

Electronic Annex:

Speciation and Natural Attenuation of Arsenic and Iron in a Tidally Influenced Shallow Aquifer

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Supplemental Information on Experimental Methods

2.2.1 *Elemental and species analyses*

Elemental concentrations were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES; Thermo Jarrel Ash IRIS ICP) and graphite furnace electro-thermal atomic absorption (GFAA) with Zeeman background correction (Perkin Elmer SIMMA 6000 GFAA; Aquatic Consulting and Testing, Inc., Tempe, AZ). Analytical blanks and spiked analytical blanks were digested with the field samples. Multi-point standard calibration curves were constructed using NIST traceable premixed standards (Fischer Scientific) prior to each analytical run. Correlation coefficients for standard curves were 0.995 or better and verified against a NIST traceable second source standard with less than $\pm 10\%$ relative difference.

Extractable sulfate was measured on sediment from Core 1 only following EPA method 375.3. Wet (but not draining) samples (20 g) were extracted with 0.5 ammonium acetate + 0.25 N acetic acid and measured gravimetrically. Concentrations are reported on a sediment dry weight basis.

2.2.2 *X-ray diffraction (XRD)*

Bulk sediment mineralogy was determined by powder XRD using both laboratory and synchrotron X-ray sources. Samples were dried at 40°C in air for 24-48 h, finely ground to ~ 5 μm grain size powders, and randomly orientated on quartz micro-slides for laboratory XRD and on aluminum mounts for synchrotron XRD. Laboratory diffractograms were collected on a Rigaku D/Max-II B X-ray Powder Diffractometer using a Cu-K α source (wavelength = 1.54184 Å) operated at 50 keV and 35 mA from 2 to 90° 2 θ in 0.020° steps. Synchrotron XRD data were collected at SSRL on beamline 2-1 at 10 keV with a Si(111) monochromator between 4 and 65° 2 θ in 0.006° or 0.008° steps. Synchrotron data were calibrated with a LaB₆ standard using non-

linear curve fit and Bragg fit equations for a calculated wavelength of 1.239 Å. Peak position error for both methods was $\pm 0.3^\circ 2\theta$. Data analysis was performed using the Jade software package (MDI Products). Mineral identification was based on matches to three dominant peaks or to two dominant peaks with multiple minor peaks in the reference database (ICDD database).

2.2.3 XAS data collection and analysis

XANES spectra were analyzed using the computer packages DATFIT and Sixpack (George and Pickering, 2000; Webb, 2006). EXAFS spectra were analyzed with the package EXAFSPAK (George and Pickering, 2000). For both XANES and EXAFS, background was subtracted using a linear fit through the pre-edge region and spectra were normalized to the average height of the post-edge absorbance. Arsenic and iron XANES spectra (either normalized or first-derivative normalized spectra) of sediment samples were fit using linear least-squares combinations of reference compound spectra. Energy was allowed to vary in fits to account for small differences in energy calibration between sediments and references, but reference spectra were linked such that energy was a single adjustable parameter. Shifts in energy of greater than 0.7 eV were rejected as spurious.

Normalization was extended into the EXAFS region using a Victoreen polynomial and tabulated McMaster coefficients (Brown et al., 1988), and spectra were weighted by k^3 (where k is the photoelectron wave vector). Normalized EXAFS spectra were filtered over a k -range of 2 to 11-14 Å⁻¹ (depending on data quality) and Fourier-transformed to produce radial structure functions (RSF's) (shown uncorrected for backscatterer phase shift). Spectra were fit by non-linear least-squares methods in k -space and the entire k -range was used in the fit (i.e., no reverse Fourier filtering was done). Theoretical phase-shift and amplitude reference functions were calculated with the program FEFF (Rehr, 1993; Ankudinov et al., 1998) for absorber-

backscatterer pairs using an atomic cluster calculated from the crystal structures of the reference compounds. In fits to the sediment arsenic EXAFS spectra, interatomic distance (R), and either backscatterer number (N) or Debye-Waller factor (σ^2) were varied in fits (because of the strong co-variance between N and σ^2). For most unknown spectra, σ^2 was fixed on a value estimated from fits to reference compounds with similar absorber-backscatters atomic pairs. For fits to iron EXAFS spectra, atomic shells were grouped by a sulfide component, represented by the local structure of pyrite, and a non-sulfide component, represented by a composite phyllosilicate-oxide, and fit according to the methods described previously (O'Day et al., 2004a; O'Day et al., 2004b). Estimated errors based on empirical fits to reference compounds are: first shell: $R \pm 0.01 \text{ \AA}$; $N \pm 10\%$; greater than first shell: $R \pm 0.02 \text{ \AA}$; $N \pm 30\%$; $\sigma^2 \pm 30\%$ (O'Day et al., 1998; O'Day et al., 2004a; O'Day et al., 2004b).

