

# Enhanced Dissolution of Cinnabar (Mercuric Sulfide) by Dissolved Organic Matter Isolated from the Florida Everglades

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Organic matter isolated from the Florida Everglades caused a dramatic increase in mercury release (up to 35  $\mu$ M total dissolved mercury) from cinnabar (HgS), a solid with limited solubility. Hydrophobic (a mixture of both humic and fulvic) acids dissolved more mercury than hydrophilic acids and other nonacid fractions of dissolved organic matter (DOM). Cinnabar dissolution by isolated organic matter and natural water samples was inhibited by cations such as  $\text{Ca}^{2+}$ . Dissolution was independent of oxygen content in experimental solutions. Dissolution experiments conducted in DI water (pH = 6.0) had no detectable (<2.5 nM) dissolved mercury. The presence of various inorganic (chloride, sulfate, or sulfide) and organic ligands (salicylic acid, acetic acid, EDTA, or cysteine) did not enhance the dissolution of mercury from the mineral. Aromatic carbon content in the isolates (determined by  $^{13}\text{C}$  NMR) correlated positively with enhanced cinnabar dissolution.  $\zeta$ -potential measurements indicated sorption of negatively charged organic matter to the negatively charged cinnabar ( $\text{pH}_{\text{pzc}} = 4.0$ ) at pH 6.0. Possible mechanisms of dissolution include surface complexation of mercury and oxidation of surface sulfur species by the organic matter.

## Introduction

Dissolved organic matter (DOM) interacts extensively with cations in natural waters and soils, with important effects on solubility, mobility, and toxicity of many trace metals (1). For example, humic substances, which represent a major fraction of DOM, have been shown to increase the solubility of several oxide and hydroxide minerals (2, 3) and to increase the mobility of gold from supergene ore minerals (4). The solubilities of relatively insoluble sulfide minerals have also been shown to increase in the presence of soil humic acids (2). Despite the ubiquitous presence of humic substances in natural waters and the toxic nature of mercury to organisms, the role of humic substances in the dissolution of cinnabar (red HgS), a major ore mineral and a sink of mercury (as black metacinnabar) in contaminated sediments (5), has not been studied before.

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In the absence of DOM, the speciation of mercury in aquatic environments is mostly controlled by chloride [ $\text{HgCl}^+$ ,  $\text{HgCl}_2^0$ ], sulfide ( $\text{HgS}^0$ ), and pH [ $\text{Hg}^{2+}$ ,  $\text{Hg}(\text{OH})^+$ ,  $\text{Hg}(\text{OH})_2^0$ ] (6, 7). However, in the presence of DOM, Hg–DOM complexes are thought to be the predominant species in oxic environments (8–10). On the other hand, even under mildly reducing conditions, mercury forms precipitates with sulfide (11). Cinnabar is an extremely insoluble solid with a solubility product of  $10^{-36.8}$  for the reaction (12, 13)



Cinnabar can dissolve, forming soluble aqueous complexes in the presence of high (7 mM) sulfide concentrations at pH > 6 (11, 13–16) or in the presence of elemental sulfur (16). The presence of  $\text{Fe}^{3+}$  in acid mine waters (pH < 2.0) has also been shown to release mercury through the oxidation of cinnabar (17). Due to the strong binding of mercury by sulfur, the solubility enhancement of cinnabar by humic substances is expected to be insignificant (2).

In this study, we show that DOM, particularly the humic fractions, enhance the release of mercury from cinnabar both under oxic and anoxic conditions. Enhanced cinnabar solubility has important geochemical significance. Recently, Barnett et al. (5) observed metacinnabar in a mercury-contaminated soil in Oak Ridge, TN. In such mercury-contaminated areas and in other conditions favorable for HgS formation, humic substances could enhance mercury mobilization and affect bioavailability.

## Materials and Methods

Analytical reagent-grade chemicals and distilled water were used in all the experiments. Cinnabar (red HgS) was purchased as a natural mineral powder from Fisher Scientific and certified to be >99.5% pure. The solid was confirmed to be cinnabar by X-ray diffraction. The surface of the cinnabar was cleaned by leaching with 1.0 M trace metal-grade HCl (Fisher) for 3 days and by subsequent washing with distilled water. The solid was separated using a 0.45- $\mu$ m Millipore filter, dried at 60  $^\circ\text{C}$ , and stored dry for later use. The surface area of unwashed cinnabar was 0.98  $\text{m}^2/\text{g}$  as determined using a multipoint BET method (Gemini model 2360).

