

Supplementary material

Arsenic binding to organic and inorganic sulfur species during microbial sulfate reduction: a sediment flow-through reactor experiment

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Methodology

General methods at the beam-lines

Flash-frozen solid materials were transported to the ESRF in N₂-filled and sealed tubes protected by O₂-free Bio-Bag (BD) chambers over dry-ice. At the beam-lines, O₂-free conditions were achieved using PE disposable glove-bags (Alfa-Aesar) under flowing N₂. The FTR samples were allowed to thaw and were mounted in a 5-position sample holder, sealed with Kapton tape and transferred from the glove-bag to the cryostat over N₂-saturated vapours boiling off a liquid N₂ Dewar. For S K-edge XANES analysis, samples were extensively ground into fine powder using agate mortar and pestle and spread as a thin layer under N₂ to yield a homogeneous particle distribution, all excess being removed to minimise the amount of sample on the S-free XRF tape. The sample was mounted on a sample holder and placed in the H₂-filled sample chamber.

Sequential extraction procedure on FTR samples

The extraction technique was based on a setup comprising PTFE extraction vessels, impingers and tubing, and used ultra-pure N₂ as a carrier gas. It comprised three main steps: (i) the extraction of Fe monosulfides as AVS using HCl 6 N along with 0.1 M ascorbic acid to prevent sulfide re-oxidation, (ii) the extraction of CRS, assumed to be predominantly composed of FeS₂, using HCl 6 N and Cr^{III} activated using Hg-amalgamated Zn mesh and Cr^{VI} and (iii) the extraction of ES by adding both activated Cr^{II} and N,N-dimethylformamide (DMF). During each step, the evolving sulfide gas was captured by 0.1 M NaOH containing traps that were then analysed for sulfide using UV/Vis at 670 nm^[1]; the instrument was

calibrated using sulfide solutions standardised by iodometric titration. For As targeted extraction, freeze-dried sediment was treated with 15 % H₂O₂ and 0.5 M NaOH to oxidise S^{-II} present in the sample.^[2] Total As concentrations in the digests were determined by HG-AFS whereas total Fe was measured by ICP-OES.

Results

Composition of the FTR outflow

Table S1. Average composition of the FTRs outflows during the acclimation (time < 21 days; in parentheses) and the steady-state (time > 35 days) phases

FTR	Inflow	pH	SO ₄ ²⁻	ΣS ^{-II} _(aq)	ΣS ⁰ _(aq)	As ^{III}	As ^V	Fe _(aq)
						(μmol L ⁻¹)		
A	As ^V	(7.1) 6.7	(47) 1.1	(1.9) 11.3	(1.2) 0.9	(2.32) 0.14	(3.02) 0.03	(8.2) 6.0
B	As ^{III}	(6.9) 6.6	(34) 1.3	(0.7) 2.5	(2.3) 1.3	(3.08) 0.65	(1.66) 0.22	(6.7) 5.5
C	As ^V	(7.4) 7.3	(103) 1.8	(4.8) 8.3	(9.8) 3.9	(1.98) 4.08	(5.69) 1.15	(1.6) 1.0
D	As ^{III}	(7.0) 6.5	(132) 3.0	(2.4) 3.7	(7.7) 2.4	(3.40) 4.54	(2.59) 1.79	(1.2) 1.0

