

Arsenic(V) incorporation in vivianite during microbial reduction of arsenic(V)-bearing biogenic Fe(III) (oxyhydr)oxides

E. Marie Muehe^{1,2*}, Guillaume Morin³, Lukas Scheer¹, Pierre Le Pape³,
Imène Esteve³, Birgit Daus⁴, Andreas Kappler¹

¹Geomicrobiology, Center for Applied Geosciences, University of Tuebingen, Germany

²Now: Environmental Soil Biogeochemistry, Earth System Science, Stanford University, USA

³Environmental Mineralogy, Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie (IMPMC), UMR7590 - CNRS - UPMC, France

⁴UFZ – Helmholtz Centre for Environmental Research, Department Analytical Chemistry, Leipzig, Germany

SUPPORTING INFORMATION

*To whom correspondence should be sent:

E. Marie Muehe, Environmental Soil Biogeochemistry, Earth System Science, Stanford University, 473 Via Ortega, Stanford, CA 94305, USA

Phone: +1-650-291-9715, email: mmuehe@stanford.edu

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Table S1: Rietveld refined Unit-cell parameters of vivianite in the biogenic samples compared to the 1 wt% As(V) substituted vivianite model compound, and available crystallographic data for vivianite and symplectite. Arsenic substitution rate in the biogenic and model compound samples could not be reliably derived from a Vegard law approach because of imprecision in the structural data reported by Mori and Ito, 1950¹ for symplectite, i.e. <As-O> ~1.655 ± 0.047, instead of an expected <As-O> = 1.679 ± 0.008 Å (Hawthorne, 1976²).

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)
Sample Fe:As(V) 50:1 - 5 days	10.13(2)	13.46(2)	4.70(1)	104.6(1)
Sample Fe:As(V) 250:1 - 5 days	10.12(4)	13.46(2)	4.70(1)	104.4(3)
Model compound 1 wt% As*(V)-vivianite	10.13(2)	13.48(3)	4.72(1)	104.4(1)
Vivianite (Mori and Ito, 1950 ¹)	10.08	13.43	4.70	104.5
Vivianite (Fedji et al., 1980 ³)	10.086	13.441	4.703	104.27
Symplectite (Mori and Ito, 1950 ¹)	10.25	13.48	4.70	103.8

Table S2: Shell-by-shell EXAFS fitting parameters for the 1 wt% As(V)-substituted vivianite model compound EXAFS data, compared to crystallographic data for the refined structure of vivianite by Fejdi et al., 1980³. * fixed parameters. (-) parameter linked to the parameter in the Table S1.

	R (Å)	<i>shell</i>	σ (Å)	ΔE_0 (eV)
vivianite As(V) 1wt%	1.695(2)	4* As-O	0.060(1)	11.3(8)
	3.1*	12* As-O-O	0.05*	-
	3.303(5)	3* As-Fe	0.067(3)	-
	3.477(5)	2* As-Fe	0.051(3)	-
vivianite (Fejdi et al., 1980 ³)	1.54(2)	4 P-O		
	3.23(1)	3 P-Fe		
	3.41(1)	2 P-Fe		

Table S3: Solubility products, ion activity products and saturation index calculations for the formation of vivianite-symplectite mixed mineral phases in the experiment. (at 25°C).

Reaction:	$\text{Fe}_3(\text{PO}_4)_{1.75}(\text{AsO}_4)_{0.25} = 3 \text{Fe}^{2+} + [1.75 \text{PO}_4^{3-} + 0.25 \text{AsO}_4^{3-}]$	
Solubility product K_{sp}	$= \frac{[\text{Fe}^{2+}]^3 \times [\text{PO}_4^{3-} + \text{AsO}_4^{3-}]^{(1.75+0.25)}}{[\text{Fe}_3(\text{PO}_4)_{1.75}(\text{AsO}_4)_{0.25}]}$	
K_{sp} (Vivianite)	$10^{-33.06} \text{ mol}^2 \text{ L}^{-2}$	(Johnston and Singer, 2007 ⁴)
K_{sp} (Symplectite)	$10^{-33.25} \text{ mol}^2 \text{ L}^{-2}$	(Johnston and Singer, 2007 ⁴)
K_{sp} (Vivianite-symplectite)	$\sim 10^{-33.15} \text{ mol}^2 \text{ L}^{-2}$	(expected from vivianite and symplectite)

