Supporting Information.

1. X-ray absorption spectroscopy methodology

Three samples at the higher Tc concentrations (~ 1000 μM) necessary for XAS were prepared. At these higher levels, chemical toxicity of Tc was a concern, so we added TcO_4^- to sediments that were already actively Fe(III)- and sulfate-reducing. In addition, in a progressive anoxia experiment, TcO_4^- was added at the high concentration (~1000 μM) prior to active Fe(III)- and sulfate reduction. Surprisingly, microbial reduction proceeded in this sediment albeit at a slow rate, and we were able to obtain a further, biotically reduced, progressive anoxia sediment sample for XAS. 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.

Background subtracted EXAFS spectra were analysed in EXCURV98 using full curved wave theory (1). Phaseshifts were derived from *ab initio* calculations using Hedin-Lundeqvist 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 charaterised 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). Shells of backscatterers were added around the Tc and by refining an energy correction E_f (the Fermi Energy), the absorber-scatterer distance, and the Debye-Waller factor for each shell, a least squares residual (the *R*-factor (5)) was minimised. Shells were only included if the overall fit (R-factor) was reduced by > 5%. For each shell

of scatterers around the Tc, the number of atoms in the shell was chosen as an integer to give the best fit, but not further refined.

Supporting Information Table 1. Major and minor element composition of Humber Estuary sediments - XRF analysis.

Sample	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	Mn_3O_4	MgO	CaO	Na_2O	K_2O	P_2O_5	Cr_2O_3	Total	LOI	Total +
	All results as %												1025 °C	LOI
BF	60.4	0.76	9.7	4.8	0.12	2.0	6.8	1.0	1.9	0.40	0.01	87.9	12.0	99.9
PL	52.0	0.92	13.0	6.1	0.15	2.5	6.7	2.4	2.4	0.36	0.02	86.6	14.6	101.1
SK	45.0	0.96	14.6	6.8	0.14	2.8	7.3	2.5	2.5	0.36	0.02	83.0	17.5	100.5

Sample	Ba	Co	Cr	Cu	La	Nd	Ni	Pb	Rb	Sr	V	Zn	Zr
	All results as ppm												
BF	598	<10	94	<30	28	23	35	85	75	155	90	188	307
PL	512	14	115	<30	35	32	45	97	97	185	123	205	289
C	472	13	123	32	37	39	50	101	110	192	135	216	213

Supporting Information Table 2. Phylogenetic affiliation of distinct RFLP types detected in a 16S rDNA clone library obtained by PCR amplification using broad-specificity primers. Amplification was from a Paull microcosm after 8 days incubation.

