (Table 3a). Indeed, the significant differences in the EXAFS spectra seen in these (and later) samples in the range 6–8 Å<sup>-1</sup> (Figs. 1, 3, 5) are almost certainly due to variability between samples in the numbers of scatterers in the outer shells. For the purposes of fitting the data, the coordination number in the outer shell was constrained to 1, but it is clear from the variation in the values of the Debye–Waller factor (from 0.004–0.017 where a low Debye–Waller factor indicates a higher relative contribution; Table 3a) that this shell makes a greater relative contribution to some spectra than others. This variation is most likely to be due to varying degrees of ordering, with some samples having a lower number of close Tc–Tc interactions than others. Overall, the spectra and modeling fits for the different reduced materials do show reasonable agreement, however, it is clear that differences do exist between the goodness of fit between samples suggesting variable degrees of ordering. Thus, although it is definite that the majority of the Tc in all samples is present as Tc(IV) octahedrally bonded to O, in the absence of appropriate standards in the literature it is not possible to rule out that some of the ligands may be, for exam-

ple, organic acids, phosphates or sulfates, which will be present in the sediment. These observations suggest that Tc is largely present as an O bound Tc(IV) phase closely resembling hydrous TcO<sub>2</sub> in a wide range of environmentally relevant reduced materials from estuarine and aquifer sediments through to synthetic Fe(II) phases but that the ordering of Tc(IV) bound within the sediment matrix may have some subtle, yet significant, differences. Modelling a first shell of 6 O atoms at 2.00 Å and a second shell of 1 Tc atom at 2.50–2.54 Å showed reasonable fits (but with some variation in goodness of fit between different samples) for all the reduced samples and was consistent with hydrous TcO<sub>2</sub>-like phases similar to those seen by other workers (Lukens et al., 2002; Maes et al., 2004). Furthermore, the lack of any pronounced peaks beyond ca. 2.5 Å confirms that in these samples crystalline TcO<sub>2</sub> was not formed on bioreduction as its three-dimensional structure has a distinctive shell of 4 Tc at 3.64 Å and 4 Tc atoms at 3.67 Å (Maes et al., 2004). When the crystalline structure is more hydrated, the three-dimensional order breaks down and this is consistent with the lack of major peaks at ca. 3.6 Å in the spectra. XANES data for samples 1–6 are given in Fig. 2, and are consistent both within the group of samples, and in shape and edge-position with previously published Tc(IV) spectra for environmentally

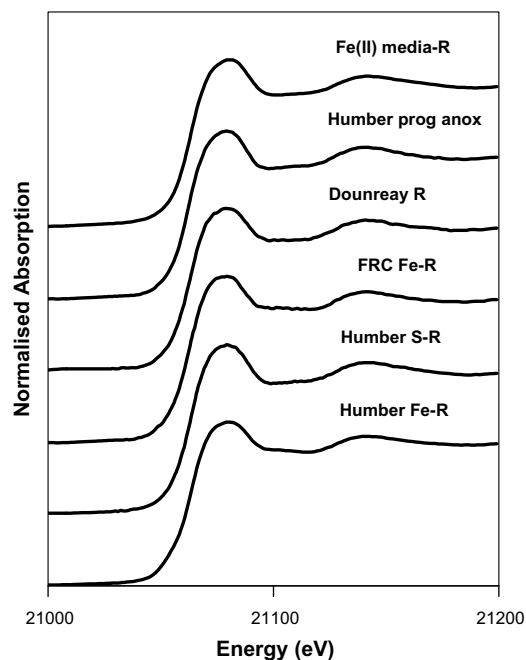


Fig. 2. Tc K-edge XANES for reduced samples.