As K-edge EXAFS spectra in R-space

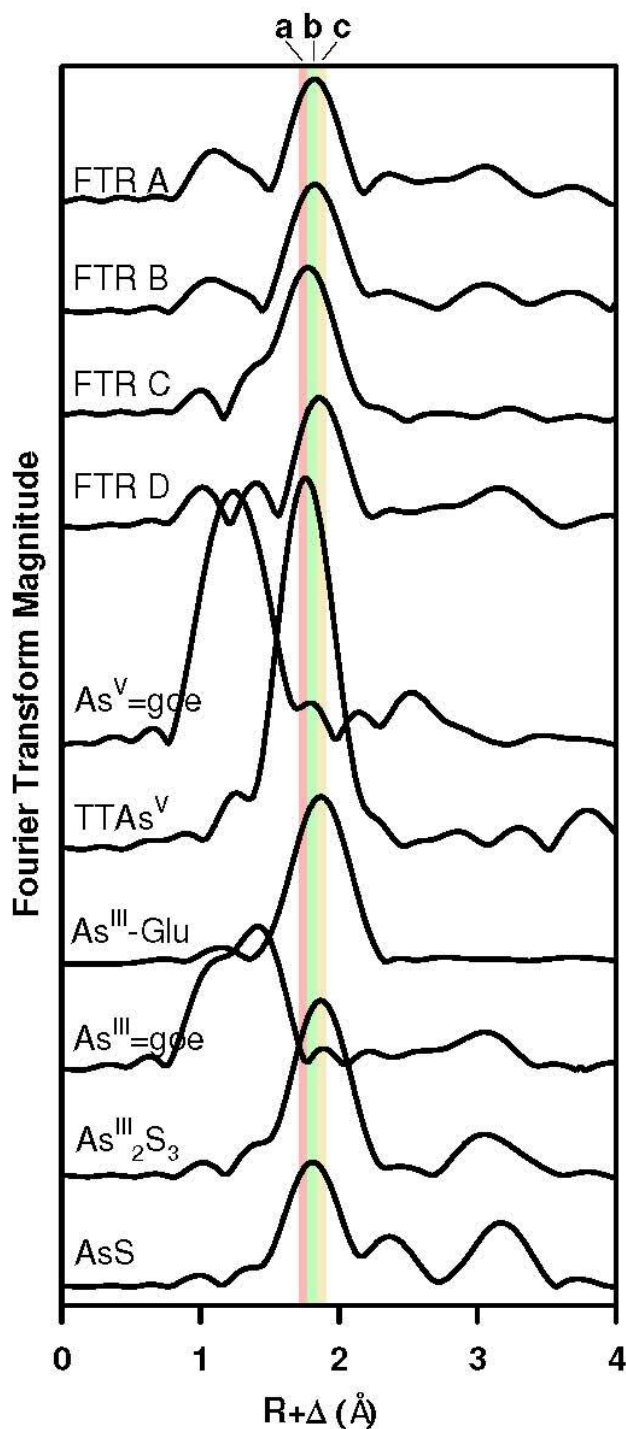


Fig. S1. Radial structure functions (uncorrected for backscattered phase shift) of As K-edge EXAFS spectra for selected reference compounds as well as for the FTR samples. The shaded areas (a–c) respectively indicate the peaks ascribed to the As–S bond distances in T₄TAs^V ($R+\Delta = 1.75$ Å), realgar (1.81 Å) and orpiment (1.85 Å).

Geochemical modelling

Thermodynamic database

The thermodynamic database WATEQ4 imbedded within PHREEQC was updated by including the equilibrium constants for (i) the ionisation of As^{III} and As^{V} oxyacid,^[3] (ii) the sulfidation of As^{III} species^[4] and of As^{V} species,^[5] (iii) As mineral solubility,^[3] (iv) elemental sulfur solubility^[6] and (v) the formation of polysulfide species.^[7]

The concentration of $\text{S}^0_{(\text{aq})}$ must be estimated in order to use the $\text{S}^0_{(\text{aq})}/\text{HS}^-$ redox couple for *pe* calculations. Using the measured values of pH, of $\Sigma\text{S}^0_{(\text{aq})}$ and of $\Sigma\text{S}^{-\text{II}}_{(\text{aq})}$ as input parameters in PHREEQC (Table S1), the concentrations of individual polysulfide species were calculated from the following mass balances and the mass action law equations for the formation of the polysulfide species:

$$\Sigma\text{S}^{-\text{II}}_{(\text{aq})} = [\text{H}_2\text{S}] + [\text{HS}^-] + \Sigma[\text{H}_x\text{S}_n\text{S}^{x-2}] \quad (1)$$

$$\Sigma\text{S}^0_{(\text{aq})} = [\text{S}^0_{(\text{aq})}] + \Sigma n[\text{H}_x\text{S}_n\text{S}^{x-2}] \quad (2)$$

where x (0–2) is the number of H atoms in the polysulfide species $\text{H}_x\text{S}_n\text{S}^{x-2}$ and n (1–7) is the number of zero-valent S atoms in the polysulfide species $\text{H}_x\text{S}_n\text{S}^{x-2}$, and $\text{S}^0_{(\text{aq})}$ is equilibrium concentration of dissolved zero-valent sulfur.

Predicted *pe*

The redox conditions prevailing in the FTRs are reflected by the trends in *pe* values. To determine which redox couple likely controlled the redox potential of the systems, the theoretical *pe* values calculated assuming equilibrium with respect to various redox couples were compared to measured values (Fig. S2). During the beginning of the acclimation phase, the measured *pe* values were lower than any of the calculated *pe* values, which were close to the theoretical values enforced by the $\text{H}_{2(\text{g})}/\text{H}_2\text{O}$ boundary (calculated *pe* ~6 assuming the formation of $\text{H}_{2(\text{g})}$). After the addition of lactate, and in particular towards the end of the experiment, only the *pe* values calculated using the $\text{S}^0/\text{S}^{-\text{II}}$ redox coupled remained within 1 *pe* unit of the measured values, suggesting that this couple may be the effective redox buffer imposing As speciation.

