

Technetium reduction and reoxidation behaviour in Dounreay soils

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Summary. Technetium is a radioactive contaminant found in groundwaters at sites where nuclear wastes have been processed or stored. The redox chemistry of technetium is a major control on its environmental mobility. Under oxic conditions, technetium exists as the pertechnetate ion, Tc(VII)O_4^- , which is poorly sorbed by minerals across a wide range of environmentally relevant pH values. Under reducing conditions pertechnetate is converted to lower valency species, of which Tc(IV) tends to predominate. Typically, the Tc(IV) oxidation state readily precipitates as insoluble hydrous Tc(IV) oxides or, at low concentrations, is removed from solution by association with mineral surfaces. Here, we present novel X-ray absorption spectroscopy (XAS) data examining Tc associations with reduced Dounreay soils. In reduced unamended microcosms and in microcosms where we added the co-contaminants ethylenediaminetetraacetic acid (EDTA) or bicarbonate to investigate their effect on Tc biogeochemistry, Tc was removed from solution on exposure to the reduced sediments and was present on solids as hydrous Tc(IV) O_2 -like phases. Furthermore, to investigate the long term stability and remobilization of solid phase associated Tc in reduced soils, we reoxidized reduced, Tc(IV)-labeled soils, in the presence of air and nitrate. The extent of remobilization of Tc to solution was dependent on the oxidant used. After reoxidation with air for 60 d, $42 \pm 6\%$ of the initial soil bound Tc was resolubilized. In the presence of 25 or 100 mmol L^{-1} nitrate as an oxidant, negligible microcosm reoxidation or remobilization of Tc to solution occurred. XAS analysis of soils treated with the two oxidants showed that in both systems, the remaining soil associated Tc was present as hydrous Tc O_2 -like phases. The recalcitrance of Tc remobilization under reoxidizing conditions has implications for the fate of Tc in contaminated environments.

Introduction

Technetium-99, a beta emitting radionuclide with a long half life (2.1×10^5 y), is a contaminant of key concern in the nuclear fuel cycle. It is highly mobile under oxic conditions as Tc(VII)O_4^- but relatively immobile under reducing conditions where the Tc(IV) oxidation state predominates [1, 2]. Bioreduction, whereby the growth of indigenous bacteria

is stimulated *via* electron donor addition to radioactively contaminated sub-surface environments to engineer immobilization of radionuclides has been explored in relation to Tc behaviour (*e.g.* [3]). Accordingly, robust reductive sorption of TcO_4^- to reduced, predominantly Tc(IV) phases has been observed in a range of different environmental matrices as bioreduction develops [4–10]. To further understand the biogeochemistry of Tc and to assess the validity of this proposed bioremediation approach it is important to understand the long-term fate of the immobilized radionuclides as redox cycling occurs. For example, air reoxidation may result after disturbance of anoxic sediments and exposure to oxygenated conditions, while microbially mediated nitrate reoxidation is likely to be important due to the presence of NO_3^- at very high levels as a co-contaminant at nuclear fuel cycle sites [10]. Indeed, the addition of both air and nitrate into Tc(IV)-labeled anoxic sediment systems has been shown to reoxidize reduced sediments and to remobilize sediment associated Tc to a variable degree [10, 11].

In microcosm experiments using soil representative of the nuclear site at Dounreay, UK, we have observed the microbially mediated removal of Tc(VII) from solution as Fe(III)-reducing conditions developed [9]. Here, we report X-ray absorption spectroscopy (XAS) characterization of the fate of Tc in unamended reduced soils, and in reduced soils in the presence of two potential co-contaminants commonly found at nuclear facilities: ethylenediaminetetraacetic acid (EDTA); and bicarbonate. Additionally, to understand the redox cycling behaviour of Tc in reduced systems, we describe reoxidation experiments with unamended reduced soils. Reduced soils which had been spiked with low levels of Tc and incubated until Fe(III)- or sulfate- reducing conditions dominated, were reoxidized with either air or nitrate and a suite of biogeochemical redox indicators monitored. A limited set of reoxidation experiments at higher Tc concentrations was also carried out to allow XAS characterization of the fate of Tc in air and nitrate reoxidized Dounreay soils.

