Geochimica et Cosmochimica Acta, Vol. 69, No. 6, pp. 1575–1588, 2005

0016-7037/05 $30.00 + .00

doi:10.1016/j.gca.2004.09.029

# Dissolution of cinnabar (HgS) in the presence of natural organic matter

JACOB S. WAPLES,[1] KATHRYN L. NAGY,[1,*] GEORGE R. AIKEN,[2] and JOSEPH N. RYAN[3]

[1]Department of Geological Sciences, 399 UCB, University of Colorado, Boulder, CO 80309, USA
[2]United States Geological Survey, Water Resources Division, 3215 Marine Street, Boulder, CO 80303, USA
[3]Department of Civil, Environmental, and Architectural Engineering, 428 UCB, University of Colorado, Boulder, CO 80309, USA

(*Received December* 22, 2003; *accepted in revised form September* 29, 2004)

**Abstract**—Cinnabar (HgS) dissolution rates were measured in the presence of 12 different natural dissolved organic matter (DOM) isolates including humic, fulvic, and hydrophobic acid fractions. Initial dissolution rates varied by 1.3 orders of magnitude, from $2.31 \times 10^{-13}$ to $7.16 \times 10^{-12}$ mol Hg (mg C)$^{-1}$ m$^{-2}$s$^{-1}$. Rates correlate positively with three DOM characteristics: specific ultraviolet absorbance ($R^2 = 0.88$), aromaticity ($R^2 = 0.80$), and molecular weight ($R^2 = 0.76$). Three experimental observations demonstrate that dissolution was controlled by the interaction of DOM with the cinnabar surface: (1) linear rates of Hg release with time, (2) significantly reduced rates when DOM was physically separated from the surface by dialysis membranes, and (3) rates that approached constant values at a specific ratio of DOM concentration to cinnabar surface area, suggesting a maximum surface coverage by dissolution-reactive DOM. Dissolution rates for the hydrophobic acid fractions correlate negatively with sorbed DOM concentrations, indicating the presence of a DOM component that reduced the surface area of cinnabar that can be dissolved. When two hydrophobic acid isolates that enhanced dissolution to different extents were mixed equally, a 20% reduction in rate occurred compared to the rate with the more dissolution-enhancing isolate alone. Rates in the presence of the more dissolution-enhancing isolate were reduced by as much as 60% when cinnabar was prereacted with the isolate that enhanced dissolution to a lesser extent. The data, taken together, imply that the property of DOM that enhances cinnabar dissolution is distinct from the property that causes it to sorb irreversibly to the cinnabar surface. 

## 1. INTRODUCTION

Interactions of mercury (Hg) in aqueous, particulate, and mineral forms with dissolved organic matter (DOM) play important roles in controlling reactivity, bioavailability and transport of Hg(II), in aquatic systems (Ravichandran, 2004). Several investigators have proposed DOM complexation of Hg(II) as a primary mechanism for the transport of mercury (Meili, 1991; Krabbenhoft and Babiarz, 1992; Driscoll et al., 1994; Shanley et al., 2002) based on a strong correlation between dissolved mercury and dissolved organic carbon (DOC) concentrations in ground, lake, and stream waters. The strongest binding sites for Hg(II) on DOM are reduced sulfur functional groups as determined from synchrotron X-ray absorption spectroscopic measurements (Xia et al., 1999; Skyllberg et al., 2000; Hesterberg et al., 2001) and binding experiments (Benoit et al., 2001; Haitzer et al., 2002; Hsu and Sedlak, 2003; Lamborg et al., 2003). Weaker binding to oxygen functional groups such as carboxyls (Reddy and Aiken, 2001) occurs only at relatively high mercury concentrations, atypical of most natural settings.

Formation of relatively insoluble solid mercury sulfides (HgS), cinnabar or metacinnabar (Martell and Smith, 1998), can inhibit Hg(II) methylation and bioaccumulation (Compeau and Bartha, 1987), and immobilize mercury Hg(II) in sediments. However, the presence of DOM enhances the solubility and dissolution of cinnabar (Ravichandran et al., 1998), which lessens the role of cinnabar in immobilizing Hg(II). DOM also inhibits the precipitation of metacinnabar (Ravichandran et al., 1999), which is conceptually consistent with the dissolution enhancement. In contrast to the spectroscopic evidence that reduced sulfur sites on DOM bind mercury most strongly, enhancement of cinnabar dissolution appears to be correlated with aromaticity, and not the sulfur content, of the DOM based on a limited number of DOM samples from the Florida Everglades examined by Ravichandran et al. (1998).