**Isolation and Characterization of DOM.** The organic matter samples used in this experiment were isolated from various locations in Water Conservation Area 2 (the latitudes and longitudes are as follow: F1 site, 26 $^\circ$ 21'35" N, 80 $^\circ$ 22'14" W; 2BS site, 26 $^\circ$ 09'17" N, 80 $^\circ$ 22'41" W; U3 site, 26 $^\circ$ 17'15" N, 80 $^\circ$ 24'41" W) in northern Everglades, FL, as a part of an ongoing research project to understand the cycling of mercury in the Everglades. For comparison, two well-characterized Suwannee River humic (SR-HA) and fulvic (SR-FA) acid standards supplied by the International Humic Substances Society (IHSS) were also used (18). DOM samples from the Everglades were separated into hydrophobic (HPoA) and hydrophilic acids (HPiA) and hydrophobic (HPoN) and hydrophilic neutrals (HPiN) using the XAD-8/XAD-4 resin method (19). In a few selected samples, the HPoA fraction of organic matter was further separated into fulvic acid (FA) and humic acid (HA) by standard techniques (20). The isolation procedure used is given in a flow diagram (Figure 1).

Elemental compositions of organic matter isolates were determined at Huffman Laboratories (Golden, CO) by the method described in Huffman and Stuber (21). Acid functional groups in hydrogen-saturated humic samples were

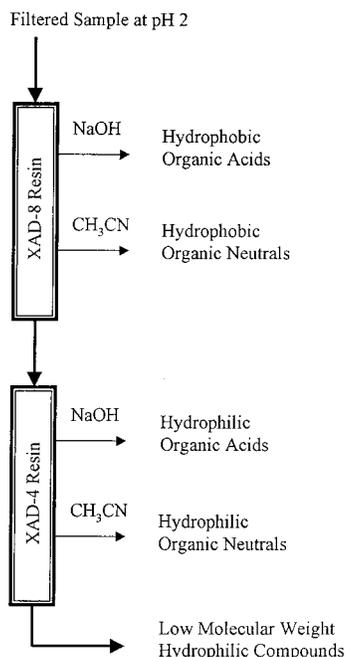


FIGURE 1. Schematic diagram of the XAD-8/XAD-4 isolation scheme.

determined by alkaline titration of samples that were dried to constant weight in a desiccator containing  $P_2O_5$ . About 10 mg of samples was dissolved in about 15 mL of 0.01 M  $KNO_3$  solution and titrated with 0.1 M NaOH to pH 12 on an autotitrator (Radiometer model ABU 93). The carboxyl group content was determined as the amount of base consumed to reach a pH of 8.0; phenol groups were estimated as twice the amount of base used to raise pH from pH 8 to pH 10 after appropriate blank subtraction (22).

Quantitative information on various functional group contents on these isolates was obtained using a liquid- or solid-state carbon-13 nuclear magnetic resonance ( $^{13}C$  NMR) technique (23). To further characterize the organic matter, the specific UV absorbance (SUVA) of organic matter was measured on isolates by dissolving a sample in distilled water and measuring DOC and SUVA (24). The DOC concentrations were measured using a TOC analyzer (O. I. Corporation model 700, College Station, TX). The UV absorbance was measured at 254-nm wavelength on a spectrophotometer (Hewlett-Packard model 8453).

The number-average molecular weight of the isolates was determined by high-pressure size exclusion chromatography (HPSEC). The instrument was comprised of a Shimadzu (Kyota, Japan) LC-600 pump, a Shimadzu SPD-6A UV detector, and a Waters (Milford, MA) Protein-Pak 125 modified silica gel column. The eluents were detected at a wavelength of 224 nm. The analytical procedures were similar to those of Chin et al. (24). The relative standard deviations from triplicate analysis were  $\sim 10$ –12%.

**Dissolution Experiments.** Stock solutions of organic matter isolates and model compounds were prepared in distilled water and adjusted to pH  $6.0 \pm 0.1$  (unless otherwise specified) with dilute NaOH and to ionic strength 0.01 M with  $NaNO_3$ . Solutions containing organic matter (50 mL of  $\sim 20$  mg C/L, unless otherwise specified) were added to cinnabar ( $100 \pm 5$  mg) in 125-mL glass Erlenmeyer flasks. All experiments were conducted in triplicate (three separate flasks). Glass beads (20 beads, 6 mm diameter) were added to each reaction vessel and were shaken in an orbital shaker at 200 rpm. Several blank dissolution experiments were also conducted in distilled water, in which cinnabar was subjected to the same experimental conditions as those in the presence of organic matter (such as pH, ionic strength, shaking