Materials and methods

Soil and groundwater

Soil was collected from close to the UKAEA Dounreay site (LAT: 58° 34' 40" N, LONG: 3° 44' 50" W) in January 2005.

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The soil was sampled from a depth of 5 cm below the surface into sterile plastic containers and stored at 4 °C prior to use in microcosms. The soil has been characterized as a sandy loam with quartz, feldspars, chlorite and mica as the dominant minerals [9]. For microcosm experiments we equilibrated the soil with an artificial groundwater representative of the Dounreay site (pH 5.1; Ca²⁺ 2.5 mmol L⁻¹; Mg²⁺ 1 mmol L⁻¹; K⁺ 0.13 mmol L⁻¹; Cl⁻ 6.4 mmol L⁻¹; SO₄²⁻ 0.42 mmol L⁻¹; [9]) under various conditions (see below).

X-ray absorption spectroscopy on reduced soils

Experiments were performed at high Tc concentrations (*ca.* 750 μmol L⁻¹) to allow XAS analysis. For bioreduced systems, microcosms (0.5 g soil, 5 mL solution) containing pre-reduced, sulfate-reducing Dounreay soil incubated for 9 months in the presence of: (a) unamended groundwater; (b) carbonate amended groundwater (10 mmol L⁻¹ bicarbonate); and (c) EDTA amended groundwater (0.2 mmol L⁻¹ EDTA), were prepared and then spiked with ~ 750 μmol L⁻¹ ammonium pertechnetate and equilibrated for 65 d under anoxic conditions. Tc labeled solid phases were then separated by centrifugation under anaerobic conditions (10 min, 15000 g) and XAS data collection and analysis on solids undertaken as described in previous studies [7, 10–12].

Low level reoxidation experiments

A number of reoxidation experiments were carried out using unamended, bioreduced soils. Unamended soil microcosms containing 12 g soil and 120 mL artificial groundwater were made up in sterile glass serum bottles. The microcosms were spiked with a stock solution of TcO₄⁻ at 3.2 × 10⁻⁷ mol L⁻¹ (20 Bq mL⁻¹), sealed with butyl rubber stoppers and aluminium crimps, and incubated anaerobically at 21 °C in the dark. Microcosms were incubated for either 90 d or 9 months. At this time, the extent of bioreduction was assessed by using a 0.5 N HCl chemical extraction technique to monitor the ratio of “bioreduced” Fe(II) to “bioavailable” Fe(III) in the solids [13]. Predominantly Fe(III)-reducing soils were characterized as containing ~ 40% of the total bioreduced iron in the sediment as reduced Fe(II). Sulfate reducing sediments were characterized by a high bioreduced Fe(II) ingrowth (> 70%–85%) and with > 98% of the sulfate originally in the oxic groundwater removed from solution, presumably due to reductive precipitation to sulfide as bioreduction proceeded. These pre-reduced Fe(III)-reducing and sulfate-reducing sediments labeled with low levels of Tc were then subject to reoxidation with air and nitrate. Air reoxidation experiments were performed in duplicate by supplying air to 120 mL of the Fe(III)- and sulfate-reducing radiolabeled soil slurries in a 500 mL conical flask capped with a porous bung and kept at 21 °C in constant motion (125 rpm) on an orbital shaker. Periodically, small volume (3 mL) samples were withdrawn and geochemical analyses were undertaken (see below).

Nitrate reoxidation experiments were performed in triplicate in sealed microcosm bottles and nitrate concentrations were chosen to reflect the elevated concentrations found at nuclear facilities [10]. Microcosms containing reduced, microbially active Tc radiolabeled soils (12 g soil; 120 mL

groundwater) were amended with a deoxygenated KNO₃ solution to a final NO₃⁻ concentration of 25 mmol L⁻¹ in Fe(III)-reducing, and 100 mmol L⁻¹ in sulfate-reducing systems. Sterile controls were established by autoclaving at 120 °C for 20 minutes prior to spiking with nitrate. The microcosms were incubated in the dark at 21 °C for 60 d with periodic sampling. At sample points, approximately 3 mL of soil slurry was withdrawn and centrifuged (7 min, 15000 g). The supernatant was then analyzed for a series of geochemical indicators (see below).

