Reoxidation behaviour of technetium, iron and sulfur in estuarine sediments.

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This section consists of 11 pages, 3 figures and 3 tables.

Section 1. XAS analysis.

Samples for XAS analysis were prepared at the higher Tc concentrations (250 - 1000 µM) necessary for detection. TcO_4^- was added to small microcosms (~ 10ml total volume containing ~ 5ml sediment slurry) made up of sediments that were already actively Fe(III)- and sulfate-reducing, and left for between 2 and 8 days when >99 % of the technetium had been reductively precipitated as hydrous TcO_2. These sediments were then reoxidised with either nitrate (to a final concentration of 100 mM NO_3^-) or air (by daily injection of air into the headspace). For 5 ml microcosms there was a maximium of ca 300 µ equivalents of electron donor from reduced Fe and sulfur (Table 1) and a maximum of ca 15 µ equivalents of electron donor from reduced Tc; NO_3^- was present at 500 µM and thus would provide 1000 µ equivalents of electron acceptor for reduction to NO_2^- and up to 4000 µ equivalents of electron acceptor for reduction to NH_4^+. Thus in nitrate reoxidation experiments, there was an excess of electron acceptor present. For sulfate-reducing sediments, reoxidation with air occurred for 26 days, at that point 37 % of the Tc had remobilized to solution; reoxidation with 100 mM nitrate occurred for 30 days, at that point 3 % of the Tc had remobilized to solution. For iron-reducing sediments, reoxidation with air occurred for 26 days, at that point 51 % of the Tc had remobilized to solution; reoxidation with 100 mM nitrate occurred for 30 days, at that point 8 % of the Tc had remobilized to solution. Therefore the reoxidation behaviour of both the air and nitrate reoxidation XAS samples was similar to the lower level microcosm experiments.

Tc K-edge spectra were collected in fluorescence mode using a 30 element solid state Ge detector on station 16.5 at the UK CLRC Daresbury SRS operating at 2 GeV with a typical current of 150mA, using a Si(220) double crystal monochromator and focussing optics. The incident beam intensity was detuned to 80% of maximum for harmonic rejection. Data were collected in fluorescence mode with a 30 element solid state Ge detector. Sediment samples were spun down to form a moist pellet and were triple contained in airtight experimental cells for radiological safety and to maintain an oxygen free

system. Experiments were performed at ambient temperature and multiple scans averaged to improve the signal / noise ratio.

Section 2 EXAFS Analysis.

Background subtracted EXAFS spectra were analysed in EXCURV98 using full curved wave theory (1). Phaseshifts were derived from *ab initio* calculations using Hedin-Lundqvist potentials and von-Barth ground states (2). 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, $2\sigma^2$. The data were fitted for each sample by defining a theoretical model and comparing the calculated EXAFS spectrum with experimental data and with published spectra for Tc-compounds (3, 4). For samples with only one Tc-O shell (A, D & E in Table 1) the number of scatterers was fixed at 4 (sample D, Tc-O distance ca. 1.7 Å) or 6 (samples A & E, Tc-O distance ca. 2.0 Å), corresponding to the coordination numbers for Tc(VII) and Tc(IV) respectively. Shells of backscatterers were added around the Tc and by refining an energy correction E_f (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, a least squares residual (the *R*-factor (5)) was minimised. The amplitude factor (or AFAC in EXCURVE 98) was retained as the default of 1 throughout. Shells were only included if the overall fit (R-factor) was reduced by > 5%. For shells of scatterers beyond the inner coordination sphere around Tc, the number of atoms in the shell was chosen as an integer to give the best fit, but not further refined. For the mixed oxidation state samples (B, C, F & G) the number of scatterers, N1, in the shorter oxygen shell (1.7 Å) was also refined, with the number of scatterers in the longer shell (2.0 Å) constrained to equal 6-1.5 x N1.

Section 3. XANES analysis.