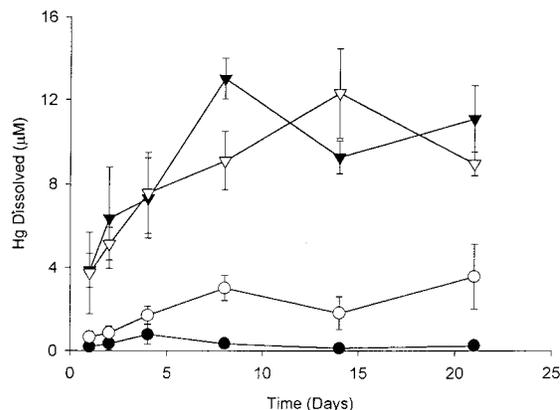


FIGURE 2. Kinetics of dissolution of cinnabar (2 g/L) by F1 hydrophobic acid at concentrations of 5 mg C/L (●), 20 mg C/L (○), 50 mg C/L (▼), and 100 mg C/L (▽). Error bars represent standard deviation from triplicate analysis.

conditions, and filtration). With or without the presence of organic matter, there was no measurable release (i.e., above the detection limit of the instrument) of Hg from cinnabar in the absence of stirring. On the basis of the results of kinetic experiments (Figure 2), dissolution was carried out for a period of 7 days after which near steady-state conditions were reached. Samples that were sparged with nitrogen and kept free of oxygen showed no difference in dissolution rate from those that were free to exchange with atmosphere. Because of this, all experiments were conducted open to the atmosphere. In the case of sulfide as a ligand, sodium sulfide ( $Na_2S \cdot 9H_2O$ ) was added after sparging the experimental solution with 99.999% pure nitrogen in a glovebox. The sample was then kept from contacting oxygen during the entire experimental period.

At the end of 7 days, the samples were filtered using 0.1  $\mu m$  pore size, 25 mm diameter, PTFE disk filters (Whatman) mounted on 60-mL syringes. Total dissolved mercury concentrations were measured using a cold vapor atomic absorption spectrophotometer (CVAAS, Buck Scientific model 400A, East Norwalk, CT). The mercury detection limit for this instrument was 2.5 nM. The instrument was calibrated using six-point mercury standards that were preserved in a 4%  $HNO_3$ –0.04%  $K_2Cr_2O_7$  mixture. The filtered samples were oxidized using  $KMnO_4$  and  $K_2S_2O_8$  and subsequently reduced using  $SnCl_2$  into  $Hg^0$ . The mercury vapor was carried in an airstream into the absorption cell, where the change in transmittance was measured at 253.7 nm by an UV-sensitive phototube.

In selected samples (F1-HPoA), organic matter was added to oxygen-free solutions containing cinnabar, and concentrations of  $Hg^0$ , sulfide, and sulfate were measured. Dissolved oxygen concentration in reaction vessels, measured by colorimetric method (CHEMetrics Inc., Calverton, VA), was 0.60–1.25  $\mu M$  (10–20 ppb).  $Hg^0$  was measured (without  $SnCl_2$  reduction) by sparging the sample with compressed air and carrying the  $Hg^0$  vapor into the absorption cell of the CVAAS. Sparging was done immediately after opening the vessel to prevent the escape of  $Hg^0$  vapor in the headspace. Sulfide was measured using a Hach DR-2000 spectrophotometer at 660 nm. Sulfate in solution was measured by ion chromatography (Dionex-QIC, Sunnyvale, CA) for anions.

The effect of unfractionated DOM on cinnabar dissolution was measured by reacting cinnabar (100 mg) with 0.45- $\mu m$  filtered water samples (50 mL) collected from the F1 (DOC = 38.9 mg/L) and 2BS (DOC = 17.6 mg/L) sites using ultraclean sampling techniques. To check the effect of polyvalent cations (e.g.,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Al^{3+}$ ) on dissolution, these samples were passed through sodium-saturated cation-

**TABLE 1. Elemental Composition, Acid Site Density, and Specific UV Absorbance (SUVA) of Organic Matter Used in Dissolution Experiments**