X-ray absorption spectroscopy on reoxidized soils

Two soil reoxidation samples were prepared for XAS characterization using unamended sulfate-reducing soils, (i) air reoxidation and (ii) nitrate reoxidation. The reduced soils (0.5 g to 5 mL unamended groundwater) were equilibrated with ~ 750 μmol L⁻¹ ammonium pertechnetate for 65 d. After this time, reoxidation was performed either by daily injection of air into the headspace of the microcosm for 49 d or by addition of deoxygenated KNO₃ to give a final concentration of 100 mmol L⁻¹ NO₃⁻ and incubation under anaerobic conditions for 49 d. The soils were then prepared for XAS and analyzed as previously described [7, 10–12].

Geochemical analyses

The supernatants from low level reoxidation experiments were analyzed for a series of geochemical indicators: pH and *E_h*; total Tc; Cl⁻, NO₃⁻, NO₂⁻, SO₄²⁻ and total dissolved Fe. Ingrowth of bioreduced Fe(II) to soils was monitored as the percentage of Fe(II) to total Fe following extraction in 0.5 N HCl for 60 min and spectrophotometric assay (see above) [13].

Results and discussion

XAS analysis of reduced soils

In XAS experiments where pre-reduced unamended, carbonate amended and EDTA amended soil microcosms were exposed to TcO₄⁻, > 99.5% removal of Tc from solution occurred after 65 d which paralleled Tc behaviour in low level experiments [9]. Additionally, solid phase Fe(II) had ingrown to > 95% in all three systems and the microcosms were black in colour suggesting that Fe(III)-reducing conditions were largely complete and that sulfate reducing conditions were beginning to predominate. For the solid phase associated Tc in these reduced systems, we were then able to characterize the fate of Tc by using Extended X-Ray Absorption Fine Structure (EXAFS). A summary of the background subtracted, normalized and *k*³ weighted EXAFS spectra, together with the Fourier transforms corresponding to the best fits are described in Table 1, and are plotted in Fig. 1 for experimental and model data. In all samples, EXAFS spectra were very similar in appearance but with clear variability between 6–8 Å⁻¹, suggesting similar but non-identical local environments for the Tc(IV) associated with these bioreduced soils. The EXAFS data were fitted by an inner shell of 6O backscatters at approximately 2.00 Å which is characteristic of

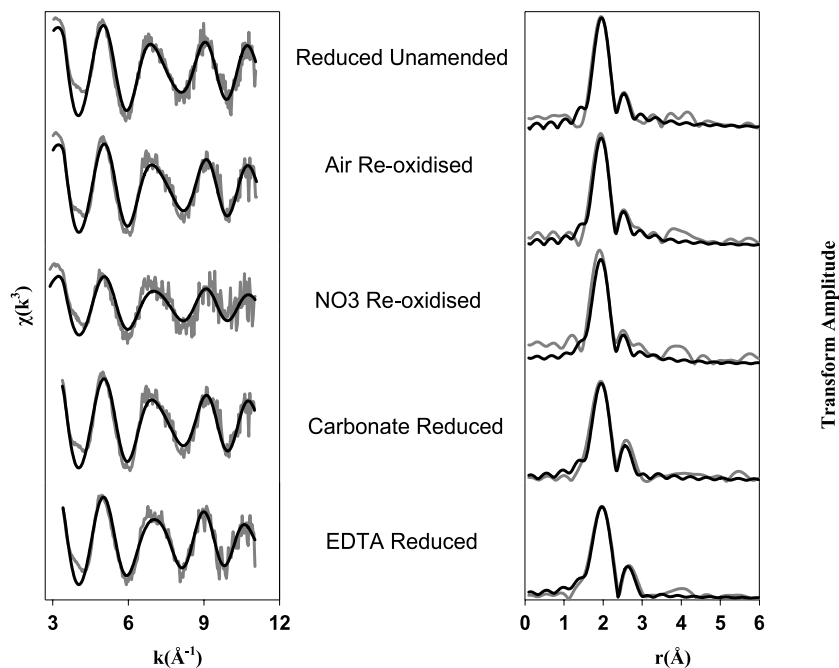


Fig. 1. Background-subtracted, normalized, and k^3 -weighted ^{99}Tc K-edge EXAFS spectra (left) and corresponding Fourier transform (right) obtained for reduced unamended; reduced carbonate-amended; reduced EDTA amended; unamended air reoxidized; and unamended nitrate reoxidized Dounreay soil microcosms for the best modeled fit described in Table 1. Grey lines are the experimental data; black lines are the best modeled fit.