	<u>Fe to As ratio 50:1 [w/w]</u>	<u>Fe to As ratio 250:1 [w/w]</u>
Ion concentration in the aqueous phase at day 5		
Fe^{2+}	0.00099 mol L ⁻¹	0.00070 mol L ⁻¹
As(V)-species	66% of aqueous As is As(V) = 0.264 mg L ⁻¹ = 0.00000352 mol L ⁻¹	66% of aqueous As is As(V) = 0.594 mg L ⁻¹ = 0.00000792 mol L ⁻¹
PO_4^{3-} -species	$\sim 0.0001 \text{ mol L}^{-1}$	$\sim 0.0001 \text{ mol L}^{-1}$
Ion activity product $\text{IAP} = [\text{Fe}^{2+}]^3 \times [\text{PO}_4^{3-} + \text{AsO}_4^{3-}]^{(1.75+0.25)}$		
	$= 3.4 \times 10^{-16} \text{ mol}^2 \text{ L}^{-2}$	$= 9.9 \times 10^{-16} \text{ mol}^2 \text{ L}^{-2}$
Saturation index $\text{SI} = \log(\text{IAP}/K_{\text{sp}})$		
	<u>$\equiv 17.7$</u>	<u>$\equiv 18.1$</u>

$\text{IAP} = K_{\text{sp}}$ or $\text{SI} = 0 \rightarrow$ solution is saturated
 $\text{IAP} < K_{\text{sp}}$ or $\text{SI} < 0 \rightarrow$ solution is undersaturated (dissolution of mineral)
 $\text{IAP} > K_{\text{sp}}$ or $\text{SI} > 0 \rightarrow$ solution is supersaturated (mineral precipitation)

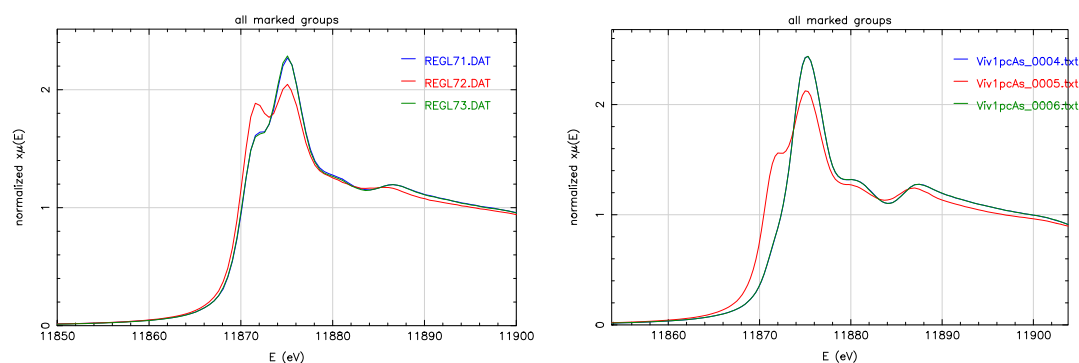


Figure S1. Synchrotron beam damage observed on the XANES region after a ~40 min long EXAFS scan at 10-20 K on the incubated sample with a Fe to As(V) ratio of 50 to 1 (w/w) (left) and on the 1 wt% As(V)-substituted vivianite model compound. The blue and red lines display two successive scans on the same spot. The green line display a scan on another spot after having shifted the sample. Since the samples were found to be sensitive to photo-reduction of As(V) to As(III), the beam position was shifted between each EXAFS scan to merge 7 and 3 scans for the biogenic and model compound sample, respectively.