sample	elemental analysis data (wt %) <sup>a</sup>						acid site density (mequiv/g)		specific UV abs (L (mg of C <sup>-1</sup> ) cm <sup>-1</sup> )	mol wt
	C	H	O	N	S	ash	-COOH <sup>b</sup>	-OH		
SR-HA	53.42	3.89	40.88	1.14	0.68	4.13	4.49	1.69	65.61	1399
SR-FA	53.46	4.29	41.00	0.70	0.56	0.85	5.50	1.16	37.02	1360
F1-HA <sup>c</sup>							3.80	1.07	57.56	1162
F1-FA	52.94	4.37	39.67	1.43	1.60	3.17	5.60	0.88	41.65	850
F1-HPoA	52.24	4.64	39.86	1.53	1.73	5.83	5.45	0.77	39.32	1031
F1-HPiA	47.69	4.14	44.01	2.52	1.63	9.37	5.41	0.84	27.97	832
2BS-HA <sup>c</sup>							3.88	1.12	43.99	944
2BS-FA	52.81	5.04	39.32	1.52	1.31	2.18	5.84	0.75	35.55	793
2BS-HPoA	52.25	4.79	40.15	1.58	1.23	7.31	5.09	0.73	31.70	953
2BS-HPiA	47.32	4.21	44.35	2.58	1.55	15.25	3.07	0.60	23.93	862
U3-HPoA	54.68	4.79	37.50	1.88	1.15	4.55	6.28	0.73	41.40	1180
U3-HPiA	48.99	4.31	42.44	2.89	1.37	29.96	5.31	0.71	27.20	926
E0-HPoN	54.68	5.37	37.00	1.82	1.12	3.61	3.91	0.75	34.62	964
F1-HPiN	55.99	6.59	30.16	6.53	0.74	0.81	2.17	0.55	14.01	196
av	52.21	4.70	39.70	2.18	1.22	7.25	4.70	0.88	37.25	961
SD	2.78	0.73	3.75	1.51	0.39	8.21	1.18	0.30	13.15	291

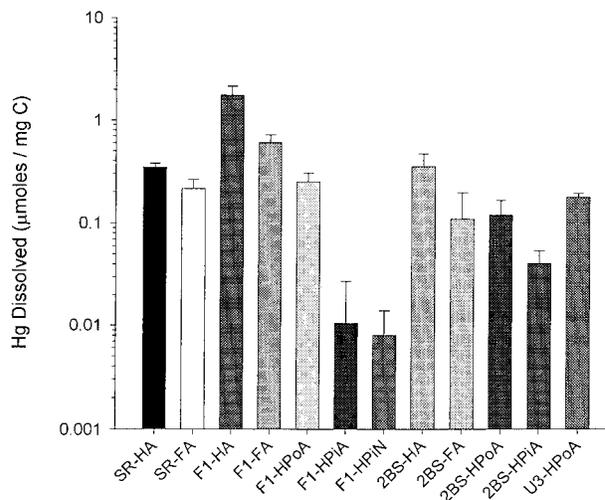
<sup>a</sup> The elemental composition was analyzed on dried samples and reported here on an ash-free basis. <sup>b</sup> Corrected for ash content. <sup>c</sup> Not analyzed for elemental composition due to insufficient sample size.

exchange resins (CER, Dowex MSC-1-H) and then reacted with cinnabar. DOC and UV absorbance measurements of water made before and after passing through the CER columns ensured that there was no change in quality and quantity of organic matter. Mercury concentrations in the organic matter isolates and in water samples (before and after passing through CER columns) were always below the detection limit (i.e., <2.5 nM).

Electrophoretic mobility (EM) measurements were made on acid-washed cinnabar using a laser Doppler microelectrophoresis instrument (Brookhaven Instruments Corp., Holtsville, NY) at a particle concentration of 50 mg/L. In the absence of organic matter, EMs were measured over a pH range of 2.5–7.0 (0.5 pH unit increments) to determine the point of zero charge (pH<sub>pzc</sub>). EM measurements were also measured at constant pH (6.0) and ionic strength (0.01 M KNO<sub>3</sub>) in the presence of various concentrations of organic matter (F1-HPoA). EMs were converted to ζ-potentials using the Smoluchowski equation (25).

## Results and Discussion

At pH 6.0, the equilibrium concentration of total dissolved mercury from the solubility of cinnabar is expected to be very low. There was no measurable (i.e., <2.5 nM) dissolution of mercury from cinnabar in distilled water (no organic matter, pH = 6.0, I = 0.01 M NaNO<sub>3</sub>) both in the presence and in the absence of oxygen. In the presence of DOM, concentrations of dissolved mercury increased for about 1 week, after which a near steady-state condition was reached (Figure 2). In the presence of various fractions of organic matter, the dissolved mercury concentrations ranged from below detection limit to about 1.7 μmol/mg C (Figure 3). At field concentrations of about 20 mg C/L, the above Hg concentrations translate to a maximum of about 35 μM. Humic acid from the F1 site in the Everglades dissolved the greatest amount of mercury. Humic acid fractions dissolved more mercury than the corresponding fulvic acids or other fractions, while the hydrophilic neutral fraction and the hydrophilic acids dissolved the least amount of mercury. There was no measurable dissolution by the hydrophobic neutral fraction. At both the F1 and 2BS sites, the humic acid constituted only about 3–4% of the total hydrophobic acid fraction, with the remaining major fraction being fulvic acid. Differences in release of mercury by F1-FA and F1-HPoA could be due to temporal differences in the sample



**FIGURE 3. Concentrations of Hg from the dissolution of cinnabar (2 g/L) by various fractions of organic matter (see Methods section for sample abbreviations). Error bars represent standard deviations from triplicate analysis.**

collection (F1-HPoA sample collected in April 1996 and F1-HA and FA collected in July 1997).