Table 1. Summary of EXAFS modeling results for: reduced unamended; reduced carbonate amended; reduced EDTA amended; unamended air reoxidized; and unamended nitrate reoxidized Dounreay soil microcosms. N is the occupancy ($\pm 25\%$), r is the interatomic distance (± 0.02 Å for the first shell, ± 0.05 Å for outer shells), $2\sigma^2$ is the Debye–Waller factor ($\pm 25\%$) and R is the normalized least squares residual (%).

Sample	Shell	N	Type	r (Å)	σ^2	R
Reduced unamended	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	
Reduced carbonate	1	6	O	2.00	0.012	42.5
	1	6	O	1.99	0.012	33.7
	2	1	Fe	2.66	0.008	
	1	6	O	2.00	0.012	34.0
	2	1	Tc	2.49	0.012	
Reduced EDTA	1	6	O	2.00	0.012	39.3
	1	6	O	2.00	0.013	33.2
	2	1	Fe	2.71	0.009	
	1	6	O	2.00	0.013	33.4
	2	1	Tc	2.53	0.012	
Air reoxidized	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	
NO_3^- reoxidized	1	6	O	1.99	0.013	57.2
	1	6	O	1.99	0.013	53.0
	2	1	Fe	2.68	0.010	
	1	6	O	2.00	0.013	52.8
	2	1	Tc	2.48	0.015	

hydrated Tc(IV) oxides coordinated in an octahedral environment [14, 15]. This is consistent with previous work modeling the speciation of Tc associated with reduced sed-

iments [7, 10, 12] and demonstrates the formation of hydrated Tc(IV)O_2 -like phases when TcO_4^- is exposed to pre-reduced Dounreay soils in unamended, carbonate- and EDTA-amended systems. Interestingly, when a second shell of 1 Tc at *ca.* 2.5 Å or 1 Fe at *ca.* 2.7 Å was modeled, this significantly improved the fits for all samples although it was impossible within the constraints of the analytical technique to define which of the second shell backscatters was actually present. To our knowledge these are the first direct, spectroscopic observations that TcO_4^- reduction in the presence of reduced, natural soils amended with high levels of the co-contaminants EDTA and carbonate leads to formation of poorly soluble hydrated TcO_2 -like phases. Overall, this confirms that microbially mediated reductive sorption of Tc is occurring in these systems, even in the presence of potential complexants. This is in agreement with recent experimental work suggesting that EDTA [9, 16] and carbonate [9] are poor solubilisers of Tc(IV) in the presence of soil surfaces under environmental conditions.

Air reoxidation results

In low level, unamended air reoxidized systems that were initially Fe(III) -reducing, there was remobilization of a significant fraction of soil bound Tc to solution from $9 \pm 5\%$ of the original spike at $t = 0$ to $45 \pm 1\%$ by 60 d (Fig. 2a), presumably *via* oxidation to Tc(VII) , of the type observed in other systems [10, 11, 17]. In experiments that were originally sulfate-reducing, both stable element and Tc behaviour was broadly similar to the Fe(III) -reducing system but with the initial rate of Tc remobilization somewhat slower than the Fe(III) -reducing system (Fig. 2a). Overall, the rate of Tc remobilization in these experiments is similar to that observed after air reoxidation in both reduced estuarine sediments [11] and in mixed $[\text{Fe(II)}/(\text{III})]/\text{Tc(IV)}$ reduced phases [17]. In both Fe(III) - and sulfate-reducing systems the amount of 0.5 N HCl extractable soil-associated Fe(II)