Table EA-1. Arsenic EXAFS fit results for reference compounds.

EXAFS Fit							Crystallographic Values		
	Atom	N	R (Å)	σ^2 (Å ⁻¹)	ΔE_0 (eV)	χ^2	Atom	N	R(Å)
Realgar (AsS) ^b	S	2 ^a	2.24	0.0034	-10.8	0.54	S	2	2.225-2.251
	As	1 ^a	2.58 ^a	0.0048			As	1	2.565-2.579
							S	1	3.415-3.513
	As	2.5 ^a	3.47 ^a	0.0057			As	2.5	3.439-3.499
							As	0.5	3.562
	As	0.75 ^a	3.63 ^a	0.012			As	0.75	3.624-3.627
Orpiment (As ₂ S ₃) ^c	S	2.5 ^a	3.67 ^a	0.0078			S	0.75	3.570-3.617
							S	2.5	3.657-3.689
	S	3 ^a	2.28	0.0040	-9.2	0.11	S	3	2.243-2.307
	As	1 ^a	3.19 ^a	0.0087			As	1	3.191
	S	1 ^a	3.22 ^a	0.014			S	1	3.219, 3.291
	S	1 ^a	3.47 ^a	0.016			S	1	3.475, 3.514
As ₂ S ₃ (am) ^d	As	1 ^a	3.52 ^a	0.0079			As	1	3.521
	As	1 ^a	3.57 ^a	0.011			As	1	3.568
	S	3 ^a	2.28	0.0026	-8.8	1.33			
	As	1 ^a	3.06	0.011					
	S	1 ^a	3.18	0.015 ^a					
	S	1 ^a	3.47 ^a	0.016 ^a					
As(III)/ HFO ^e	As	1 ^a	3.52	0.0057					
	As	1 ^a	4.11	0.0090					
As(III)/ HFO ^e	O	3.0	1.78	0.0044 ^a	-1.9	0.69			
	Fe	0.6	2.93	0.0049 ^a					
	Fe	0.6	3.41	0.0049 ^a					
As(V)/ HFO ^f	O	4 ^a	1.70	0.0023	0.34	0.98			
	MS ^g	1	3.16	0.0058/					
	Fe	2 ^a	3.32	0.010					

^aParameter fixed in least-squares fit based on the known coordination or distance in the reference compound; / parameter linked in fit to the parameter directly above.

^bFrom O'Day et al. (2004b). Realgar structure from Mullen and Nowacki (1972); distances give the range for the four unique arsenic sites. Disordered sulfur shells at 3.415-3.513 Å and 3.570-3.617 Å cancel and do not contribute to EXAFS amplitudes. Scale factor (S_0^2) fixed at 0.9.

^cFrom O'Day et al. (2004b). Orpiment crystal structure from Mullen and Nowacki (1972); distances give the range for the two unique arsenic sites. Scale factor (S_0^2) = 0.9.

^dFreshly precipitated sample by the method given in Eary (1992); X-ray amorphous.

^eAs(III) sorbed to hydrous ferric oxide (HFO; see Table EA-2) equilibrated with 10⁻⁴ M arsenite solution. Debye-Waller factor from Ona-Nguema et al. (2005).

^fAs(V) sorbed to hydrous ferric oxide (HFO; see Table EA-2) equilibrated with 10⁻³ M arsenate solution.

^gSpectrum fit with a multiple scattering path from As-O-O-As in arsenate tetrahedra.

Table EA-2. Iron EXAFS fit results for reference compounds.