**Effect of Chemical Characteristics of DOM on Dissolution.** To understand the differences in reactivities of various fractions of organic matter with cinnabar and to possibly elucidate the mechanisms of interaction, the chemical characteristics of different fractions of organic matter were determined (Table 1). The elemental composition of various fractions of organic matter changed very little between different samples. Carbon content was slightly lower in hydrophilic acids than in hydrophobic acids, and oxygen content showed the opposite trend. Mercury is considered to be a soft acid, and it forms very strong complexes with soft bases such as sulfur and nitrogen (Table 2; 26). However, the amount of Hg dissolved (Figure 3) was not strongly correlated with either the N or S contents of the isolates (Table 1).

Among the different metal binding sites in DOM, carboxylic acid groups constitute as much as 90% of the total sites (27) and are known to facilitate the adsorption and surface complexation of organic matter to mineral surfaces (28). Fulvic acids generally had a higher carboxyl group

**TABLE 2. Stability Constants for Complexes between Hg and Various Inorganic and Organic Ligands**

ligand	log $K^a$	stoichiometry	concn used (M)
<b>Inorganic Ligands</b>			
hydroxide	21.8	HgL <sub>2</sub>	0.01
chloride	14.0	HgL <sub>2</sub>	0.01
sulfate	2.5	HgL	0.01
bromide	18.0	HgL <sub>2</sub>	0.01
sulfide (HS <sup>-</sup> )	36.8	HgL(aq)	0.001
<b>Organic Ligands</b>			
acetate	8.4	HgL <sub>2</sub>	0.001
salicylate			0.001
EDTA	20.1	HgL	0.001
mercaptoacetic acid	43.8	HgL	0.001
cysteine	14.2	HgL	0.001

<sup>a</sup> These values are from Martell and Smith (31).

content than the humic acids. The hydrophobic and hydrophilic neutral fractions had low acid densities (Table 1). There was no clear correlation between the carboxyl content and the amount of mercury dissolved.

Specific UV absorbance has been correlated with the degree of aromaticity and the molecular weight of DOM (24). In this study, there was a positive correlation ( $R^2 = 0.84$  significant at 95% confidence level) between SUVA (Table 1) and aromatic carbon content determined by <sup>13</sup>C NMR (Table 3). When organic matter is reacted with mineral surfaces, such as ferric oxides, the hydrophobic, high molecular weight, and high SUVA fraction of organic matter interacts preferentially with the surface and becomes fractionated (28, 29). The molecular weight of isolates did not correlate with the amount of Hg dissolved. There was a positive correlation between the aromatic carbon content and the amount of Hg dissolved ( $R^2 = 0.82$ ) if the two highest mercury concentration samples (F1-HA and F1-FA) were not considered (with the two points included  $R^2 = 0.23$ ). This indicates that fractions higher in aromatic carbon may preferentially sorb to the cinnabar surface and promote Hg dissolution.

**Surface Properties of Cinnabar.** To elucidate the mechanism of interaction between cinnabar and organic matter, the surface properties of cinnabar were explored. For cinnabar, the pH at which the solid surfaces have no net charge (pH<sub>pzc</sub>) occurs at about pH 4.0 (Figure 4a). Thus, the cinnabar surface is negatively charged at experimental pH conditions (pH 6.0). Balsley et al. (30) obtained a pH<sub>pzc</sub> of 3.0 for cinnabar in their iodide sorption experiments and attributed the negative surface to the deprotonation of exposed sulfhydryl groups.

When humic substances (F1-HPoA) were added to a solution containing HgS particles at pH 6.0, the negative potential on the surface increased (-35 to -55 mV) with increasing concentration of humic material (Figure 4b), indicating sorption of organic matter to the surface. Similarly, when F1-HPoA (10.6 mg C/L) was reacted with 2 g/L cinnabar, the DOC concentration decreased by about 15% (to 9.1 mg C/L), as a result of sorption onto the solid surface. The surface charge on cinnabar became less negative as a function of calcium concentration, both in the presence and in the absence of organic matter (Figure 4c). This would indicate that calcium interacts with exposed sulfur groups on cinnabar surface, passivating (blocking) the active surface sites.