After identification of Tc(VI) and Tc(VII) as constituents 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, XANES data were also modeled using least squares fitting of the XANES spectra (21000 - 21200 eV) with linear combinations of the spectra of hydrous TcO_2 and TcO_4 (6, 7; Supporting Information Table 3; Supporting Information Figure 1).

Supporting Information Table 1. Redox ladder for key biogeochemical redox couples in sediment microcosms at pH = 7 (Eh, mV)

Redox Couple	Eh (mV)
[a]O_2 / H_2O	+800
[a]NO_3/N_2	+720
[a]MnO_2/Mn^{2+}	+530
[b]TcO_4^-/ hydrous TcO_2	+20
[a]$Fe(OH)_3$ / Fe^{2+}	0
[a]SO_4^{2-} / H_2S	-200

[a] Data from (8); [b] Calculated for 1 x 10^{-8} mol l^{-1} Tc(VII) / hydrous TcO_2 using data from the Nuclear Energy Agency Database Project, www.nea.fr.

Supporting Information, Table 2.

|	Eh (mV)	pH	Fe (aq) (µM)	% HCl Extractable Fe as $Fe(II)$	HS^- (µM)	NO_3^- (µM)	SO_4^{2-} (mM)
A. Sediment Reduction							
Surface sediment (day 0)	+50 – +164	7.6 – 7.8	0.7 – 1.2	17 – 39	n.d.	119 – 247	14.0 – 19.1
Fe(III)-reducing sediment (day 60)	-112 – -243	7.5 – 7.8	199 – 644	52 – 71	n.d – 0.1	n.d.	13.4 – 19.0
Sulfate-reducing sediment (day 270)	-260 – -347	7.5 - 7.7	520 – 599	96 – 100	0.5 – 6	n.d.	n.d. – 1.2
B. Air Reoxidation							
Fe(III)-reducing sediment (reoxidised for 66 days)	+120 – +259	7.8 – 8.0	1.5 – 3.0	8 – 11	n.d.	n.d.	16.3 – 18.5
Sulfate-reducing sediment (reoxidised for 60 days)	+205 – +225	7.8 – 8.4	n.d. – 5.0	21 – 24	n.d.	n.d.	4.5 - 4.7
C. Nitrate Reoxidation							
Fe(III)-reducing sediment (25 mM NO_3^- for 60 days)	+85 – +184	7.6 – 8.0	2.6 – 4.7	25 – 28	n.d.	19.8 – 21.2	13.0 – 14.2
Sulfate-reducing sediment (100 mM NO_3^- for 60 days)	+121 – +160	7.4 – 7.8	n.d. – 6.2	<0.3	n.d.	80.8 – 83.5	4.9 – 5.5

Supporting Information Table 2. Range of values for geochemical indicators obtained during sediment reduction and reoxidation experiments. (A) Reduction experiments: surface sediment (day 0); Fe(III)-reducing sediment, 60 day reduction; and sulfate-reducing sediment, 270 day reduction; (B) Air reoxidation experiments: Fe(III) and sulfate-reducing sediments after 66 and 60 days reoxidation respectively. (C) Nitrate reoxidation experiments: Fe(III)-reducing and sulfate-reducing sediments after 60 days reoxidation.

| Experiment	Percentage Spectrum A	Percentage Spectrum F	[*]Fit index
A. TcO_4^-	100	-	-
B. NO_3^- (Fe-R)	33	67	0.36
C. AIR (Fe-R)	30	70	0.33
D. NO3- (S-R)	18	82	0.11
E. AIR (S-R)	15	85	0.032
F. S-R	-	100	-

[*] The fit index of the calculated XANES spectra with experimental XANES spectra is defined as Σ $[(I_{obs} - I_{calc})^2]/n$ where n is the number of points in each spectrum.