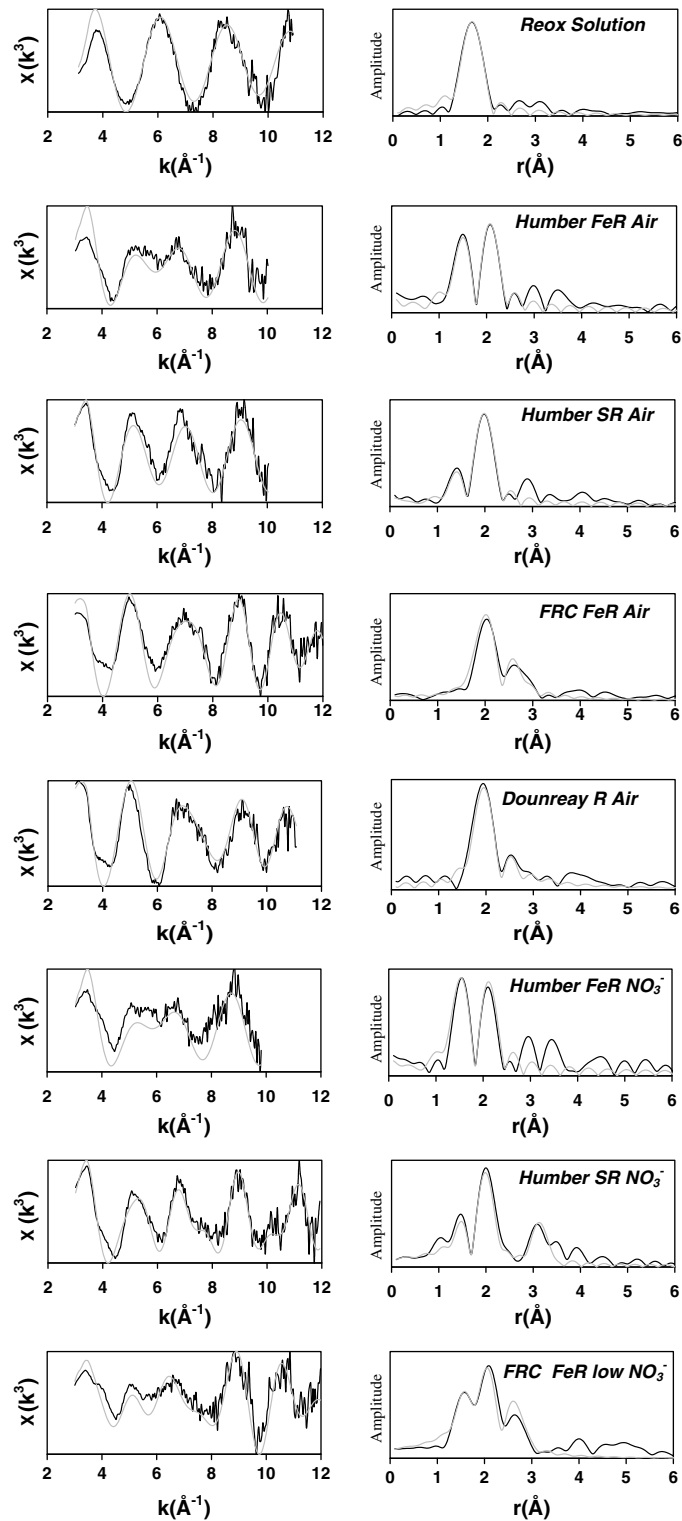


Fig. 3. Background-subtracted, normalized, and  $k^3$ -weighted  $^{99}\text{Tc}$  K-edge EXAFS spectra (left) and corresponding Fourier transform (right) obtained for reoxidised samples and for the best modeled fit obtained in Table 3b. Fourier transforms are phase shifted for Tc–O and were performed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

relevant samples (Lloyd et al., 2000; Wharton et al., 2000; Lukens et al., 2002; Maes et al., 2004).