The importance of sorption of organic matter to cinnabar surfaces is demonstrated by the inhibition of mercury dissolution in the presence of Ca<sup>2+</sup>. When small quantities ( $2.5 \times 10^{-4}$  M) of Ca<sup>2+</sup> were added to solutions of F1-HPoA, the dissolution of mercury decreased almost by 85% (reduced from 0.25 to 0.04  $\mu$ mol/mg of C; Figure 5). Similarly, when natural water samples (from F1 and 2BS sites) containing polyvalent cations and unfractionated DOM were reacted with cinnabar, there was no measurable (i.e., <2.5 nM) release of mercury. On the other hand, after the polyvalent cations were removed using cation-exchange resins, the DOM in water caused significant release of mercury from cinnabar (Figure 5). Thus in natural systems, polyvalent cations may be an important factor in inhibiting the dissolution of cinnabar.

**Interactions of Model Ligands with Cinnabar.** Possible reactions between organic matter and cinnabar were modeled using various organic and inorganic ligands having varying binding strengths with mercury (31; Table 2). The presence of chloride, bromide, and sulfate in experimental solutions did not enhance the dissolution of mercury under experimental conditions (pH = 6.0; I = 0.01 M; ligand concentrations = 0.01 M). There was a small ( $0.07 \pm 0.11 \mu$ M) release of mercury when cinnabar was reacted with  $10^{-3}$  M sulfide. On the other hand, when  $10^{-4}$  M sulfide was added to the organic matter (F1-HPoA)-cinnabar system, the amount of mercury released did not change as compared to the system with only the organic matter (Figure 5). Only the hydroxide ligand (not shown) dissolved significant quantities ( $1.28 \pm 0.44 \mu$ M) of mercury from cinnabar. The hydroxide concentration used (0.01 M or pH 12) is not representative of natural environments.

Among the organic ligands used in this experiment (Table 2), acetic acid and salicylic acid did not release significant amount of mercury into solution (not shown). Even strong chelating agents such as EDTA had no significant effect on

**TABLE 3. Results of Quantitative <sup>13</sup>C NMR Analysis on Organic Matter Used in Dissolution Experiments<sup>a</sup>**

sample ID	region (ppm)					
	0-62 aliphatic I	62-90 aliphatic II	90-110 acetal	110-160 aromatic	160-190 carboxyl	190-230 ketone
SR-HA <sup>b,c</sup>	21.3	7.3	6.6	35.1	20.7	9.0
SR-FA <sup>b,c</sup>	35.0	10.1	5.0	22.9	21.3	5.6
F1-HA	37.9	17.5	7.4	25.2	8.8	3.2
F1-FA	43.4	15.0	5.4	20.1	13.8	2.2
F1-HPoA	45.0	17.0	5.6	18.2	11.6	2.7
F1-HPiA	43.5	20.6	6.4	13.1	14.6	1.8
2BS-FA	45.8	15.9	5.2	16.5	13.5	3.2
2BS-HPoA	48.5	14.9	4.1	15.4	15.4	1.8
U3-HPoA <sup>c</sup>	42.3	15.0	5.3	19.0	14.4	4.1
E0-HPoN	62.0	13.0	3.2	12.4	8.3	1.0
F1-HPiN	51.8	19.0	4.4	12.0	11.3	1.4

<sup>a</sup> Each carbon fraction is given as % of the total. <sup>b</sup> Thorn et al. (40). <sup>c</sup> These samples were analyzed by liquid-state <sup>13</sup>C-NMR, and all other samples were analyzed by solid-state NMR.