EXAFS Fit							Crystallographic Values		
	Atom	N	R (Å)	σ^2 (Å ⁻¹)	ΔE_0 (eV)	χ^2	Atom	N	R(Å)
Pyrite ^a (FeS ₂)	S	6 ^c	2.25	0.0013	-5.3	2.84	S	6	2.2566
	S	6 ^c	3.45	0.0041			S	6	3.4449
	Fe	12 ^c	3.83	0.0037			Fe	12	3.8212
Illite ^b (IMt-1)	O	6 ^c	2.01	0.0072	-0.3	0.39	O	6	1.9157-1.9588
	Al	3 ^c	3.02	0.0088			Al	3	2.9963, 3.0022, 3.0154
	Fe	1 ^c	3.02	0.0059			Fe	1	
	Si	4 ^c	3.26	0.0045			Si	1	3.1574, 3.1581, 3.2234, 3.2280
Synth. GR1 ^c (carb)	O	5.8	2.11	0.0077	-2.0	0.44			
	Fe	5.7	3.23	0.0069					
Synth. GR2 ^c (sulf)	O	5.8	2.12	0.0063	-2.2	0.28			
	Fe	5.1	3.25	0.0052					
Synth. HFO ^d	O	3.4	1.94	0.0050 ^e	-2.2	0.28			
	O	1.0	2.05	0.0040 ^e					
	Fe	2.2	3.02	0.009 ^e					
	Fe	2.0 ^e	3.24 ^e	0.018 ^e					
	Fe	4.4	3.48	0.018 ^e					

^aEXAFS fit from O'Day et al. (2004a); XRD crystallographic values from Elliot (1960).

^bEXAFS fit from O'Day et al. (2004a); XRD crystallographic values not reported for IMt-1. Values shown are for an iron-bearing muscovite from Guggenheim et al. (1987).

^cSynthetic green rust (fougerite) prepared as the carbonate (GR1 (carb)) and sulfate (GR 2 (sulf)) forms using the method of Drissi et al. (1995). Numerical fit result from Root et al. (2007).

^dSynthetic HFO prepared by neutralizing a 0.2 M ferric chloride solution with 1 M KOH to a pH of 7-8 in the presence of CO₂ according to the 2-line ferrihydrite method of Schwertmann and Cornell (1991). Numerical fit result from Root et al. (2007).

^eParameter fixed in least-squares fit.

Table EA-3. Total element concentrations in Bay Road sediment cores (kg⁻¹ sediment dry wt.).