Supporting Information Table 3. XANES analysis of sediment spectra as linear combinations of "end member" spectra A and F. (A) TcO_4^- solution from air reoxidation of sulfate reducing sediment; (B) Fe(III)-reducing sediment amended with 250 µM Tc, then reoxidised with 100 mM nitrate for 30 days; (C) Fe(III)-reducing sediment amended with 250 µM Tc, then reoxidised with air for 26 days; (D) Sulfate-reducing sediment amended with 250 µM Tc, then reoxidised with 100 mM nitrate for 30 days; (E) sulfate-reducing sediment amended with 250 µM Tc, then reoxidised with air for 26 days; (F) sulfate-reducing sediment amended with 1000 µM Tc**.**
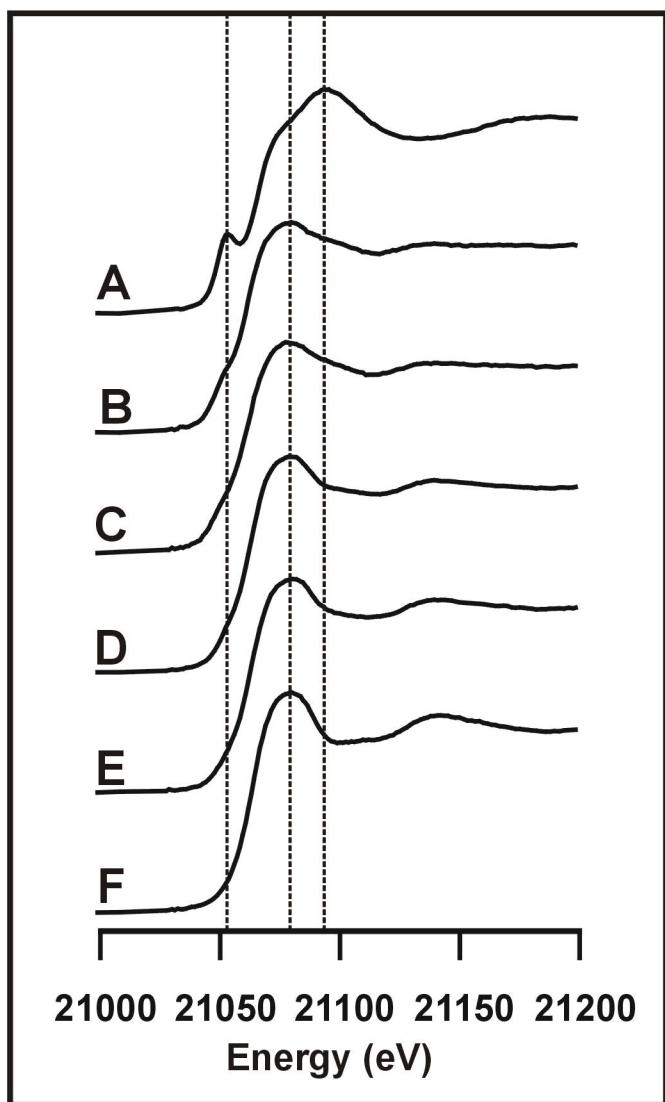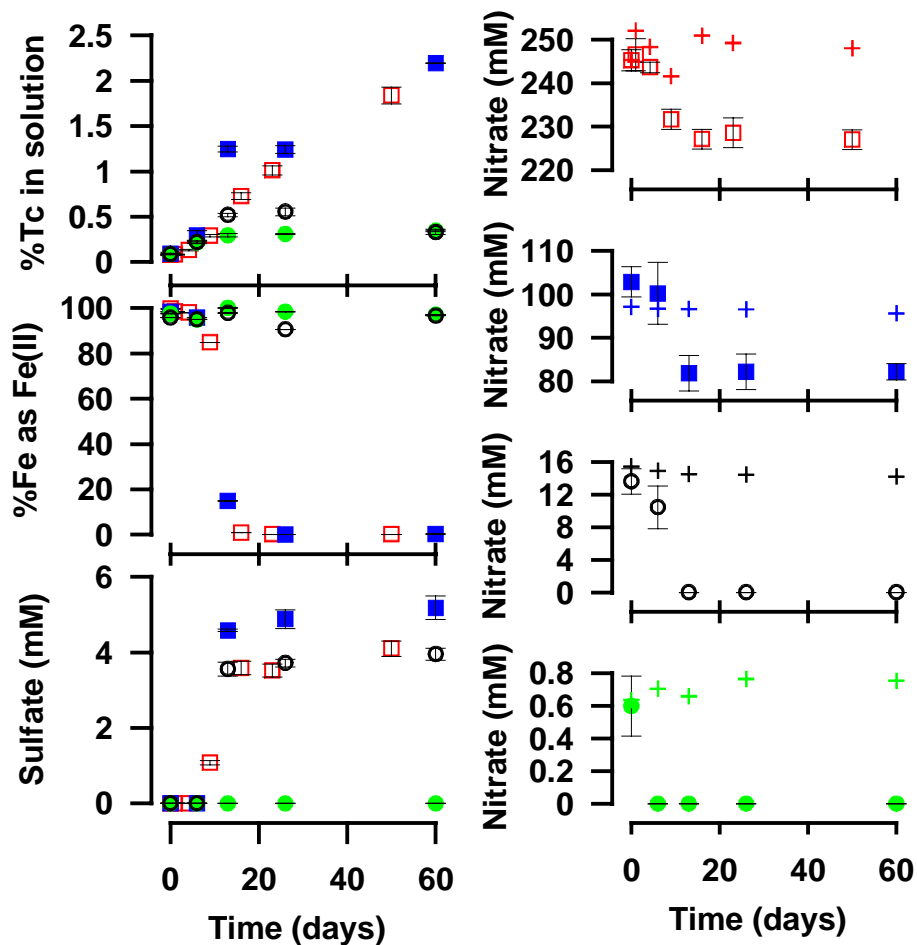
Supporting Information, Figure 1. Normalised Tc-K edge XANES spectra for (from top to bottom) samples: (A) TcO_4^- solution from air reoxidation of sulfate reducing sediment; (B) Fe(III)-reducing