RFLP Type	Closest Matching Microorganism (Accession Number)	% Match (Identities)	% Present	Phylogenetic
P8-GEN-7	*Novosphingomonas* sp. ARI-1 (AB070237)	99% (435/438)	2.3%	Alpha Proteobacteria
P8-GEN-8	*Rhodobacter capsulatus* (D16428)	95% (152/159)	2.3%	Alpha Proteobacteria
P8-GEN-24	Alpha proteobacterium P498 (AF414879)	94% (32/34)	2.3%	Alpha Proteobacteria
P8-GEN-11	*Nitrosomonas cryotolerans* (AF272423)	93% (482/516)	2.3%	Beta Proteobacteria
P8-GEN-10	*Pelobacter* sp. (AJ271656)	97% (518/531)	2.3%	Delta Proteobacteria
P8-GEN-28	*Desulfovibrio senezii* (AF050100)	87% (244/278)	2.3%	Delta Proteobacteria
P8-GEN-1	Sulfur-oxidizing bacterium NDII1.1 (AF170424)	90% (461/508)	7.0%	Gamma Proteobacteria
P8-GEN-2	*Lucina nassula* gill symbiont (X95229)	88% (363/410)	7.0%	Gamma Proteobacteria
P8-GEN-3	*Acidithiobacillus ferrooxidans* (AJ459800)	91% (388/423)	2.3%	Gamma Proteobacteria
P8-GEN-4	*Lucina nassula* gill symbiont (X95229)	94% (478/505)	16.3%	Gamma Proteobacteria
P8-GEN-6	*Thiobaca trueperi* (AJ404007)	89% (288/322)	2.3%	Gamma Proteobacteria
P8-GEN-9	*Marinobacter* sp. (AJ292528)	89% (444/495)	7.0%	Gamma Proteobacteria
P8-GEN-12	*Methylomonas* sp. LW13 (AF150792)	91% (376/411)	2.3%	Gamma Proteobacteria
P8-GEN-15	*Methylomicrobium album* (X72777)	92% (413/446)	9.3%	Gamma Proteobacteria
P8-GEN-20	Arsenite-oxidizing bacterium MLHE-1 (AF406554.1)	88% (349/396)	2.3%	Gamma Proteobacteria
P8-GEN-22	*Xylella fastidiosa* strain PE.PLS (AF203392)	92% (473/514)	2.3%	Gamma Proteobacteria
P8-GEN-23	Arsenite-oxidizing bacterium MLHE-1 (AF406554.1)	89% (282/314)	2.3%	Gamma Proteobacteria
P8-GEN-25	*Nevskia ramosa* (AJ001343)	91% (44/48)	2.3%	Gamma Proteobacteria
P8-GEN-26	*Marinobacter lutaoensis* (AF288157)	90% (387/427)	4.7%	Gamma Proteobacteria
P8-GEN-5	*Cytophaga* sp. (AB015532)	94% (480/510)	2.3%	Sphingobacteria
P8-GEN-14	*Cytophaga* sp (AB015525)	94% (365/388)	2.3%	Sphingobacteria
P8-GEN-13	*Prosthecobacter* FC1 (U60012)	95% (407/426)	2.3%	Verrucomicrobiae
P8-GEN-16	*Gyrosigma fasciola* (AF514847)	97% (259/265)	2.3%	Bacillariophyta
P8-GEN-17	*Anaerobranca bogoriae* (AF203703)	86% (249/287)	2.3%	Clostridia
P8-GEN-19	*Flavobacterium* sp. V4.MO.31 (AJ244697)	89% (291/324)	2.3%	Flavobacteria
P8-GEN-27	Uncultured bacterium (X84472)	93% (390/415)	2.3%	Chloroflexi
P8-GEN-29	*Nitrospira* sp. (AF035813)	98% (429/437)	2.3%	Nitrospirales

Supporting Information Table 3. Phylogenetic affiliation of distinct RFLP types detected in a 16S rDNA clone library obtained by PCR amplification, using primers designed to target gene sequences in members of the family *Geobacteracea* (6). Amplification was from a Paull microcosm after 8 days incubation.

RFLP Type	Closest Matching Micro Organism (Accession number)	**%Match (Identities)**	**% Present**	**Phylogenetic Division**
P8-GEO-13	*Caulobacter* species (M83811)	87% (130/148)	2.22%	Alpha Proteobacteria
P8-GEO-7	*Thalassospira lucentensis* (AF358664)	87% (149/171)	2.22%	Alpha Proteobacteria
P8-GEO-1	*Dechloromonas* species SIUL (AJ318917)	98% (320/324)	24.44%	Beta Proteobacteria
P8-GEO-18	*Dechloromonas* species SIUL (AF170356)	91% (300/328)	2.22%	Beta Proteobacteria
P8-GEO-3	*Geobacter chapellei* (U41561)	95% (316/332)	22.22%	Delta Proteobacteria
P8-GEO-5	*Pelobacter acetylenicus* (X70955)	96% (319/332)	2.22%	Delta Proteobacteria
P8-GEO-10	*Pelobacter* species (AJ271656)	85% (149/175)	2.22%	Delta Proteobacteria
P8-GEO-2	*Desulfuromonas michiganensis* (AF357915)	93% (306/326)	4.44%	Delta Proteobacteria
P8-GEO-11	*Desulfuromonas acetexigens* (U23140)	87% (209/238)	2.22%	Delta Proteobacteria
P8-GEO-17	*Desulfuromonas* species (AF019933)	76% (184/239)	2.22%	Delta Proteobacteria
P8-GEO-15	*Desulfuromusa kysingii (*X79414)	88% (201/226)	2.22%	Delta Proteobacteria
P8-GEO-6	*Desulfobacterium anilini* (AJ237601)	88% (234/264)	2.22%	Delta Proteobacteria
P8-GEO-8	*Syntrophus* species (AJ133796)	90% (293/324)	2.22%	Delta Proteobacteria
P8-GEO-9	*Desulfosarcina variabilis* (M34407)	97% (317/324)	13.33%	Delta Proteobacteria
P8-GEO-12	*Olivius algarvensis* Sulfate reducing endosymbiont (AF328857)	95% (241/253)	2.22%	Delta Proteobacteria
P8-GEO-4	*Olivius algarvensis* Sulfate reducing endosymbiont (AF328857)	97% (326/336)	6.66%	Delta Proteobacteria
P8-GEO-16	*Olivius algarvensis* Sulfate reducing endosymbiont (AF328857)	96% (314/327)	2.22%	Delta Proteobacteria
P8-GEO-14	*Thermomonospora chromogena* (AF116559)	95% (166/174)	2.22%	Actinobacteridae