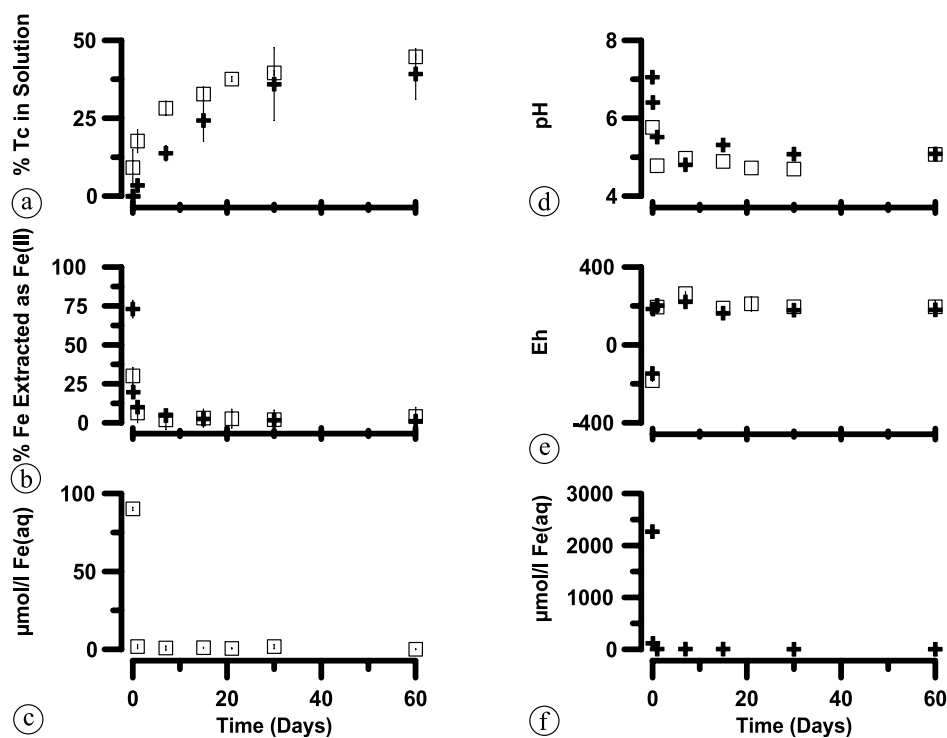


Fig. 2. Remobilization of Tc to solution and change in redox indicators during air reoxidation of initially iron-reducing (□) and initially sulfate-reducing (+) unamended Dounreay soils containing Tc. Error bars are the range of duplicate results.

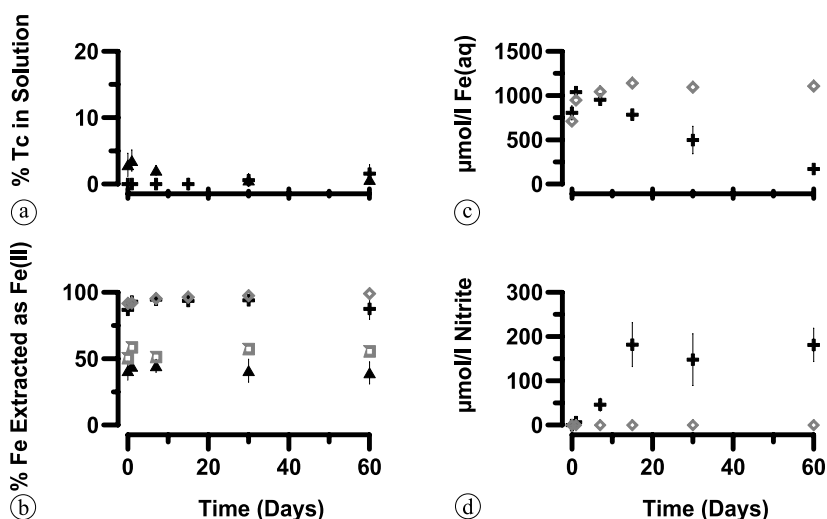


Fig. 3. Remobilization of Tc to solution and change in redox indicators during nitrate reoxidation of: microbially active, unamended Fe(III)-reducing soils ($25 \text{ mmol L}^{-1} \text{ NO}_3^-$) (▲); sterile, unamended Fe(III)-reducing soils ($25 \text{ mmol L}^{-1} \text{ NO}_3^-$) (□); microbially active unamended sulfate-reducing soils ($100 \text{ mmol L}^{-1} \text{ NO}_3^-$) (+) and sterile, unamended sulfate-reducing soils ($100 \text{ mmol L}^{-1} \text{ NO}_3^-$) (◇). Error bars are 1 σ of triplicate results.