sediment amended with 250 μM Tc, then reoxidised with 100 mM nitrate for 30 days; (C) Fe(III)-reducing sediment amended with 250 μM Tc, then reoxidised with air for 26 days; (D) Sulfate-reducing sediment amended with 250 μM Tc, then reoxidised with 100 mM nitrate for 30 days; (E) sulfate-reducing sediment amended with 250 μM Tc, then reoxidised with air for 26 days; (F) sulfate-reducing sediment amended with 1000 μM Tc.
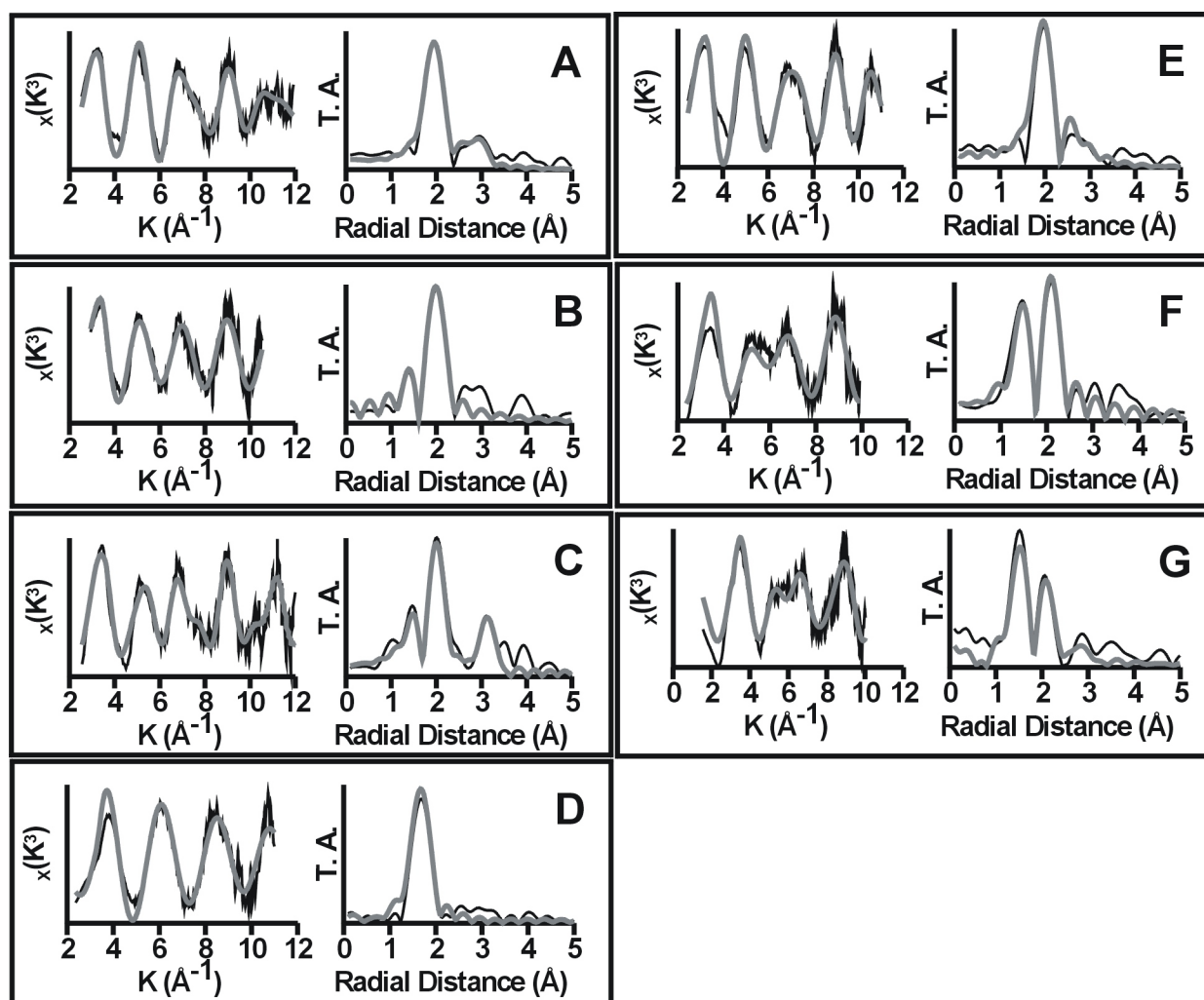
Supporting Information, Figure 2. k^3-weighted Tc K-edge EXAFS spectra and Fourier transforms for: (A). Sulfate-reducing sediments amended with 1000 µM Tc; (B). Sulfate-reducing sediments amended with 250 µM Tc, then reoxidised with air for 26 days; (C). Sulfate-reducing sediments amended with 250 µM Tc, then reoxidised with nitrate for 30 days; (D). Pore-water solution from sulfate-reducing sediments amended with 1000 µM Tc, then reoxidised with air for 42 days; (E). Fe(III)-reducing sediments amended with 1000 µM Tc; (F). Fe(III)-reducing sediments amended with 250 µM Tc, then reoxidised with air for 26 days; (G). Fe(III)-reducing sediments amended with 250 µM Tc, then reoxidised with nitrate for 30 days. The black lines represent experimental data and grey lines represent the best fit using parameters listed in Table 3. T.A. – transform amplitude.

Supporting Information Figure 3. Remobilisation of Tc(VII) to solution and change in redox indicators during the nitrate reoxidation of sulfate reducing sediments with 1 mM (★), 15 mM (▨), 100 mM (⊞) and 250 mM (⊠) sodium nitrate solutions respectively. Sterilised control experiments shown as: (+), (+), (+) and (+) respectively. Error bars show standard deviation of triplicate experiments.

Supporting Information References

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