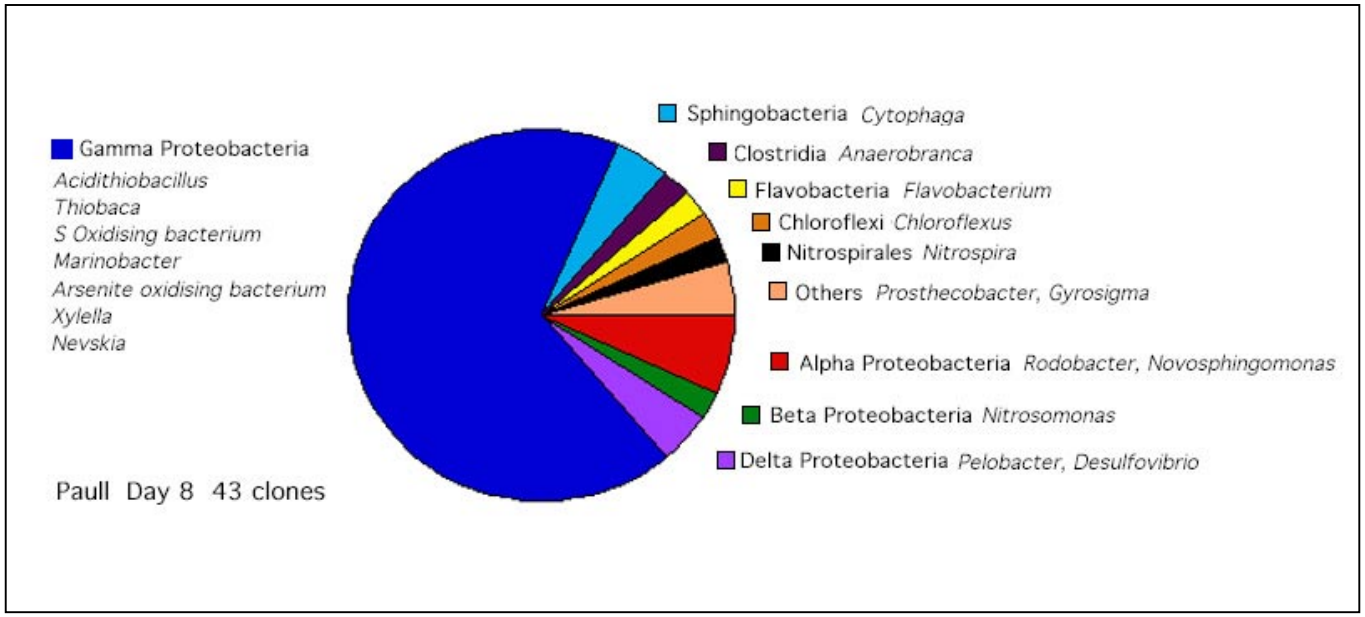
Supporting Information Table 4. Phylogenetic affiliation of distinct RFLP types detected in a 16S rRNA clone library obtained by PCR amplification using broad specificity primers. Amplification was from the lowest dilution Fe(III)-NTA MPN tube scored positive for growth. The MPN series was inoculated with sediment from a Paull microcosm that had been incubated for 8 days.

RFLP Type	Closest Matching micro-organism (Accession number)	% match	%Present	Phylogenetic Division
P8-NTA-1	*Shewanella putrefaciens* (X81623)	94% (492/518)	66.7%	Gamma Proteobacteria
P8-NTA-2	*Shewanella putrefaciens* (X81623)	98% (417/423)	2.1%	Gamma Proteobacteria
P8-NTA-4	*Shewanella putrefaciens* (X81623)	97% (425/435)	2.1%	Gamma Proteobacteria
P8-NTA-3	*Pseudomonas marginalis* strain NZCX27 (AF364098)	99% (512/516)	4.2%	Gamma Proteobacteria
P8-NTA-5	*Klebsiella planticola* strain ATCC 33531T (AF129443)	100% (509/509)	25%	Gamma Proteobacteria