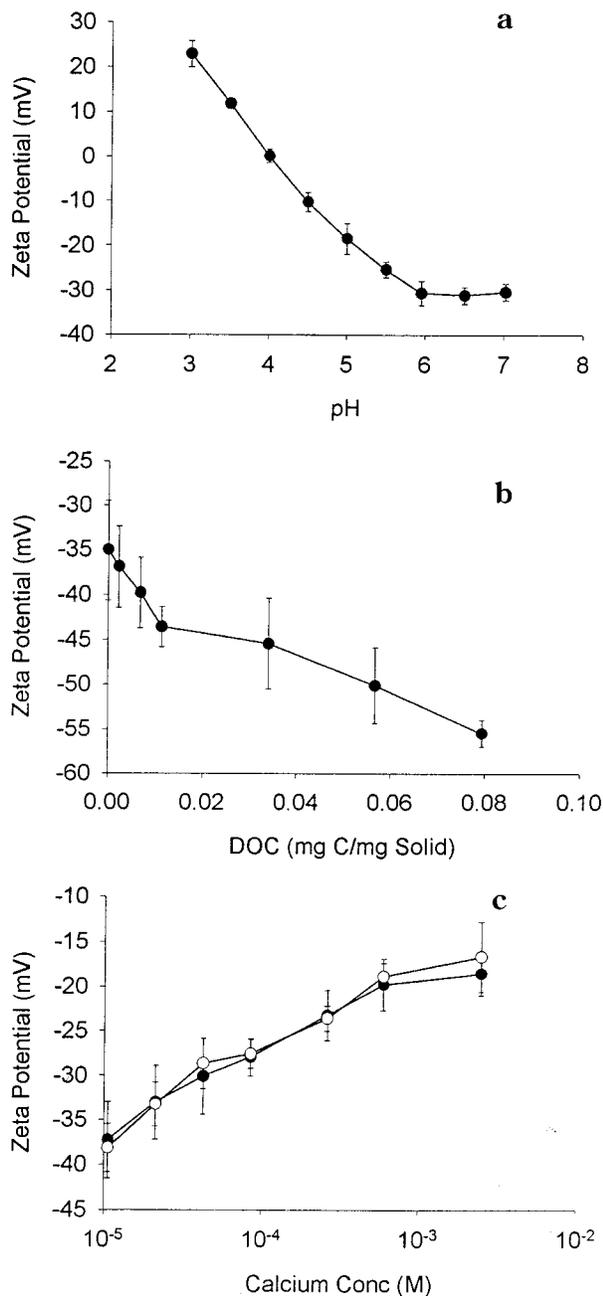


FIGURE 4. Results of electrophoretic mobility measurements ( $\zeta$ -potential) on cinnabar surfaces. (a) pH titration of cinnabar to determine  $\text{pH}_{\text{pzc}}$ . (b) Change in  $\zeta$ -potential as a function of organic matter (F1-HPoA) concentration. (c) Change in  $\zeta$ -potential as a function of calcium concentration in the absence of organic matter (●) and in the presence of F1-HPoA at 0.05 mg C/mg cinnabar (○).

the dissolution of cinnabar (Figure 5). This is in direct contrast to their role in oxide surface dissolution (32, 33), where low molecular weight acids such as salicylic acid have the highest effect on dissolution as compared to the almost null effect of humic substances. Weak interactions of these simple organic acids with cinnabar could be a result of strong covalent bonds between mercury and sulfur in cinnabar.

Cysteine reacted with cinnabar produced measurable quantities ( $\sim 0.002 \mu\text{mol}/\text{mg C}$ ) of mercury in solution (Figure 5). The other sulfur-containing ligand, mercaptoacetic acid, solubilized a significant amount of mercury ( $\sim 0.02 \mu\text{mol}/\text{mg C}$ ) from cinnabar. This might be a result of the extremely high binding strength between mercury and this compound (log  $K = 43.8$  at 25 °C and 1.0 M ionic strength; 31). The

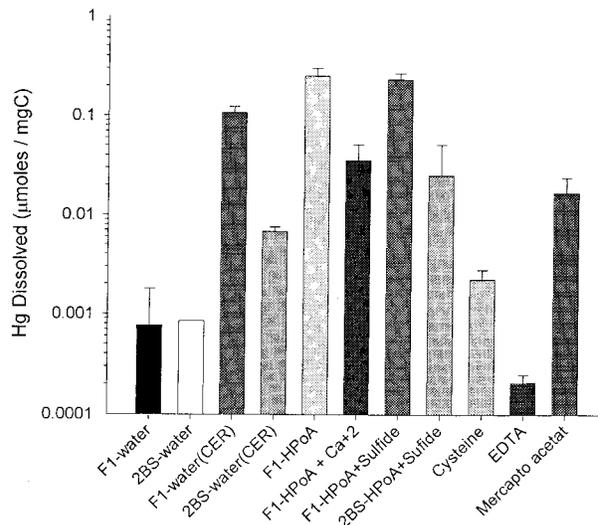
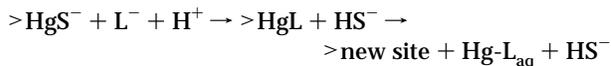


FIGURE 5. Concentrations of Hg from dissolution of cinnabar (2 g/L) by unfractionated organic matter in water samples (CER: samples passed through cation-exchange resins) from Florida Everglades, by model ligands, and in the presence of calcium and sulfide (see text for concentrations used). Error bars represent standard deviation from triplicate analysis.

mercury concentration, when normalized to organic carbon concentration, is still much smaller than when reacted with F1-HPoA. Thus, the humic fractions of organic matter appear to interact very strongly with the cinnabar surface releasing significant quantities of mercury, and this interaction could not be modeled with the weakly interacting model compounds studied here.