declined very quickly with $\sim 80\%$ of the original Fe(II) inventory reoxidized within 1 d and $> 90\%$ reoxidized after 7 d in both cases (Fig. 2b). Total iron in solution also fell rapidly, most likely due to reoxidation of soluble Fe(II) to poorly soluble Fe(III) over 1 d (Figs. 2c and 2f). There was an initial fall in pH from 5.7 to 4.9 and 7.1 to 5.5 after one day in Fe(III)- and sulfate-reducing systems respectively (Fig. 2d) presumably linked to hydrolysis of Fe *via* oxidative precipitation of Fe(III) phases. The E_h in both systems increased rapidly after one day of oxidation with values well above the theoretical Tc(VII)/Tc(IV) couple at pH 7 of *ca.* +20 mV [11] (Fig. 2e). This suggests that at equilibrium Tc would be present as soluble Tc(VII) species on air reoxidation. Nonetheless, despite elevated E_h values and clear evidence for substantial Fe(II) oxidation in the air reoxidized microcosms, Tc remobilization was only 40%–45% at 60 d in reoxidized Fe(III)- and sulfate-reducing systems. This recalcitrance to reoxidation may be explained by ki-

netic inhibition of Tc(IV) reoxidation to Tc(VII) [17, 18] and/or by inhibition of Tc release to solution *via* “armouring” of Tc(IV) from molecular oxygen by precipitation of Fe(III) phases [17].

EXAFS data for the parallel air reoxidized system were fitted by an inner shell of 6 O backscatterers at approximately 2.00 \AA indicating that hydrous Tc(IV) O_2 -like phases which were originally formed during microbial reduction, dominate the soil bound Tc that is recalcitrant to oxidative remobilization (Fig. 1; Table 1). The retention of Tc(IV) as hydrous Tc O_2 -like phases in these soils was similar to that observed for Tc associated with reoxidized-mackinawite (FeS) [19], -green rusts (mixed Fe(II)/Fe(III) hydroxides) [20], an amorphous -Fe(II)-rich gel [12] and -aquifer sediments [10] that were exposed to air. However, this is in contrast to the solid phase associated, mixed Tc(VII)/Tc(IV) phase observed in air reoxidized, estuarine sediments [11].

Nitrate reoxidation

No significant remobilization of technetium to solution was seen in Fe(III)-reducing microcosms amended with 25 mmol L⁻¹ nitrate throughout the experiment (Fig. 3a). Similarly, there was no oxidation of 0.5 N HCl extractable Fe(II) in soils (Fig. 3b) or decline in total Fe in solution suggesting that microbially mediated oxidation was not occurring in this system. In the absence of a clear geochemical signal for reoxidation it appears that microbially mediated NO₃⁻ reoxidation of Fe(II) of the type previously observed in mineral phases, freshwater and estuarine sediments [10, 11, 21, 22] and which leads to formation of NO₂⁻ [21], is not fully active in these systems. In sulfate-reducing microcosms spiked with 100 mmol L⁻¹ NO₃⁻, no significant change in solution technetium concentration was observed during the experiment (Fig. 3a). Similarly, the percentage of 0.5 N HCl extractable Fe(II) in soils showed no change (Fig. 3b). Interestingly however, the concentration of total iron in solution declined from 800 ± 80 μmol L⁻¹ at *T* = 0 to 170 ± 30 μmol L⁻¹ by the end point suggesting that low-levels of Fe(II) bio-oxidation were occurring in the microbially active experiment (Fig. 3c). Despite the lack of significant decline in NO₃⁻ values in these microcosms, the accumulation of measurable NO₂⁻ in porewaters (Fig. 3d) as Fe_(aq) values fell suggests that microbially mediated NO₃⁻ reduction coupled to Fe²⁺ oxidation may have occurred at very low levels in these systems. Overall, even though there was some evidence for minor Fe(II) bio-oxidation in the reoxidized sulfate-reducing system, no significant remobilization of Tc to solution was observed. Additionally, it is unclear why these microcosms did not develop robust, microbially mediated NO₃⁻ reduction and Fe(II)-oxidation which has been observed in a range of sediment systems [11, 12, 22]. EXAFS data for parallel experiments where sulfate-reducing soils were reoxidized with 100 mmol L⁻¹ nitrate were fitted with an inner shell of 6 O backscatterers at approximately 2.00 Å with a single atom of either Tc at 2.50 Å or Fe at 2.7 Å. Again this suggested that hydrous Tc(IV)O₂-like phases predominate in the nitrate spiked soils (Fig. 1; Table 1). Overall, nitrate was a poor oxidant in these microcosms presumably due to the lack of relevant microbial activity in these systems and unsurprisingly, EXAFS showed that Tc was present in similar hydrous TcO₂-like phases that were observed in the reduced, unamended soils.