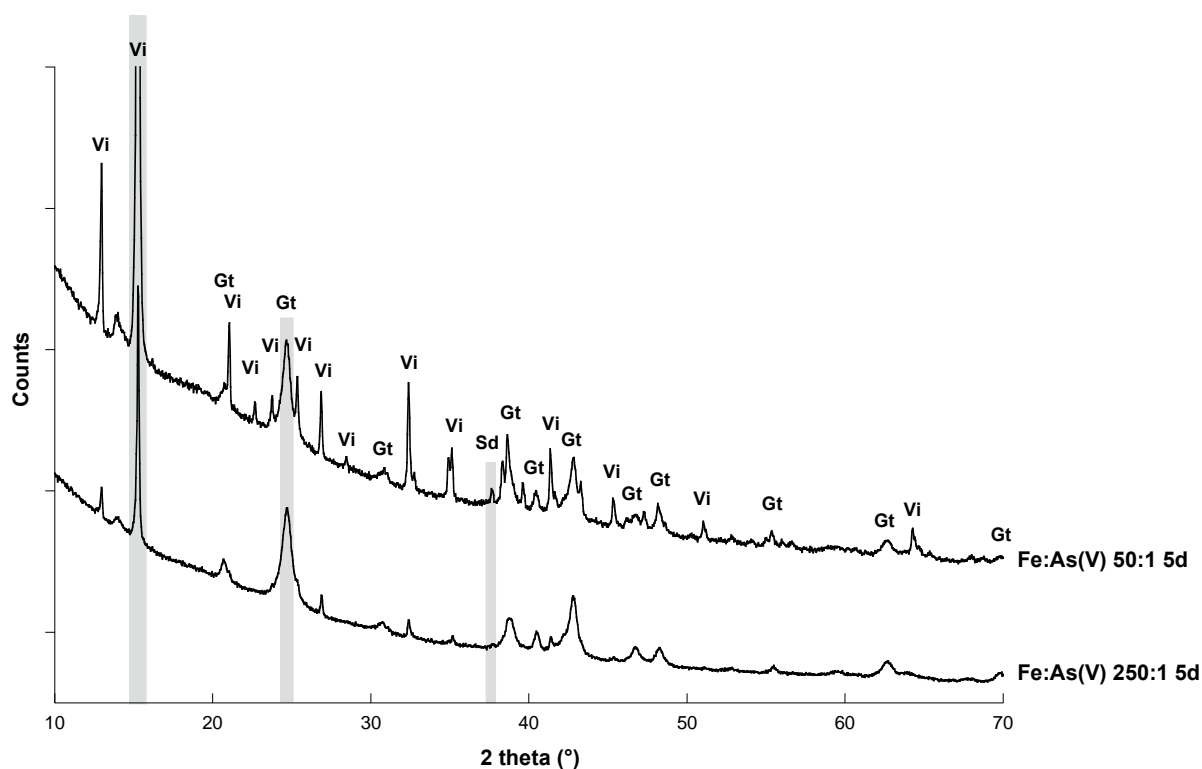


Figure S2: Powder X-ray diffraction patterns of As(V)-bearing biogenic Fe(III) (oxyhydr)oxides synthesized with a Fe to As ratio of 50 to 1 and 250 to 1 (w/w) after 5 days of reduction by *S. oneidensis* strain MR-1. The strongest Bragg reflections of vivianite (Vi), goethite (Gt), and siderite (Sd) are depicted in grey.

