Electronic Supplementary Material (ESI) for Metallomics

Supplemental Material

Stabilities of Thiomolybdate Complexes of Iron; Implications for Retention of Essential Trace Elements (Fe, Cu, Mo) in Sulfidic Waters.

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I. Details Concerning Experimental Methods

Synthesis of Pyrrhotite. Synthetic pyrrhotite was prepared according to the method of Kullerud and Yoder (1959) from equimolar amounts of iron powder (99.999% pure, Johnson Mathey) and elemental sulfur powder (99.998%, Aldrich Gold Label). Prior to mixing with the sulfur, the iron powder was heated to 500 °C under a continuous stream of 95% Ar–5% H_2 for two hours in order to reduce any oxides from the surface of the iron. The iron was allowed to cool to room temperature while still under Ar/H_2 and was then immediately mixed with the sulfur. The iron-sulfur mixture was finely ground with a mortar and pestle, transferred into a quartz tube, and fusion sealed under vacuum. The contents in the evacuated quartz tube were allowed to react at room temperature for one day. The tube was then heated in a furnace, increasing the temperature 50 °C per day, to a final temperature of 550 °C. After holding at 550 ^{o}C for one week, the mixture was cooled to room temperature, and was finely ground to increase homogeneity. The solid was then reheated to 550 °C in a new evacuated quartz tube for an additional three days. In the final product, the atomic Fe deficiency that is characteristic of pyrrhotite was not greater than 2% based on the d_{102} spacing (Arnold, 1966). Within uncertainty, the material was stoichiometric, hexagonal $Fe_{1.00}S$ (troilite).

Reagents. Solutions were prepared from N_2-purged deionized water. The N_2 was passed through a Ridox oxygen absorbing column prior to entering solutions. Sulfide stock solutions were prepared by bubbling H_2S gas through deoxygenated NaOH. This approach minimizes the polysulfide contamination found in $Na_2S{\cdot}9H_2O$ reagents. All Mo-containing solutions were prepared from $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ reagent. Glassware was soaked overnight in 5% nitric acid to remover trace metals before rinsing with deionized water.

Thiomolybdate solutions of varying pH, ΣS^{2-}, ΣMo, and ΣCl^{-} were prepared from two 0.01 M ΣMo/ 0.1 M ΣS^{2-} stock solutions that had been allowed to react for a week beforehand. One stock solution contained no NH_3/NH_4^+ beyond that in the Mo reagent whereas the other was buffered with an additional 0.19 M NH_3/NH_4^+. In both stock solutions, MoS_4^{2-} was the most stable form of Mo^{VI} because of the high sulfide concentration. Based on UV-vis spectra, MoS_4^{2-} indeed predominated in the high-NH_4 stock solution, but owing to slower sulfidation kinetics at low NH_4^+, $MoOS_3^{2-}$ and $MoO_2S_2^{2-}$ predominated in the other stock solution at the time when the samples were prepared. Sulfidation↔hydrolysis equilibrium among thiomolybdates is facilitated by NH_4^+, which acts as an acid catalyst (Erickson and Helz, 2000).

Sulfide gains and losses. In most but not all samples, dissolved ΣS^{-II} in the final solutions differed relative to blank solutions containing no pyrrhotite. The ΣS^{-II} differences were biased in the direction of losses from the pyrrhotite-containing solutions by an average of 6%, but in a few samples there were apparent gains. The losses, which did not vary systematically with solution composition, were generally too large to be explained by reduction of Mo^{VI} to Mo^{V} or to Mo^{IV}, a process that would transform S^{-II} to S^0 in polysulfides. We are uncertain of the explanation for the losses, but H_2S off-gassing during sample handling may have contributed. A procedural artifact of this kind is indicated by the fact that batches of samples processed at the same time tended to have similar, though not identical ΣS^{-II} losses. The data that we report below are the measured ΣS^{-II} in the pyrrhotite-equilibrated solutions.

Procedures. Individual test samples were prepared in a N_2-filled glove box. Aliquots of Mo stock solutions were combined with aliquots of a freshly prepared 1.00 M NaHS stock solution to give desired concentrations of Mo and HS^-. Sufficient NaCl was added to give desired Cl^- concentrations, and the solutions were brought to volume with deoxygenated, deionized water. In some solutions, the pH was adjusted with 2 M HCl and/or 3 M NaOH to give the desired initial pH.