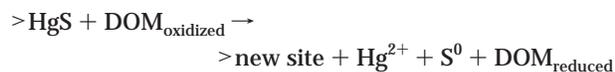
**Proposed Reaction Mechanisms.** The dissolution of cinnabar by organic ligands could be brought about by several pathways. The elementary steps involved in ligand-promoted dissolution are a fast ligand adsorption step, a slow detachment of activated surface complex, and a regeneration of initial surface sites (33). At fixed solid concentration, the dissolved mercury concentration did not increase linearly with the organic matter concentration (Figure 2). This may be a result of monolayer coverage (saturation) of surface sites by organic matter. Rapid adsorption of DOM was observed in electrophoretic mobility experiments. The necessity of mechanical stirring to bring about dissolution of mercury from cinnabar suggests that regeneration of new sites could be rate limiting in these experiments. If dissolution occurs by the formation of surface complexes, the binding between mercury and organic matter must be very strong to compete with mercury-sulfur bonds. The following equations can be written for ligand-promoted dissolution:



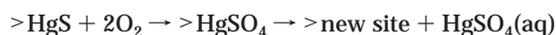
Apart from simple ligand-promoted dissolution, minerals made up of redox-sensitive elements (e.g., sulfides and oxides of Mn, Fe, and U) can also dissolve by reduction and oxidation reactions (34). At the cinnabar mineral surface, both mercury and sulfur can be affected by redox reactions. The mechanism of reductive or oxidative dissolution follows these basic steps: adsorption of the reductant or oxidant, transfer of electrons, release of the reduced or oxidized surface species, and regeneration of the initial surface (31, 34). Some of the released Hg may also be re-adsorbed to the cinnabar surface (17). The role of humic substances in the abiotic reduction

of  $\text{Hg}^{2+}$  to  $\text{Hg}^0$  has long been known (8, 35, 36). However, this seems to be an unlikely mechanism of cinnabar dissolution because generation of  $\text{Hg}^0$  could not be detected even with micromolar quantities of Hg in solution. Past studies of Hg reduction by humic substances have been conducted in aqueous solutions, where mercury is already complexed strongly by organic matter. No evidence exists for humic-mediated, abiotic reduction of mercury from soils or other solid surfaces. Moreover, if dissolution was through the reduction of mercury, one might expect to see equimolar quantities of mercury and sulfide in solution, which was not the case. Sulfide concentration in solution was only about 5% of the molar concentration of mercury.

Oxidation of sulfide on cinnabar surface would weaken the sulfur-mercury bonds facilitating surface complexation and subsequent release of mercury from the surface:



Sulfur could be further oxidized to sulfate or other species of intermediate oxidation states (e.g., sulfite, polythionate, thiosulfate). Oxidative dissolution of cinnabar by  $\text{Fe}^{3+}$  has been proposed to take place in acid mine waters (17). Potential electron-accepting groups (e.g., quinone moieties) are known to occur in humic molecules and are thought to be important in microbially mediated reactions (37). When cinnabar was reacted with solutions of organic matter (F1-HPoA) that were carefully sparged with nitrogen (0.60–1.25  $\mu\text{M O}_2$ ), the measured sulfide concentrations were only about 5% of the total molar concentrations of mercury. On the other hand, the sulfate concentrations were much higher (20.6  $\pm$  0.8  $\mu\text{M}$  after 7 days) than the total dissolved Hg concentrations (3.0  $\pm$  0.6  $\mu\text{M}$ ). This would seem to indicate oxidation of sulfide on the surface by organic matter. To test this, deoxygenated (0.60–1.25  $\mu\text{M O}_2$ ) solutions containing sulfide (0.001 M  $\text{Na}_2\text{S}$ ) and organic matter (~20 mg C/L of F1-HPoA) were reacted in the absence of cinnabar. We did not detect any generation of sulfate in this reaction. Thus, it seems unlikely that organic matter could be directly oxidizing sulfur on mineral surface. It may be possible that organic matter could be catalyzing the reaction between trace oxygen in solution and sulfur on the surface by the following reaction:



High concentrations of sulfate could also be a result of contamination from organic matter (the sulfate concentration in 20 mg C/L of organic matter solution was ~4.5  $\mu\text{M}$ ) or readsorption of dissolved mercury on cinnabar surface (17).

Additional work is required to explain the nature of interaction between sulfide and organic matter. Future research work could involve experiments carried out under strict anoxic conditions, measuring concentrations of various sulfur species in solution (38), and identifying sulfur species on mineral surface by various spectroscopic methods (39). Irrespective of which mechanism is responsible for the dissolution of cinnabar, the ubiquitous presence of humic substances in natural waters makes the organic matter-enhanced solubilization of mercury a potentially important source of mercury in contaminated and pristine soils, sediments, pore waters, and surface waters.

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