Sample	Depth(cm)	As	Al	B	Ba	Ca	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Ti	V	Zn
	<i>Detection limit</i>	<i>0.003</i>	<i>0.074</i>	<i>0.0925</i>	<i>0.00723</i>	<i>0.0499</i>	<i>0.0192</i>	<i>0.0157</i>	<i>0.0179</i>	<i>0.0512</i>	<i>0.0823</i>	<i>0.0182</i>	<i>0.0435</i>	<i>0.0170</i>	<i>0.0209</i>	<i>0.0196</i>	<i>0.0153</i>
Core 1: April 26, 2002		10 ⁻³ mol kg ⁻¹	mol kg ⁻¹	10 ⁻³ mol kg ⁻¹	10 ⁻³ mol kg ⁻¹	mol kg ⁻¹	10 ⁻³ mol kg ⁻¹	10 ⁻³ mol kg ⁻¹	mol kg ⁻¹	mol kg ⁻¹	mol kg ⁻¹	10 ⁻³ mol kg ⁻¹	mol kg ⁻¹	10 ⁻³ mol kg ⁻¹	10 ⁻³ mol kg ⁻¹	10 ⁻³ mol kg ⁻¹	10 ⁻³ mol kg ⁻¹
1-1	15-30	0.574	1.90	<DL	1.89	0.265	2.89	3.89	0.953	0.523	0.842	13.2	0.479	0.392	3.49	3.42	10.4
1-2	30-46	1.76	1.57	<DL	1.32	0.146	1.16	1.39	0.960	0.244	0.822	16.3	0.137	0.414	1.29	2.69	3.81
1-3	46-61	3.74	1.56	<DL	1.11	0.210	2.53	1.91	0.904	0.245	0.810	15.2	0.392	1.99	4.47	2.81	3.88
1-4	61-76	2.74	0.891	<DL	0.925	0.564	1.27	0.891	0.500	0.151	0.518	8.17	0.243	1.14	1.94	1.89	2.06
1-6	122-137	1.57	1.37	3.49	1.11	0.172	2.41	2.26	0.786	0.192	0.698	13.9	0.434	2.01	3.82	2.53	3.00
1-7	152-168	0.814	0.782	<DL	1.21	0.281	1.48	0.423	0.528	0.0928	0.557	5.86	0.131	1.08	39.8	2.36	1.50
1-8	168-183	1.03	0.603	1.16	0.816	0.216	1.16	0.228	0.345	0.0846	0.336	3.60	0.142	0.900	24.8	1.51	1.04
1-10	193-205	5.19	0.432	0.721	1.47	0.128	0.767	0.242	0.299	0.0613	0.260	3.33	0.0645	0.550	20.1	1.10	1.06
1-11	206-213	4.35	0.611	<DL	2.51	0.178	1.03	0.455	0.385	0.0971	0.362	3.80	0.108	0.794	21.5	1.35	1.51
1-12	284-295	5.65	0.821	1.88	1.56	0.113	1.13	0.522	0.533	0.113	0.425	8.72	0.141	0.981	18.1	1.72	1.53
1-13	295-305	3.59	0.620	1.86	1.93	0.132	0.917	0.364	0.401	0.0866	0.344	4.06	0.105	0.806	16.7	1.44	1.27
1-14	305-315	4.71	0.680	2.26	1.95	0.116	1.03	0.606	0.521	0.126	0.433	4.86	0.144	0.954	17.8	1.66	1.87
1-15	315-325	2.43	0.811	2.14	2.19	0.0992	1.10	0.508	0.517	0.117	0.433	5.26	0.151	1.01	17.5	1.67	1.58
1-16	325-335	3.83	0.931	2.52	2.29	0.104	1.20	0.567	0.596	0.140	0.480	5.08	0.171	1.05	19.0	1.96	1.84
1-18	345-357	1.55	1.19	3.19	1.47	0.147	1.41	0.982	0.710	0.204	0.610	6.33	0.186	1.14	23.3	2.65	2.86
Core 2: January 3, 2002																	
2-1	15-30	1.44	2.51	15.6	1.35	0.159	3.45	0.872	1.28	0.284	0.893	8.76	0.626	1.97	33.9	2.73	3.15
2-2	46-61	1.07	0.922	9.12	0.386	0.237	1.32	0.417	0.543	0.111	0.572	3.97	0.382	0.682	17.2	1.14	1.58
2-3	76-91	0.294	1.06	8.22	1.98	1.71	1.66	0.408	0.527	0.145	0.495	6.21	0.413	0.750	18.8	1.48	1.13
2-4	107-122	0.243	0.976	5.40	1.41	1.01	1.27	0.279	0.514	0.110	0.421	4.57	0.253	0.596	16.9	1.24	0.765
2-5	138-152	0.220	1.25	8.15	1.50	0.196	1.84	0.378	0.619	0.156	0.493	2.95	0.397	0.854	21.9	1.65	1.28
2-6	168-183	0.178	1.05	7.02	1.43	1.42	1.52	0.310	0.557	0.126	0.480	3.59	0.374	0.770	21.1	1.51	1.09
2-7	198-203	0.300	1.05	6.49	1.46	1.28	1.50	0.318	0.596	0.125	0.483	3.13	0.332	0.760	19.2	1.41	0.963
2-8	229-244	0.659	1.17	7.65	1.38	0.933	1.68	0.307	0.746	0.132	0.551	3.35	0.400	0.837	19.2	1.54	1.07
2-9	259-274	1.53	1.09	7.32	1.38	0.222	1.58	0.279	0.656	0.119	0.433	2.91	0.299	0.733	17.4	1.42	1.06
2-10	290-305	0.854	0.902	7.09	1.24	0.215	1.48	0.326	0.552	0.0885	0.378	3.02	0.427	0.729	20.5	1.38	1.19
Core 3: January 3, 2002																	
3-1	0-15	0.573	0.959	12.2	0.706	0.115	1.96	0.674	0.819	0.153	0.623	23.5	0.416	1.64	14.9	1.42	2.19
3-2	15-30	0.593	0.878	10/6	0.699	0.105	2.01	0.807	0.740	0.140	0.584	12.2	0.495	1.49	13.8	1.28	2.43
3-3	30-46	1.60	0.740	12.7	1.41	0.134	1.64	1.08	0.704	0.142	0.563	5.55	0.687	1.56	13.9	1.12	3.79
3-4	46-61	1.72	0.603	10.6	1.52	0.178	1.18	1.18	0.612	0.125	0.550	5.92	0.584	1.31	11.9	0.876	5.47
3-5	62-76	1.40	0.485	12.0	0.561	0.407	0.965	0.659	0.455	0.111	0.541	6.17	0.584	0.942	7.41	0.730	3.18
3-6	77-91	0.717	0.545	9.15	0.947	0.481	1.12	0.552	0.500	0.105	0.490	7.99	0.381	0.923	10.0	0.907	1.87
3-7	91-107	0.351	0.489	6.83	0.961	0.632	0.900	0.401	0.375	0.0988	0.377	4.71	0.332	0.729	9.23	0.879	1.04
3-8	107-122	0.188	0.457	5.73	1.93	0.516	0.890	0.327	0.379	0.0974	0.335	4.33	0.328	0.743	7.66	0.736	0.719
3-9	122-137	0.342	0.476	6.50	1.35	0.525	0.921	0.404	0.430	0.0916	0.342	4.53	0.234	0.813	10.4	0.852	0.918
3-11	168-183	0.258	0.409	8.88	0.706	0.328	0.798	0.373	0.431	0.0824	0.309	3.46	0.220	0.724	9.61	1.42	7.03
3-13	198-203	0.117	0.342	4.62	1.30	0.769	0.687	0.233	0.315	0.0618	0.296	3.15	0.210	0.641	9.17	2.29	6.71
3-16	259-274	0.136	0.407	5.05	1.49	0.179	0.840	0.393	0.383	0.0683	0.287	4.15	0.199	0.736	9.54	0.842	6.99
3-17	290-305	0.153	0.391	5.47	1.55	0.0908	0.804	0.478	0.404	0.0695	0.277	3.70	0.177	0.763	9.98	0.681	7.31
3-18	320-335	0.155	0.565	6.24	1.72	0.123	0.992	0.549	0.491	0.111	0.362	4.68	0.225	0.847	11.1	1.20	8.15
South Bay muds ^b		0.147	2.05	<DL	<DL	<DL	<DL	0.699	0.874	<DL	<DL	0.0289	<DL	1.20	<DL	<DL	1.79