The interaction between DOM and cinnabar in both promoting dissolution and enhancing aqueous Hg solubility contrasts with observations of the interactions between humic substances and metal oxides. Whereas strong binding of DOM to a dissolved cation generally accounts for the mobility of metals in the aqueous phase of the natural environment, there is no simple relationship between humic substances and oxide mineral dissolution rates despite the fact that low molecular weight organic ligands tend to promote oxide mineral dissolution in the laboratory (Hering, 1995). Furthermore, interactions of DOM with oxide mineral surfaces also can remove DOM and metals from solution via sorption (Jardine et al., 1989; McKnight et al., 1992) and inhibit solid dissolution and precipitation (Hering, 1995). Processes that control sorption interactions of DOM with mineral surfaces are complex with evidence for hysteresis (Gu et al., 1994), different sorption affinities (Davis, 1982; Jardine et al., 1989; Gu et al., 1995; Wang et al., 1997), and competition among different DOM fractions (Ochs et al., 1994; Gu et al., 1996).

We describe the results of experiments on the interactions of

* Author to whom correspondence should be addressed, at Department of Earth and Environmental Sciences, University of Illinois at Chicago (MC-186), 845 West Taylor Street, Chicago, IL 60607-7059, USA (klnagy@uic.edu).
† *Present address:* Golder Associates Inc., 44 Union Blvd., Suite 300, Lakewood, CO USA 80228.

Table 1. Site descriptions for aquatic organic matter isolates.

| Sample | Site description |
|---|---|
| Suwannee River Humic Acid (SRHA)<br>Suwannee River Fulvic Acid (SRFA) | Black water river draining the Okeefenokee Swamp. Sampled at Fargo, Georgia. Vegetation types: Southern Floodplain Forest (Quercus, Nyassa, Taxodium); International Humic Substances Society standards. |
| Ogeechee River Humic Acid (OgRHA)<br>Ogeechee River Fulvic Acid (OgRFA) | Small river draining the Piedmont in Eastern Georgia. Sampled at Grange, Georgia. Vegetation types: Oak-Hickory-Pine Forest (Quercus, Carya, Pinus). |
| Coal Creek Fulvic Acid (CCFA) | Small mountain stream draining the Flattops Wilderness Area, Colorado. Vegetation type: Spruce-Fir Forest (Picea, Abies). |
| F1 Hydrophobic Acid (F1HpoA) | Eutrophied marshland located in Water Conservation Area 2A in the northern Everglades. Vegetation dominated by cattails. (26°21′35″ N; 80°22′14″ W). |
| 2BS Hydrophobic Acid (2BSHpoA) | Relatively pristine marshland located in Water Conservation Area 2B in the northern Everglades. Vegetation dominated by saw grass. (26°09′00″ N; 82°22′30″ W). |
| Ohio River Fulvic Acid (OhRFA) | Major river draining east-central United States. Sampled at Cincinnati, Ohio. Vegetation types: Appalachian Oak Forest, Mixed Mesophytic Forest, Oak Hickory Forest. |
| Missouri River Fulvic Acid (MRFA) | Major river draining north-central United States. Sampled at Sioux City, Iowa. Vegetation types: Northern Floodplain Forest and Wheatgrass, Needlegrass, and Bluestem Grasslands. |
| Pacific Ocean Fulvic Acid (POFA) | Sample collected from 100 m depth, 170 km southwest of Honolulu, Hawaii, Marine organic matter. |
| Lake Fryxell Fulvic Acid (LFFA) | Ice-covered lake in the McMurdo Dry Valleys, Antarctica. Organic matter dominated by autochthonous sources (algae, bacteria). |
| Williams Lake Hydrophobic Acid (WLHpoA) | Seepage lake in north-central Minnesota. Organic matter dominated by autochthonous sources (algae, bacteria, emergent vegetation). |