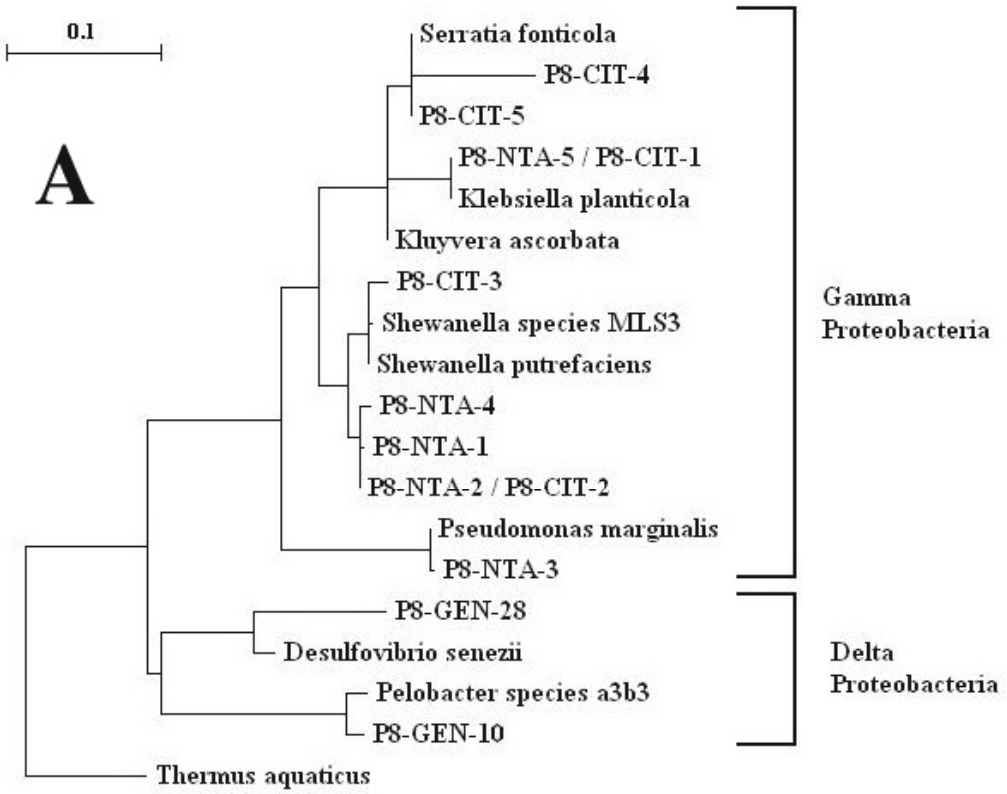
Supporting Information Table 5. EXAFS fits for reduction and reoxidation experiments. (i) Sulfate reducing sediment amended with 1000 μM TcO_4^-; (ii) Iron reducing sediment amended with 1000 μM TcO_4^-; and (iii) progressive anoxia sediment biotically reduced with 1000 μM TcO_4^-. N is the occupancy (± 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 (± 25%), and *R* is the least squares residual.