^aAll concentrations reported on the basis of dry sediment weight.

^bSouth Bay mud reference sediment sampled August 15, 2001 by San Francisco Estuary Institute (Gandesbery et al., 1999).

<DL = below detection limit, i.e., analyte was observed at concentrations statically indistinguishable from laboratory blank. Additional parameters analyzed but not detected above the limit of detection and therefore not tabulated include Ag, Be, Cd, Co, Hg, Mo, Pb, Sb, Se, and Sn. Analytical recoveries for spiked samples were between 85-115% and replicate analyses of sediments had relative standard deviations of less than 15.0.

Table EA-4. Total organic carbon and extractable sulfur in Bay Road sediment cores (kg⁻¹ sediment dry wt.).

Sample	Depth(cm)	TOC ^a	Extractable S ^b	Reactive Sulfide
	<i>Detection limit</i>	<i>0.2%</i>	<i>0.10</i>	<i>0.30</i>
Core 1: April 26, 2002		%	10 ⁻³ mol kg ⁻¹	10 ⁻³ mol kg ⁻¹
1-1	15-30	2.4	8.1	<DL
1-2	30-46	9.9	15.8	1.5
1-3	46-61	7.2	n.a.	n.a.
1-4	61-76	8.1	10.3	8.2
1-6	122-137	11.5	9.7	<DL
1-7	152-168	3.2	9.8	<DL
1-8	168-183	2.2	8.9	<DL
1-10	193-205	1.8	5.8	<DL
1-11	206-213	1.9	15.3	<DL
1-12	284-295	2.0	23.5	<DL
1-13	295-305	2.1	15.1	<DL
1-14	305-315	3.5	n.a.	n.a.
1-15	315-325	2.7	4.8	<DL
1-16	325-335	5.0	5.8	<DL
1-18	345-357	5.1	3.2	<DL
Core 2: January 3, 2002				
2-1	15-30	n.a.		
2-2	46-61	11.4		
2-3	76-91	12.2		
2-4	107-122	4.6		
2-5	138-152	4.7		
2-6	168-183	6.0		
2-7	198-203	7.2		
2-8	229-244	7.0		
2-9	259-274	6.7		
2-10	290-305	n.a.		
Core 3: January 3, 2002				
3-1	0-15	11.4		
3-2	15-30	11.8		
3-3	30-46	12.1		
3-4	46-61	12.8		
3-5	62-76	11.9		
3-6	77-91	12.7		
3-7	91-107	9.0		
3-8	107-122	5.3		
3-9	122-137	3.9		
3-11	168-183	2.8		
3-13	198-203	2.5		
3-16	259-274	4.2		
3-17	290-305	3.5		
3-18	320-335	5.7		