Summary

In microcosm experiments containing unamended Dounreay soil, and in carbonate- and EDTA-amended microcosms, Tc(VII) was removed from solution during the development of microbially reducing conditions [9]. In this study, we describe XAS results from parallel samples in microbially reduced unamended, carbonate- and EDTA-amended microcosms. In all of these reduced soil systems, formation of hydrous Tc(IV)O₂-like phases occurred on bioreduction. In low level air reoxidation experiments with Fe(III)- and sulfate-reducing soils labeled with Tc(IV), only partial oxidative remobilization of Tc occurred over 60 d de-

spite near complete reoxidation of solid phase Fe(II). XAS characterization of these sediments confirmed that Tc associated with soils after air reoxidation was present as hydrous Tc(IV)O₂-like phases. In the presence of nitrate as an oxidant in pre-reduced Fe(III)- and sulfate-reducing soils, there was evidence only for very minor Fe(II) bio-oxidation and only in the sulfate-reducing system. The lack of any significant oxidative remobilization of Tc in these systems is therefore unsurprising. The differences in the biogeochemistry and associated speciation of Tc in these experiments compared to other studies illustrates the difficulties in identifying key factors controlling the redox cycling behaviour of Tc(IV) in complex soil systems and reinforces the need for site specific studies. Nonetheless, results from this work do indicate that sorbed Tc(IV) will remain solid associated in Dounreay soils provided aerobic oxidation is avoided.

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References

- Bondietti, E. A., Francis, C. W.: Geologic migration potentials of technetium-99 and neptunium-237. *Science* **203**, 1337 (1979).
- Lloyd, J. R., Sole, V. A., van Praagh, C. V. G., Lovley, D. R.: Direct and Fe(II)-mediated reduction of technetium by Fe(III)-reducing bacteria. *Appl. Environ. Microbiol.* **66**, 3743 (2000).
- Lloyd, J. R., Renshaw, J. C.: Bioremediation of radioactive waste: radionuclide-microbe interactions in laboratory and field-scale studies. *Curr. Opin. Biotechnol.* **16**, 254 (2005).
- Fredrickson, J. K., Zachara, J. M., Kennedy, D. W., Kukkadapu, R. K., McKinley, J. P., Heald, S. M., Liu, C., Plymale, A. E.: Reduction of TcO₄⁻ by sediment-associated biogenic Fe(II). *Geochim. Cosmochim. Acta* **68**, 3171 (2004).
- Istok, J. D., Senko, J. M., Krumholz, L. R., Watson, D., Bogle, M. A., Peacock, A., Chang, Y. J., White, D. C.: *In situ* bioreduction of technetium and uranium in a nitrate-contaminated aquifer. *Environ. Sci. Technol.* **38**, 468 (2004).
- Wildung, R. E., Li, S. W., Murray, C. J., Krupka, K. M., Xie, Y., Hess, N. J., Roden, E. E.: Technetium reduction in sediments of a shallow aquifer exhibiting dissimilatory iron reduction potential. *FEMS Microbiol. Ecol.* **49**, 151 (2004).
- Burke, I. T., Boothman, C., Lloyd, J. R., Mortimer, R. J. G., Livens, F. R., Morris, K.: Effects of progressive anoxia on the solubility of technetium in sediments. *Environ. Sci. Technol.* **39**, 4109 (2005).
- Michalsen, M. M., Goodman, B. A., Kelly, S. D., Kemner, K. M., McKinley, J. P., Stucki, J. W., Istok, J. D.: Uranium and technetium bio-immobilization in intermediate-scale physical models of an *in situ* bio-barrier. *Environ. Sci. Technol.* **40**, 7048 (2006).
- Begg, J. D. C., Burke, I. T., Morris, K.: The behaviour of technetium during microbial reduction in amended soils from Dounreay, UK. *Sci. Total Environ.* **373**, 297 (2007).
- McBeth, J. M., Lear, G., Lloyd, J. R., Livens, F. R., Morris, K., Burke, I. T.: Technetium reduction and reoxidation in aquifer sediments. *Geomicrobiol. J.* **24**, 189 (2007).
- Burke, I. T., Boothman, C., Lloyd, J. R., Livens, F. R., Charnock, J. M., McBeth, J. M., Mortimer, R. J. G., Morris, K.: Reoxidation behavior of technetium, iron, and sulfur in estuarine sediments. *Environ. Sci. Technol.* **40**, 3529 (2006).
- Morris, K., Livens, F. R., Charnock, J. M., Burke, I. T., McBeth, J. M., Begg, J. D. C., Boothman, C., Lloyd, J. R.: An X-ray