### 3.2. Tc fate on reoxidation of reduced sediments

For all reoxidised materials from sediment samples, a summary of the background subtracted, normalised and  $k^3$  weighted EXAFS spectra and the best fit Fourier transforms are given in Fig. 3 for experimental (black) and model (grey) data. Model fits are provided in Table 3b. The reoxidised solution from air reoxidation of the Humber SR sediment was fitted with 4 O atoms at 1.72 Å, diagnostic for  $\text{TcO}_4^-$ . This spectroscopic measurement confirmed that remobilisation of reduced hydrous  $\text{TcO}_2$  in the sediments was mediated via reoxidation to Tc(VII) (Burke et al., 2006). Interestingly, for a number of sediment samples, EXAFS data were best modelled using the constrained fitting approach described above for reoxidised samples, with O atoms at both ca. 1.7 Å and ca. 2.0 Å. This suggested that both hydrous  $\text{TcO}_2$  and  $\text{TcO}_4^-$  were present in selected reoxidised samples (Table 3b; Fig. 3). Within the constraints of the fitting approach, for Humber estuarine sediments, the biogeochemistry of the sample prior to reoxidation seemed to affect the final composition of the sediment-associated Tc on reoxidation. For Fe(III)-reducing Humber sediments reoxidised with air and  $\text{NO}_3^-$ , the “best fit” modelled occupancy of O atoms at 1.7 Å (1.8 and 2.1 atoms, respectively, for a model including 1 Tc backscatterer at 2.52 Å; Table 3b) suggested ca.  $50 \pm 10\%$  of sediment-associated Tc was present as Tc(VII). Whilst for  $\text{SO}_4$ -reducing Humber sediments reoxidised with air and  $\text{NO}_3^-$ , the occupancies at 1.7 Å (1.0 and 1.3 Å respectively; Table 3b) suggested a lower average percentage of Tc(VII) in these reoxidised samples (ca.  $30 \pm 10\%$ ). These observations were reinforced by XANES fitting for these samples (see Table 4). For freshwater and aquifer sediments the situation was more complex. In the reduced FRC aquifer sediment reoxidised with air there was no evidence for a mix of Tc(IV) and Tc(VII) and the data could be fitted with 6 O atoms at ca. 2.00 Å, diagnostic for octahedrally coordinated Tc(IV) oxides. This pattern was repeated for the reduced Dounreay freshwater sediment reoxidised with air, with a hydrous  $\text{TcO}_2$ -like phase predicted from modelling the EXAFS spectra (Table 3b). By contrast, in the reduced FRC aquifer sediment reoxidised with 25 mmol  $\text{L}^{-1}$   $\text{NO}_3^-$ , EXAFS modelling gave O occupancies at both ca. 1.7 Å and ca.

Table 4

XANES analysis of reoxidised sediment spectra as linear combinations of representative “end member” spectra  $\text{TcO}_4^-$  (1) and the hydrous  $\text{TcO}_2$ -like phase in the Humber SR sediment (2)

Sample	Percentage spectrum 1	Percentage spectrum 2	Fit index <sup>a</sup>
1. $\text{TcO}_4^-$	100	0	–
A. Humber Fe-R air	30	70	0.33
B. Humber S-R air	15	85	0.032
C. FRC Fe-R air	0	100	–
D. Dounreay R air	0	100	–
E. Humber, Fe-R, $\text{NO}_3^-$	33	67	0.36
F. Humber $\text{NO}_3^-$ (S-R)	18	82	0.11
G. FRC low $\text{NO}_3^-$ (Fe-R)	52	48	0.33
H. FRC high $\text{NO}_3^-$ (Fe-R)	33	68	0.24
2. Hydrous $\text{TcO}_2$	0	100	–

Modeled results are for samples: (A) Humber Fe-R air; (B) Humber S-R air; (C) FRC Fe-R air; (D) Dounreay Fe-R air; (E) Humber Fe-R  $\text{NO}_3^-$ ; (F) Humber S-R  $\text{NO}_3^-$ ; (G) FRC Fe-R low  $\text{NO}_3^-$ ; (H) FRC Fe-R high  $\text{NO}_3^-$ .

<sup>a</sup> The fit index of the calculated XANES spectra with experimental XANES spectra is defined as  $\Sigma [(I_{\text{obs}} - I_{\text{calc}})^2]/n$  where  $n$  is the number of points in each spectrum.

2.00 Å of 2 and 3 atoms, respectively, (Table 3b) suggesting ca.  $50 \pm 10\%$  of the sediment bound Tc was present as Tc(VII).