Approximately 35 mL aliquots of each prepared thiomolybdate solution were transferred into glass ampoules containing approximately 50 mg of pyrrhotite. The ampoules were capped with rubber balloons, removed from the N_2 glove box, and immediately sealed using a propane/O_2 flame. Sealed samples were allowed to react at room temperature (23-27 ^{o}C) with periodic shaking by hand to aid mixing. Reaction times in the ampoules ranged from 22 to 264 days.

After the reaction time, ampoules were opened in a N_2 filled glove box. Solutions were filtered (0.02 µm pore diameter, Whatman Anotop 25), and the pH and total sulfide immediately determined. In some cases, a UV-visible absorption spectrum was obtained. Residual pyrrhotite was washed with deionized water and methanol, and dried by vacuum filtration in the glove box. Selected samples were examined by X-ray diffraction, confirming that the pyrrhotite composition did not change during the experiments.

Analyses. Sulfide was determined by potentiometric (Ag/Ag_2S electrode) titration with $HgCl_2$ after raising the sample pH to 13 with NaOH. This titration determines not only free sulfide (H_2S+HS^-), but also sulfide bound to thiomolybdates and polysulfides, if any. Titrations were performed on an automatic titrator and have an estimated precision of ±5%. The pH was determined by glass electrode against a double junction reference electrode. Total molybdenum was determined by flame (N_2O-acetylene) atomic absorption at a wavelength of 313.3 nm. Samples for Mo determination were diluted volumetrically to give ΣMo = 3–5 ppm. Sulfide was oxidized to sulfate with BrCl and then 1000 ppm Al was added to suppress interference from Fe (David, 1968). The Al content of samples and standards were matched. Total iron was determined using flame (air-acetylene) atomic absorption at 248.3 nm. In only a few cases, dilution with deionized water was necessary to keep sample concentrations within the optimum working range. Precision in both Mo and Fe determinations is estimated to be ±5%.

II. Solubility Data.

Table S-1. Solubility data

Run No.	pH	ΣS^{-II} (M)	ΣMo (M)	ΣFe (M)	I (M)	ΣNH_3 (M)	Reaction time (d)
5.1	8.73	3.00E-03	3.84E-04	1.00E-05	0.71	6.24E-03	24
5.2	8.73	4.80E-03	3.84E-04	1.50E-05	0.71	6.24E-03	28
5.3	8.82	6.50E-03	4.12E-04	7.00E-06	0.71	6.00E-03	28
5.4	8.85	8.40E-03	3.84E-04	1.80E-05	0.71	5.91E-03	28
12.1	9.08	3.86E-02	4.03E-04	5.00E-06	0.05	4.62E-03	26
12.2	9.00	2.06E-02	4.03E-04	3.00E-06	0.03	4.94E-03	26
12.3	8.92	1.15E-02	4.12E-04	1.00E-06	0.02	5.25E-03	26
9.1	9.15	1.22E-02	4.13E-04	3.60E-05	1.41	5.21E-03	22
9.2	9.14	1.25E-02	4.13E-04	1.80E-05	0.71	4.91E-03	22