^aSamples dried at 105°C for 48 hours and ashed at 400°C for 45 min. Sulfur measured only on Core 1. n.a. = not analyzed; <DL = below detection limit.

^bMeasured as sulfate by EPA Method 375.3. ^c Measured as reactive sulfide by EPA Method 846-9031.

Table EA-5. Sequential extractions from sediments for arsenic and iron (10^{-3} mol kg⁻¹ sediment dry wt.)^a.

Arsenic					
<i>Reduced</i>	depth (cm)	1	2	3a + 3b	4
1-2	30 - 46	0.050	0.114	1.12	1.76
1-3	47 - 60	0.089	0.468	b.d.	3.74
1-4	61 - 76	0.037	0.368	0.707	2.74
1-7	152 - 168	0.112	<DL	0.706	0.814
2-3	76 - 91	0.211	0.116	<DL	0.294
3-2	15 - 30	0.118	0.170	<DL	0.593
<i>Transition</i>					
2-7	198 - 203	0.119	<DL	0.094	0.300
3-11	168 - 183	0.141	0.291	<DL	0.342
3-13	198 - 203	0.184	<DL	<DL	0.258
<i>Oxidized</i>					
1-1	15 - 30	0.041	0.100	0.339	0.574
1-10	193 - 205	0.338	<DL	3.82	5.19
1-11	206 - 213	0.332	0.854	2.97	4.35
1-13	295 - 305	0.206	1.37	2.44	3.59
1-16	325 - 335	0.343	2.03	2.35	3.83
1-18	345 - 357	0.127	0.119	1.23	1.55
2-9	259 - 274	0.278	0.522	0.131	1.52
2-10	290 - 305	0.292	<DL	<DL	0.854

Iron					
<i>Reduced</i>	depth (cm)	1	2	3a + 3b	4
1-2	30 - 46	0.666	7.45	138.0	960.3
1-3	47 - 60	0.616	8.77	135.7	904.4
1-4	61 - 76	0.605	9.71	168.5	500.5
1-7	152 - 168	0.582	6.79	167.5	527.6
2-3	76 - 91	0.313	5.55	121.4	543.0
3-2	15 - 30	0.285	4.91	99.7	739.9
<i>Transition</i>					
2-7	198-203	0.646	4.19	144.0	558.3
3-11	168-183	0.867	3.60	62.3	430.5
3-13	198-203	0.621	3.24	200.5	430.6
<i>Oxidized</i>					
1-1	15 - 30	0.652	0.53	155.2	952.5
1-10	193 - 205	0.643	5.21	189.7	299.4
1-11	206 - 213	0.629	6.21	228.7	385.4
1-13	295 - 305	0.623	7.05	249.1	401.1
1-16	325 - 335	0.684	4.44	279.1	595.9
1-18	345 - 357	0.620	4.44	256.6	710.5
2-9	259 - 274	0.637	1.43	107.2	656.2
2-10	290 - 305	0.507	1.14	126.6	552.1

^aSediment aliquots (~400 mg) sequentially treated with each extractant solution (solid:solution = 0.01): (1) 1.0 M MgCl₂; (2) 1.0 M NaH₂PO₄; (3a) 0.2 M ammonium oxalate and oxalic acid; (3b) 1.0 M HCl; (4) Aqua-regia reflux (12 M HCl+HNO₃) was done on a separate 500 mg sample split. HF digestion was performed on selected samples; no additional As released. <DL = below detection limit. ($0.013 \cdot 10^{-3}$ mol kg⁻¹).

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