For all reoxidised samples that showed evidence for both Tc(IV) and Tc(VII) in the sediments, addition of a third shell of 1 Tc or 1 Fe scatterer at ca. 2.5 Å or ca. 2.7 Å, respectively, and concordant with the modelling approach described above for Tc(IV) in reduced sediments, improved the fits for the EXAFS modelling (Table 3b). Overall, the fits with a Tc atom were marginally better than with an Fe atom and addition of the modelled outer shell of either Fe or Tc decreased the  $R$  value significantly compared to fitting without the outer shell. Interestingly, the improvement in the modeled fit between Tc and Fe was generally less striking than in the reduced samples (Table 3b). In addition, for the reduced FRC aquifer and Dounreay freshwater sediments reoxidised with air which contained only Tc(IV), modelling with a second shell of 1 Tc or 1 Fe atom at ca. 2.5 Å or 2.7 Å, respectively, significantly improved the fit. Again, in both cases the applied fits were marginally better with Tc suggesting hydrous  $\text{TcO}_2$ -like phases may dominate on reoxidation. Finally, as with the reduced samples

and in the absence of appropriate standards for these natural environmental materials, it is not possible to exclude the possibility that some of the reduced Tc is present as, e.g. polymeric species (Zachara et al., 2007) or bound by sediment components such as organic acids, phosphates or sulfates. In summary, EXAFS analysis suggests that in air- and  $\text{NO}_3$ -reoxidised estuarine sediments and in a  $\text{NO}_3$ -reoxidised aquifer sediment a mix of both Tc(IV) and Tc(VII) is present. Additionally, for the freshwater sediments described here, Tc is retained on air reoxidation as hydrous  $\text{TcO}_2$ -like phases. Overall, it is difficult to draw any further conclusion about the nature of the reoxidised Tc in these environmental samples due to lack of relevant standards in the literature.

The XANES spectra for the reoxidised samples are provided in Fig. 4. The reoxidised solution was very different from the reduced samples with a clear “pre-edge” signal characteristic of the forbidden  $1s \rightarrow 4d$  transition seen in  $\text{TcO}_4^-$  XANES (Maes et al., 2004). For the reoxidised sediments, the XANES spectra were intermediate between the representative  $\text{TcO}_4^-$  and hydrous  $\text{TcO}_2$  end members. For example, the Fe(III)-reducing Humber sediment reoxidised with  $\text{NO}_3$  clearly shows a “pre-edge”

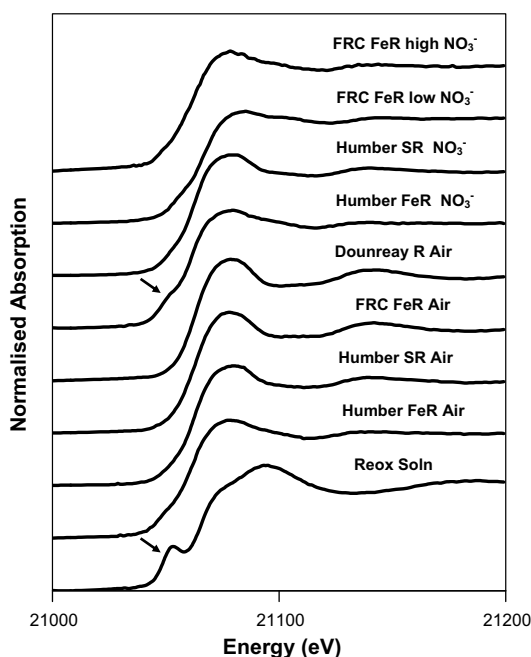


Fig. 4. Tc K-edge XANES for reoxidised sediment samples. Arrows are used to indicate the pre-edge shoulder in the reoxidised solution which is also clearly seen in the Humber FeR  $\text{NO}_3^-$  sample.