9.3	9.14	1.23E-02	4.13E-04	1.40E-05	0.36	4.46E-03	22
9.4	9.12	1.24E-02	3.77E-04	7.00E-06	0.01	4.46E-03	22
13.1	8.03	8.90E-03	3.50E-04	2.10E-05	0.71	7.24E-03	68
13.2	8.12	9.70E-03	3.50E-04	1.50E-05	0.71	7.17E-03	68
13.3	8.36	9.80E-03	3.76E-04	3.10E-05	0.71	6.92E-03	68
13.4	8.58	1.01E-02	3.53E-04	1.40E-05	0.71	6.57E-03	68
14.1	8.12	8.90E-03	3.39E-04	8.00E-06	0.02	7.05E-03	50
14.2	8.46	1.03E-02	3.21E-04	6.00E-06	0.02	6.55E-03	50
14.3	8.77	1.09E-02	3.68E-04	4.00E-06	0.02	5.76E-03	50
14.4	9.21	1.09E-02	3.86E-04	4.00E-06	0.02	4.07E-03	50
3.9	8.76	1.02E-02	1.08E-04	3.10E-05	0.71	2.31E-03	35
3.1	8.78	9.80E-03	7.30E-05	3.00E-05	0.71	1.53E-03	35
3.11	8.78	9.90E-03	7.70E-05	3.00E-05	0.71	1.38E-03	42
3.12	8.77	9.50E-03	6.20E-05	2.90E-05	0.71	1.07E-03	42
3.13	8.77	9.20E-03	6.20E-05	2.40E-05	0.71	7.70E-04	47
15.1	8.72	1.09E-02	3.22E-04	8.00E-06	0.02	5.91E-03	63
15.5	8.67	9.90E-03	3.31E-04	4.00E-06	0.01	3.03E-03	60
15.6	8.78	8.70E-03	2.32E-04	3.00E-06	0.01	1.43E-03	60
15.2	8.80	9.60E-03	1.66E-04	4.00E-06	0.01	7.10E-04	63
15.7	8.85	8.40E-03	1.19E-04	2.00E-06	0.01	4.40E-03	60
15.3	8.88	9.00E-03	9.30E-05	3.00E-06	0.01	3.24E-03	63
15.4	9.02	8.70E-03	4.30E-05	3.00E-06	0.01	9.70E-04	63
7.8	8.26	1.16E-03	9.80E-05	3.30E-05	0.70	8.0E-05	99
7.3	8.49	1.23E-03	1.02E-04	2.20E-05	0.70	8.74E-05	99
7.7	8.11	7.03E-03	9.00E-06	5.00E-06	0.70	7.71E-06	100
7.2	8.99	7.70E-03	1.00E-05	2.00E-06	0.70	8.57E-06	100
1.2	9.29	1.84E-02	1.09E-03	9.80E-05	0.70	9.31E-04	264
1.4	9.19	1.45E-02	7.69E-04	9.80E-05	0.70	6.59E-04	264
1.5	9.17	1.35E-02	5.76E-04	7.00E-05	0.70	4.94E-04	264
1.6	9.11	1.27E-02	4.52E-04	6.60E-05	0.70	3.87E-04	264
1.7	9.14	1.22E-02	4.00E-04	5.30E-05	0.70	3.43E-04	192
1.9	9.00	1.04E-02	1.77E-04	4.30E-05	0.70	1.52E-04	192
2.1	9.25	1.08E-02	2.85E-04	2.70E-05	0.70	2.44E-04	27
2.5	9.17	1.07E-02	2.43E-04	1.50E-05	0.70	2.08E-04	57
2.2	9.11	1.00E-02	1.99E-04	2.60E-05	0.70	1.71E-04	27
2.6	9.20	9.70E-03	1.49E-04	2.50E-05	0.70	1.28E-04	62
2.3	9.03	9.10E-03	9.60E-05	2.10E-05	0.70	8.23E-05	28
2.4	9.16	8.70E-03	9.10E-05	1.90E-05	0.70	7.80E-05	56
2.7	9.05	9.00E-03	6.30E-05	1.90E-05	0.70	5.40E-05	63
2.8	8.97	8.70E-03	5.40E-05	1.70E-05	0.70	4.63E-05	64

III. Comparison of peaks in Figure 2A, main paper, to peaks for known compounds.

Table S-2. For each entry, the leading 3-digit number is the wavelength (nm) of an absorption peak and the number in parentheses is the molar extinction coefficient ($M^{-1}cm^{-1}$).

Anglin 1987		McDonald 1980	Coucouvanis 1980	This Work
$[(Fe_2S_2)(MoO_2S_2)_2]^{4-}$		$[Fe(MoS_4)_2]^{3-}$	$[Fe(MoS_4)_2]^{3-}$	Figure 2A
H_2O	MeCN[a.]	MeCN[a.]	DMF[a.]	H_2O
290	290(23100)	no data	290(21350)	288(13150)
350		347(26920)	348(25546)	348(15750)
	372(14600)	372(sh16070)	375(sh)	378(sh)
		409(sh9150)	409(9848)	
				440(sh)
510	526(12200)	507(18970)	510(18254)	506(7900)
		577(7750)	583(8360)	574(5740)

[a.] MeCN=acetonitrile solvent; DMF=dimethylformamide solvent.

IV. Trends in ΣFe and ΣMo in Well-Studied Modern Euxinic Basins.

Table S-3 gives representative ΣFe and ΣMo concentrations in the deep waters of three well-studied euxinic basins. The basins are organized in the table so that ΣS^{-II} in the deep waters increases downward. Going downward in the ΣFe_{aq} column, the values are seen to flatten whereas in the ΣMo_{aq} column the values pass through a minimum. These are the trends predicted in Figure 5 of the main paper.

Table S-3. Compositions of deep waters in three well-studied euxinic basins.*

Basin	ΣS^{-II} (mM)	ΣFe_{aq} (μM)	ΣMo_{aq} (μM)
Cariaco	0.030	0.300	0.084
Black Sea	0.400	0.038	0.003
Framvaren Fjord	6.000	0.025	0.018

* Data from: Helz et al. 2011; Emerson and Huested, 1991;Landing and Westerlund, 1988;Lewis and Landing, 1991, 1992; and Li et al. 2011.

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