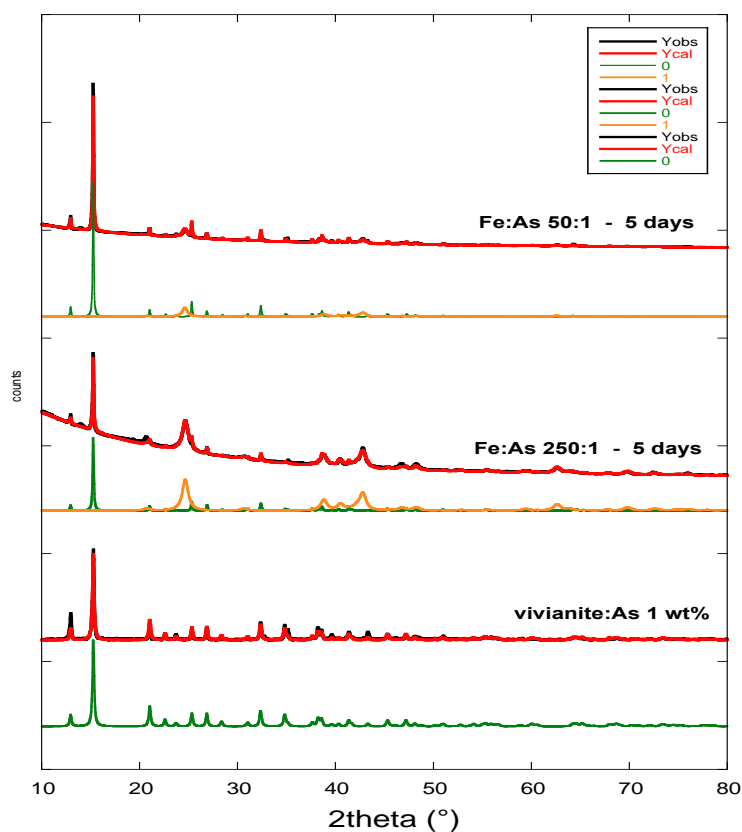


Figure S3: Rietveld refinement of the Powder X-ray diffraction patterns of microbially reduced As(V)-bearing biogenic Fe(III) (oxyhydr)oxides (with Fe to As ratios of 50 to 1 and 250 to 1, respectively), and of the 1 wt% As-substituted vivianite reference compound. Experimental data are plotted in black line. The calculated patterns (red) include vivianite (green line) and goethite (orange line). Refined unit-cell parameters for vivianite in the samples are reported in Table S1. Rietveld refinement was performed using the XND1.3 code (Berar et al., 1998⁵).

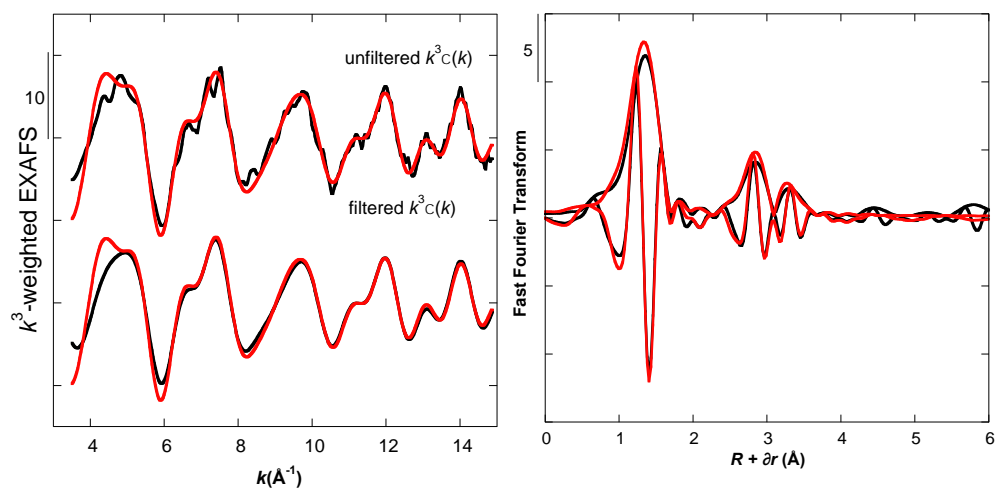


Figure S4: Shell-by-shell fitting of the 1 wt% As(V)-substituted vivianite model compound EXAFS data using parameters reported in Table S1. The fit curve (red) is shown for experimental data (black line), either unfiltered or filtered within the $0.8 - 4 R + \Delta r$ range. The Fast Fourier Transform of the unfiltered data and of the fit is plotted on the right side of the figure, uncorrected for phase shift. The unfitted long distance peaks in the FT at $R + \Delta r \sim 4.5$ and 6 \AA are assigned to contributions from multiple scattering within the vivianite structure.

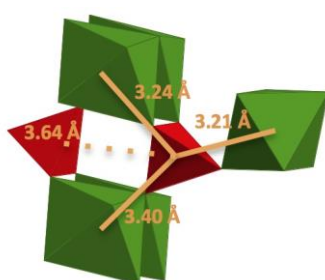


Figure S5: Local structure around the PO_4^{3-} group in the vivianite structure according to Fejdi et al., 1980³.