- absorption study of the fate of technetium in reduced and re-oxidized sediments and mineral phases. *Appl. Geochem.* **26**, 603 (2008).
13. Lovley, D. R., Phillips, E. J. P.: Availability of ferric iron for microbial reduction in bottom sediments of the freshwater tidal Potomac River. *Appl. Environ. Microbiol.* **52**, 751 (1986).
 14. Almahamid, I., Bryan, J. C., Bucher, J. J., Burrell, A. K., Edelstein, N. M., Hudson, E. A., Kaltsoyannis, N., Lukens, W. W., Shuh, D. K., Nitsche, H., Reich, T.: Electronic and structural investigations of technetium compounds by X-ray absorption spectroscopy. *Inorg. Chem.* **34**, 193 (1995).
 15. Wharton, M. J., Atkins, B., Charnock, J. M., Livens, F. R., Patrick, R. A. D., Collison, D.: An X-ray absorption spectroscopy study of the coprecipitation of Tc and Re with mackinawite (FeS). *Appl. Geochem.* **15**, 347 (2000).
 16. Maset, E. R., Sidhu, S. H., Fisher, A., Heydon, A., Worsfold, P. J., Cartwright, A. J., Keith-Roach, M. J.: Effect of organic co-contaminants on technetium and rhenium speciation and solubility under reducing conditions. *Environ. Sci. Technol.* **40**, 5472 (2006).
 17. Zachara, J. M., Heald, S. M., Jeon, B.-H., Kukkadapu, R. K., Liu, C., McKinley, J. P., Dohnalkova, A. C., Moore, D. A.: Reduction of pertechnetate [Tc(VII)] by aqueous Fe(II) and the nature of solid phase redox products. *Geochim. Cosmochim. Acta* **71**, 2137 (2007).
 18. Cui, D., Eriksen, T. E.: Reduction of pertechnetate in solution by heterogeneous electron transfer from Fe(II)-containing geological material. *Environ. Sci. Technol.* **30**, 2263 (1996).
 19. Livens, F. R., Jones, M. J., Hynes, A. J., Charnock, J. M., Mosselmans, J. F. W., Hennig, C., Steele, H., Collison, D., Vaughan, D. J., Patrick, R. A. D., Reed, W. A., Moyes, L. N.: X-ray absorption spectroscopy studies of reactions of technetium, uranium and neptunium with mackinawite. *J. Environ. Radioact.* **74**, 211 (2004).
 20. Pepper, S. E., Bunker, D. J., Bryan, N. D., Livens, F. R., Charnock, J. M., Patrick, R. A., Collison, D.: Treatment of radioactive wastes: An X-ray absorption spectroscopy study of the reaction of technetium with green rust. *J. Colloid Interface Sci.* **268**, 408 (2003).
 21. Weber, K. A., Picardal, F. W., Roden, E. E.: Microbially catalyzed nitrate-dependent oxidation of biogenic solid-phase Fe(II) compounds. *Environ. Sci. Technol.* **35**, 1644 (2001).
 22. Wilkins, M. J., Livens, F. R., Vaughan, D. J., Beadle, I., Lloyd, J. R.: The influence of microbial redox cycling on radionuclide mobility in the subsurface at a low-level radioactive waste storage site. *Geobiology* **5**, 293 (2007).