shoulder similar to that seen in the reoxidised solution (see black arrows on Fig. 4) whilst both the reduced FRC aquifer and Dounreay freshwater sediments reoxidised with air are consistent with the hydrous  $\text{TcO}_2$  XANES spectra seen in all the reduced samples in Fig. 2. The results of the least squares analysis of the XANES spectra for reoxidised sediment samples are presented in Table 4. Each spectrum was modeled as a combination of two “end-member” representative phases, pertechnetate and the hydrous  $\text{TcO}_2$ -like phase seen in the most reduced, Humber SR sediment, although without using a wider database of model spectra it is not possible to be definitive that these are the only phases present. Note, although the data quality for the reduced FRC sediment reoxidised with  $100 \text{ mmol L}^{-1} \text{ NO}_3$  meant that EXAFS interpretation was inappropriate, XANES analysis and least squares fitting was possible. Overall, the XANES modeling agreed with EXAFS modeling results, with Fe(III)-reducing Humber estuarine sediments reoxidised with air and  $\text{NO}_3$  and reduced FRC aquifer sediments reoxidised with  $\text{NO}_3$  displaying a higher percentage Tc(VII) retained in solids after reoxidation than the  $\text{SO}_4$ -reducing Humber estuarine sediments reoxidised with air and  $\text{NO}_3$ . Additionally, XANES analysis suggested that the reduced FRC and Dounreay sediments reoxidised with air contained only Tc(IV) in agreement with EXAFS modeling (Fig. 4).

In summary, both EXAFS and XANES modeling suggests that in Humber estuarine sediments reoxidised with air and  $\text{NO}_3$  and FRC aquifer sediments reoxidised with  $\text{NO}_3$ , both Tc(VII) and Tc(IV) were present in the solid phase. Interestingly, all of the  $\text{NO}_3$ -reoxidised sediment samples contained significant quantities of Tc(VII) in their solid phases even though remobilisation of Tc to solution in these systems was very low in both XAS experiments (<8%) and in parallel, lower ( $\mu\text{mol L}^{-1}$ ) Tc concentration experiments (Burke et al., 2006; McBeth et al., 2007). Indeed, the mechanism(s) by which Tc(VII), in particular, is retained in the solid phase in both estuarine and aquifer sediments would repay further investigation.

### 3.3. Tc fate on reoxidation of the amorphous Fe(II) phase

For the amorphous Fe(II) phase reoxidised with air or  $\text{NO}_3$ , a summary of the background subtracted, normalised and  $k^3$  weighted EXAFS spectra and the associated Fourier transforms for the

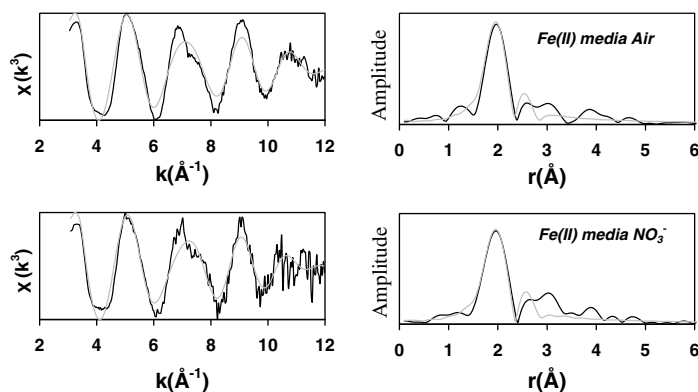


Fig. 5. Background-subtracted, normalized, and  $k^3$ -weighted  $^{99}\text{Tc}$  K-edge EXAFS spectra (left) and corresponding Fourier transform (right) obtained for reoxidised mineral samples and for the best modeled fit obtained in Table 3b. Fourier transforms are phase shifted for Tc–O and were performed over the whole  $k$ -range shown. Black lines are the experimental data, grey lines are the best fit.