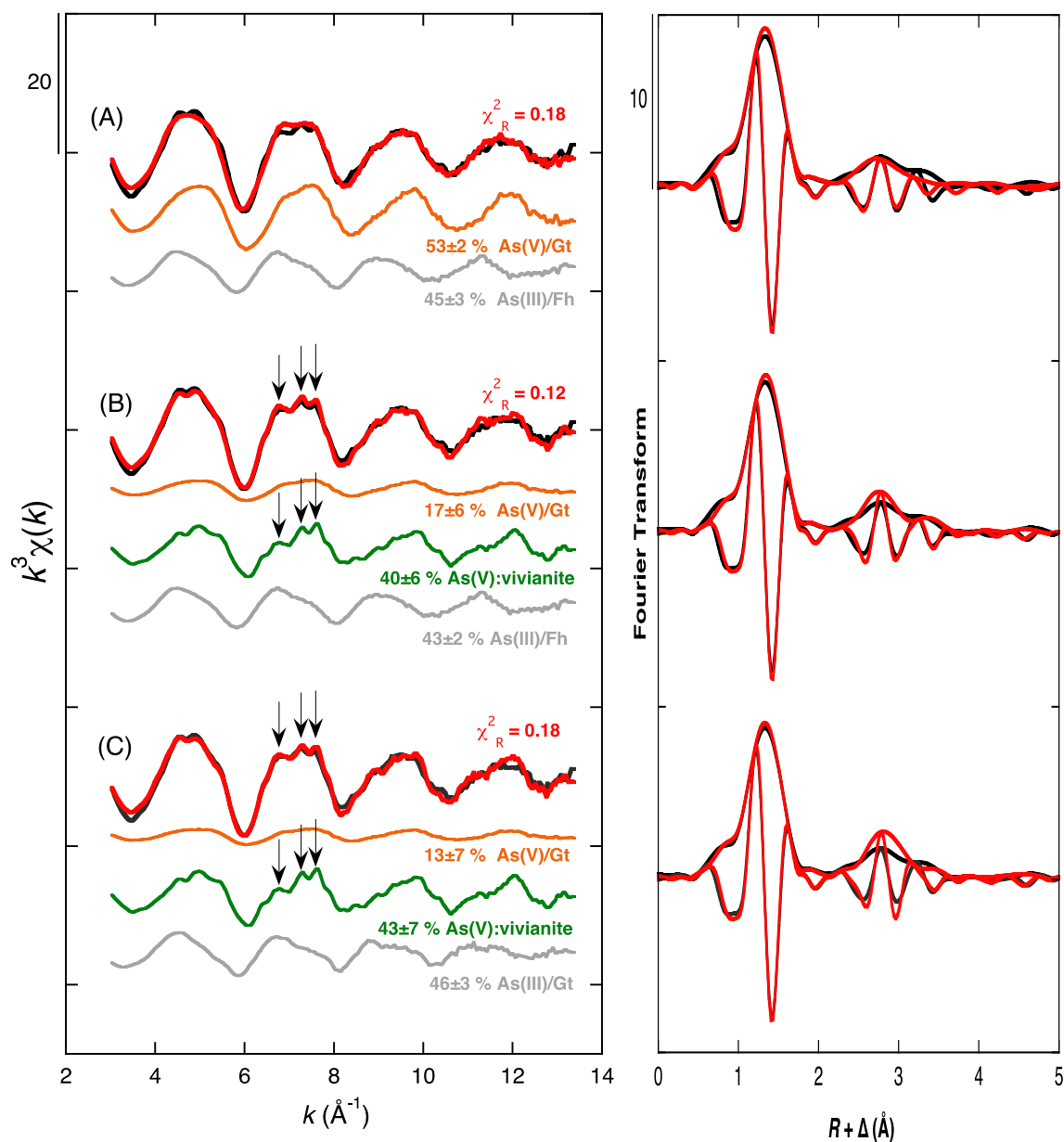


Figure S6: Alternative Linear Combination Fit solutions for the As K-edge data of As-bearing biogenic Fe(III) (hydroxide) with a Fe to As ratio of 50 to 1 (w/w) after 5 days of reduction. (A) Fit without As(V)-substituted vivianite (As(V):vivianite); (B) Fit with As(V)-substituted vivianite retained as the best fit solution; (C) Fit with As(V)-substituted vivianite and with As(III)-sorbed goethite (As(V)/Gt) instead of As(III)-sorbed ferrihydrite (As(III)/Fh). The vertical arrows indicate contributions from multiple scattering within the vivianite structure (see Fig. S3).