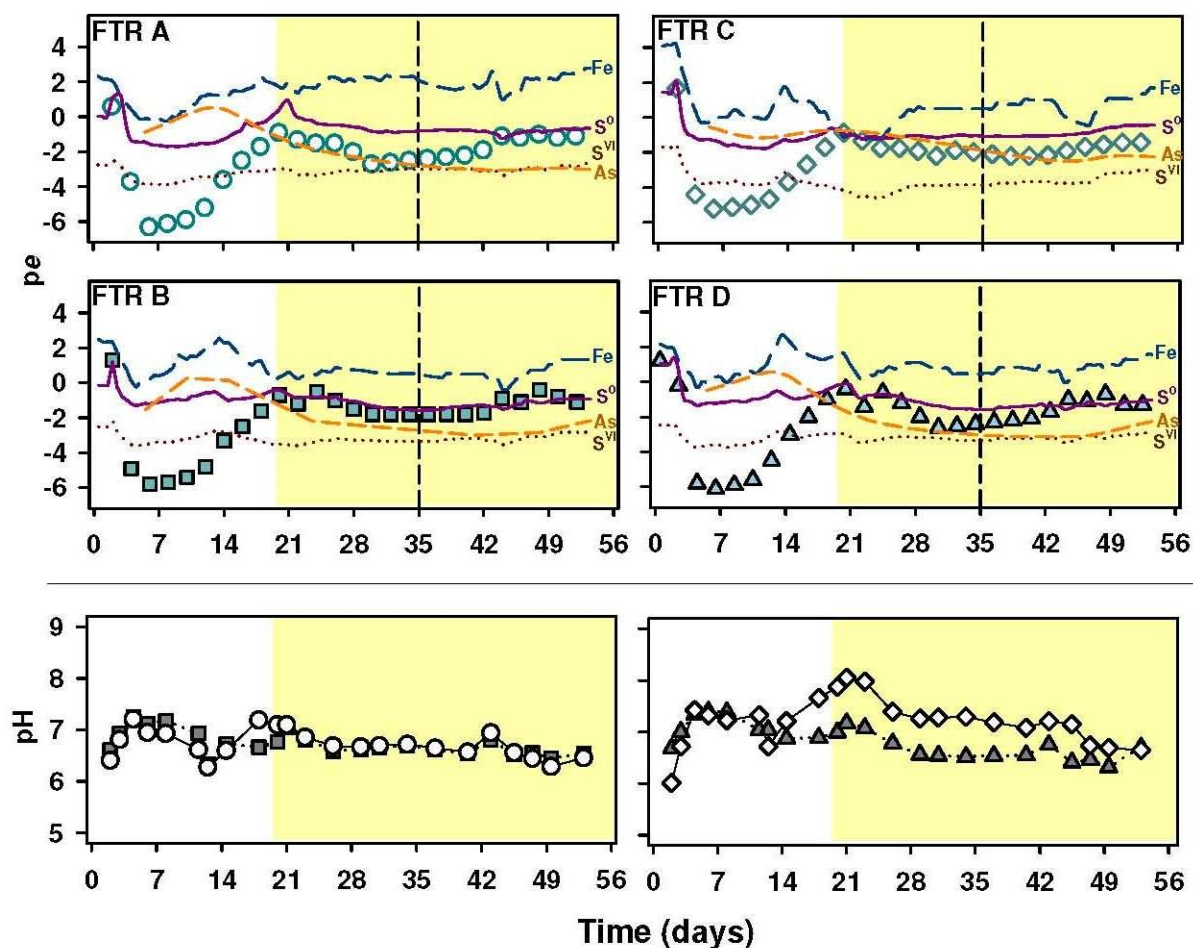


Fig. S2. Upper panel: redox potential (pe) calculated using Pt-electrode measurements and modelled using the S^{VI}/S^{-II} (dotted lines), S^0/S^{-II} (solid lines), As^{III}/As^V (short dashed) and $Fe^{II}/Fe^{III}(OH)_3(s)$ (long dashed lines) redox couples in the outflow of the labile OM-rich FTRs A (○) and B (■) in the left panels and of the labile OM-poor FTRs C (◇), and D (▲) in the right panels. Lower panel: pH in the outflow of the FTRs A (○) and B (■) in the left panels and of FTRs C (◇) and D (▲) in the right panels. Open symbols denote the As^{III} -fed FTRs and solid symbols denote As^V -fed FTRs, whereas the shaded area indicates the lactate-supply phase.

References

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