samples are given in Fig. 5 for experimental (black) and model (grey) data and in Table 3b. The extent of oxidation between samples differed; with air after 1 week, ca. 13% Tc was remobilised whilst with  $\text{NO}_3^-$  after 57 days, only ca. 4% of Tc was remobilised to solution even though the Fe(II) remaining in the partially reoxidised samples was similar (33% and 39% Fe(II)) in air- and  $\text{NO}_3^-$ -reoxidised experiments, respectively. Both air- and  $\text{NO}_3^-$ -reoxidised amorphous Fe(II) phase samples gave very similar spectra with a dominant peak in the Fourier transform at ca. 2.00 Å, minor peaks between ca. 2–3 Å, and with no significant spectral features below 2.00 Å. Again, this suggests that on reoxidation of this Fe(II)-containing phase, Tc forms hydrous  $\text{TcO}_2$ -like phases with a first shell coordination environment of 6 O atoms at ca. 2.00 Å, similar to the behaviour observed on air reoxidation of FRC aquifer and Dounreay freshwater sediments. A significant improvement in fit for the model was observed by addition of a second shell coordination environment for the samples of 1 Tc at ca. 2.50 Å or 1 Fe at ca. 2.7 Å with the Tc fit being the most improved in both cases (Table 3b). This, in combination with the lack of amplitude in the EXAFS spectra at ca. 3.6 Å again suggests that Tc is most likely retained in these samples as hydrous  $\text{TcO}_2$ -like phases and with parallels to the phases seen in the reduced samples and in the air oxidised FRC and Dounreay freshwater sediments. Furthermore, a similar hydrous  $\text{TcO}_2$ -like environment has been observed on air oxidation of a Tc(IV)-doped, Fe(II)-containing mackinawite (FeS) sample (Wharton et al., 2000) and polymeric octahedrally coordinated Tc(IV) oxide phases have been observed on air oxidation of chemically precipitated Fe(II)/

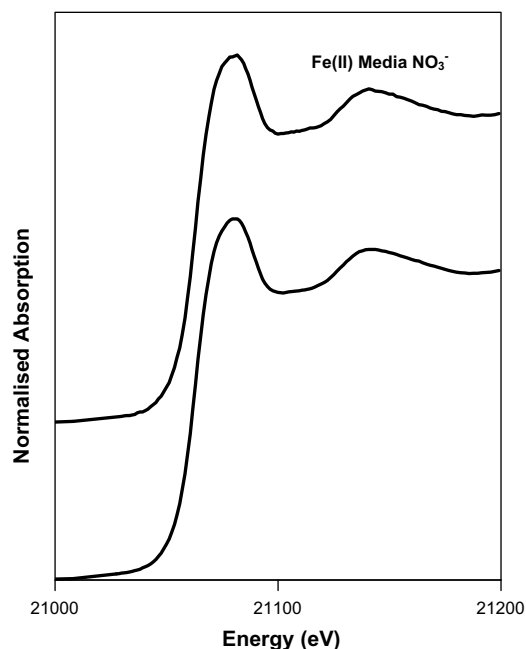


Fig. 6. Tc K-edge XANES for reoxidised mineral samples.

Tc(IV) phases (Zachara et al., 2007). Again, in agreement with the EXAFS data, the XANES spectra for the amorphous Fe(II) phase samples described here were consistent with Tc(IV) dominating the environment (Fig. 6).

Thus, reoxidation of the amorphous Fe(II) phase described here apparently leads to formation of an oxidation resistant Tc(IV) hydrous oxide-like phase in the residual, Fe(III) containing solid. Interestingly, recent work has suggested that Tc(IV) polymeric species incorporate into ferrihydrite lattices on air reoxidation of chemically precipitated Fe(II)–Tc(IV) phases and that the Tc(IV) in these systems is

resistant to reoxidation because of this intimate association with the reoxidation products (Zachara et al., 2007). Indeed, the amorphous Fe(II) phase described here may be undergoing a similar “armouring” process, and certainly Tc(IV) reoxidation is hindered in this Fe(II) phase in both air and nitrate reoxidation systems. The observations on the amorphous Fe(II) systems are in contrast to the reduced Humber estuarine sediments that were reoxidised with air and  $\text{NO}_3$  and the reduced FRC aquifer sediments that were reoxidised with  $\text{NO}_3$  where both Tc(IV) and Tc(VII) phases were seen associated with the reoxidised solids. This suggests that caution should be applied when choosing sediment analogs to study the redox cycling behaviour of Tc and that Tc fate on reoxidation of sediments will be site specific.