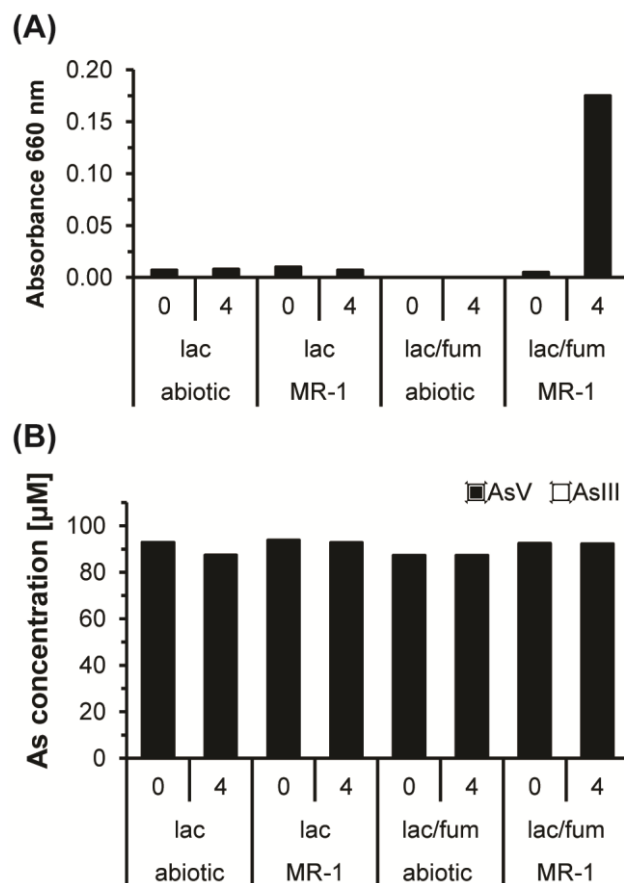


Figure S7: The ability of *Shewanella oneidensis* MR-1 to reduce As(V) when grown on mineral medium in the presence of 100 μ M As(V) as electron acceptor and 20 mM lactate (lac) as electron donor. For some setups, 40 mM fumarate (fum) was amended as an additional electron acceptor. Growth was determined via quantification of the absorption at 660 nm at 0 and 4 days (A); aqueous As(V) (black) and As(III) (white) concentrations after 0 and 4 days are given in μ M (B). No reduction of As(V) was observed in any setup, so no white bars are shown in B. n=3.

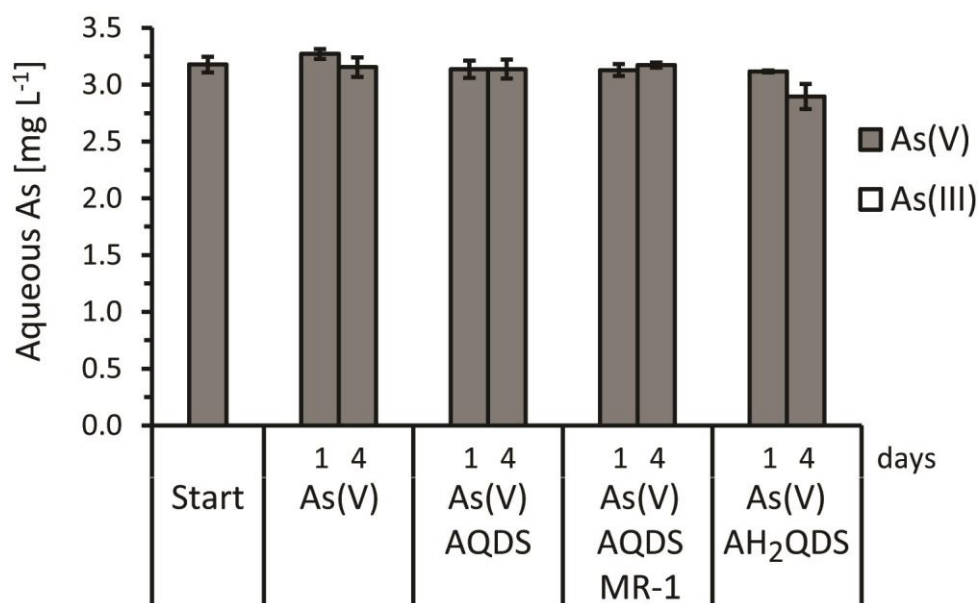


Figure S8: Reduction of As(V) by AH₂QDS. This control setup was conducted under the same experimental conditions as applied in the main experiment (mineral medium at pH 7, 20 mM lactate, 40 mM fumarate, incubation in the dark at 28°C). Approximately 3 mg L⁻¹ of aqueous As(V) were added, as this was in the range of the aqueous As concentration present at the end of incubation of the main experiment. 100 µM of AH₂QDS was used (the AH₂QDS was synthesized from AQDS by chemical reduction at pH 7 using H₂ and a palladium catalyst). Additional controls were: no AQDS/AH₂QDS, 100 µM of AQDS, and 100 µM of AQDS plus *Shewanella oneidensis* MR-1. Total As was quantified by ICP-MS, the speciation of As was determined with HPLC-ICP-MS. Aqueous As(V) (grey) and As(III) (white) concentrations after 1 and 4 days are given in mg L⁻¹. No reduction of As(V) was observed in any setup, so no white bars are shown. n=3.

Supporting Information References

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