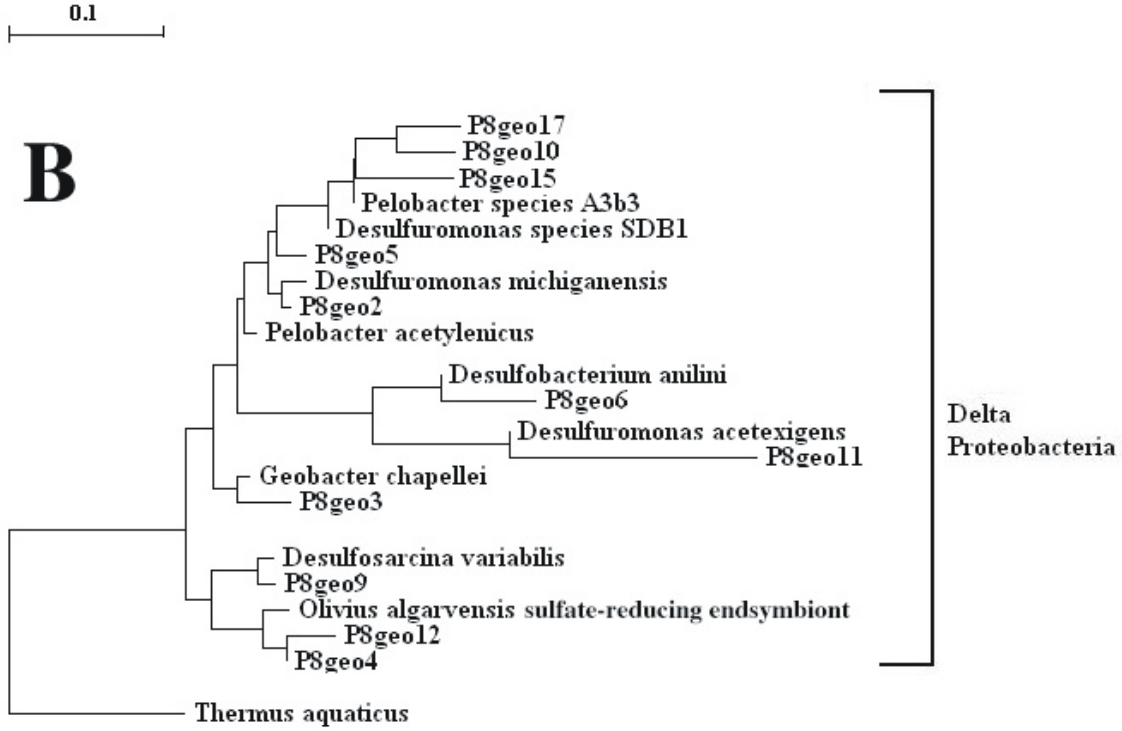
Scatterer	N	r (Å)	$2\sigma^2$ (Å^2)	**R**
(i) O	6	2.00	0.010	30.9
S	1	2.84	0.013	
(ii) O	6	2.00	0.013	42.9
Fe	1	2.72	0.010	
(iii) O	6	2.00	0.015	33.1
Fe	1	2.67	0.006	

Supporting Information Figure 1. Phylogenetic affiliation of distinct RFLP types detected in a 16S rRNA gene clone library obtained by PCR amplification using broad-specificity primers. Amplification was from a Paull microcosm after 8 days incubation. 43 clones were analysed.



Supporting Information Figure 2. A. Phylogenetic tree showing taxonomic affiliations of γ- and δ-Proteobacteria with potential to reduce Fe(III), and by inference Tc(VII) in Paull microcosms. Sequences with codes including CIT or NTA were identified in MPN tubes containing Fe(III)-citrate or Fe(III)-NTA respectively. In some cases the same organism was detected growing in both types of media (e.g. P8-NTA-5 and P8-CIT-1 yielded identical sequences). P8-GEN-28, and P8-GEN-10 were identified in a clone library obtained directly from sediments by PCR amplification of a 500 bp (approx.) portion of the 16S rRNA gene using broad-specificity primers. B. Taxonomic affiliations of 16S rDNA sequences of δ-Proteobacteria with the potential to reduce Fe(III) and Tc(VII), detected by PCR with primers designed to target members of the family *Geobacteraceae*. For both figures (A and B) closest known relatives identified by BLAST searches are included. *Thermus aquaticus* was used as the outgroup. Scale bars represent substitutions per site.


0.1
A
Serratia fonticola
P8-CIT-4
P8-CIT-5
P8-NTA-5 / P8-CIT-1
Klebsiella planticola
Kluyvera ascorbata
P8-CIT-3
Shewanella species MLS3
Shewanella putrefaciens
P8-NTA-4
P8-NTA-1
P8-NTA-2 / P8-CIT-2
Pseudomonas marginalis
P8-NTA-3
P8-GEN-28
Desulfovibrio senezii
Pelobacter species a3b3
P8-GEN-10
Thermus aquaticus
Gamma Proteobacteria
Delta Proteobacteria


0.1
B
P8geo17
P8geo10
P8geo15
Pelobacter species A3b3
Desulfuromonas species SDB1
P8geo5
Desulfuromonas michiganensis
P8geo2
Pelobacter acetylenicus
Desulfobacterium anilini
P8geo6
Desulfuromonas acetexigens
P8geo11
Geobacter chapellei
P8geo3
Desulfosarcina variabilis
P8geo9
Olivius algarvensis sulfate-reducing endsymbiont
P8geo12
P8geo4
Thermus aquaticus
Delta Proteobacteria

Supporting Information References

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