#### 4. Conclusions

It is clear that at the elevated concentrations of Tc required for XAS, in a range of estuarine, aquifer and freshwater sediments and in an amorphous Fe(II) phase,  $\text{TcO}_4^-$  is reduced to hydrous  $\text{TcO}_2$ -like phases with variable ordering through either microbially-mediated or abiotic reduction with Fe(II). This interpretation is supported by the similar EXAFS modelling fits for first shell interactions and XANES spectra across all reduced samples. For EXAFS analysis, the variability between spectra particularly between 6 and  $8 \text{ \AA}^{-1}$  suggested varying degrees of order in the Tc(IV) precipitates between different samples, although when modelling EXAFS a second shell of 1 Tc at ca.  $2.5 \text{ \AA}$  significantly improved the fit in all samples supporting the evidence for hydrous Tc(IV)-like phases bonded to O across the range of samples. On reoxidation of sediments containing hydrous  $\text{TcO}_2$ -like phases, in the reduced Humber estuarine sediments reoxidised with air and  $\text{NO}_3$  and in the FRC aquifer sediments reoxidised with  $\text{NO}_3$  both Tc(VII) and Tc(IV) were observed in association with the solid phase using both EXAFS and XANES approaches. Interestingly, in all the  $\text{NO}_3$ -reoxidised sediments, high levels of  $\text{TcO}_4^-$  (30–50%) were associated with sediments even though minimal (<8%) remobilisation of Tc(VII) to solution had occurred over the reoxidation period. This suggests that, in these systems when significant  $\text{NO}_3$ -mediated oxidation of sediments is occurring and even with Fe(II) oxidation occurring in vast molar excess to Tc, that Tc can be recalcitrant to remobilisation under  $\text{NO}_3$  reoxidising conditions.

In the case of air-reoxidised sediments, significant remobilisation of Tc to solution mediated by reoxidation of Tc(IV) to Tc(VII) occurred over the duration of the experiments and both Tc(IV) and Tc(VII) were present in air oxidised Humber sediments. Clearly, the biogeochemistry of the sediments influences the final fate of Tc on reoxidation. This warrants further study to ascertain the mechanism(s) of reoxidation of Tc and the nature of the mixed hydrous  $\text{TcO}_2/\text{TcO}_4^-$  species observed in selected sediments analysed here.

In the FRC aquifer and Dounreay freshwater sediment samples reoxidised with air, and on both air and microbially-mediated  $\text{NO}_3$  oxidation of an amorphous Fe(II) phase, only Tc(IV) (as hydrous  $\text{TcO}_2$ -like phases) was observed in the reoxidised solid material. The mechanism of retardation of Tc(IV) reoxidation remains unexplained in these systems but may be due to armouring of Tc(IV) by its incorporation into Fe(III) phases formed on reoxidation similar to those seen by Zachara et al. (2007). These observations suggest that Fe(II) bearing mineral phases alone may not always be appropriate analogs for reduced sediments when considering Tc redox cycling behaviour and that site specific studies are necessary. Overall, the mechanisms leading to sediment bound Tc(VII) and Tc(IV) in selected sediments on reoxidation and only Tc(IV) on air reoxidation of the freshwater sediments and both air and  $\text{NO}_3$  reoxidation of the amorphous Fe(II) phase are as yet unclear. Nonetheless, XAS has provided direct insights into the complex biogeochemical redox cycling behaviour of Tc. These observations are directly relevant to “near field” radioactively contaminated environments such as those found at nuclear facilities like Hanford which has abnormally high concentrations of Tc (Lukens et al., 2002). Additionally, the XAS samples generally behaved in a similar way to parallel experiments run at lower ( $\mu\text{mol L}^{-1}$ ) concentrations (Burke et al., 2005, 2006; McBeth et al., 2007; Begg et al., 2007) giving confidence that these XAS observations have relevance to lower level environmental scenarios.

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