cinnabar with 12 samples of DOM obtained from a variety of aquatic systems and having a wide range in chemical composition and reactivity. The goals were to quantify the rate of cinnabar dissolution as a function of DOM composition and determine the role of sorption of DOM onto cinnabar in the dissolution mechanism. The results are important for understanding the dynamics of Hg-cycling in the environment, including sites heavily contaminated with Hg such as at Oak Ridge, TN (Barnett et al., 1997), sites that contain naturally occurring or mined deposits of cinnabar (Covelli et al., 2001), sites where cinnabar-containing sediments are transported to organic-rich water bodies such as the Sacramento River and the Sacramento-San Joaquin delta in California (Domagalski, 2001), and sites containing sulfide and atmospherically deposited mercury, such as the Florida Everglades (Hurley et al., 1998; Benoit et al., 1999; Krabbenhoft et al., 2000).

## 2. MATERIALS AND METHODS

### 2.1. Materials

Certified A.C.S. or trace-metal grade reagents and deionized (DI) water (>18.0 MΩ; DOC < 0.2 mg C $L^{-1}$) were used. Glassware was cleaned with 10 wt% NaOH to remove DOM, and an aqua regia solution (three parts concentrated HCl, one part concentrated $HNO_3$, and two parts water) to remove cinnabar and mercury, and then rinsed at least 15 times with DI water.

Powdered cinnabar ($HgS_{red}$), 99.5+% (Acros Organics), was soaked in $HNO_3$ (10% by volume) for 3 d and then rinsed with 100 mL aliquots of DI water until a pH of 6 to 7 was measured for at least 10 successive rinses. For each rinse, the mixture was stirred vigorously with a glass rod and then left to settle for 2 min. Fine suspended particles were removed by decanting. Cinnabar was oven-dried at 60°C and then sieved (30–70 $\mu$m fraction) using Spectra/Mesh nylon filters. X-ray diffraction (Scintag PADV powder diffractometer with graphite beam monochrometer; Cu-K$\alpha$ radiation; 10° to 80° 2$\theta$ at 2° 2$\theta$ $min^{-1}$) was used to confirm mineral purity. A surface area of 0.23 $m^2$ $g^{-1}$ was measured by BET $N_2$ adsorption (Gemini 2360). Scanning electron microscopy (SEM; ISI SX-30) showed particles of irregular shape varying in maximum dimension from about 2 to 40 $\mu$m.

Natural organic matter (NOM) isolates in freeze-dried form were obtained from a variety of environments (Table 1) using methods described by Aiken et al. (1992). NOM isolates were characterized by determining elemental composition (Huffman and Stuber, 1985), molecular weight by high-pressure size exclusion chromatography (HPSEC) (Chin et al., 1994), specific ultraviolet (UV) light absorbance (Weishaar et al., 2003), and by $^{13}$C-NMR spectroscopy (Wershaw, 1985) (Table 2). Select samples were examined for sulfur speciation using X-ray absorption spectroscopy (XANES) (Vairavamurthy et al., 1997) (Table 2).

Dried NOM isolates were dissolved in 0.01 M $NaNO_3$ and the solutions were adjusted to pH 6.0 (±0.2) using either NaOH or $HNO_3$ while in contact with the atmosphere. DOC concentrations were determined using Oceanography International Model 700 and 1010 carbon analyzers. UV light absorbance measurements were made with a Hewlett-Packard 8453 spectrophotometer. Specific UV absorbance at 280 nm ($SUVA_{280}$), an indicator of the degree of aromaticity (Weishaar et al., 2003), was determined for each DOM isolate solution as:

$$\left(\frac{\text{UV absorbance}}{\text{DOC}}\right) = \text{SUVA}_{280} \quad (1)$$

where UV absorbance is expressed as absorbance per cm of path length and DOC concentration is in mg C $L^{-1}$. Errors in $SUVA_{280}$ values were calculated using an error of ±0.005 absorbance units for the UV absorbance measurement and the standard deviation between duplicate measurements for the DOC concentration. Values of $SUVA_{280}$ for the DOM solutions in 0.01 M $NaNO_3$ were corrected for interfering absorbance (with a peak absorbance observed at 207 nm) from a solution of 0.01 M $NaNO_3$. Average values for $SUVA_{280}$ errors were ±0.0020 for solutions from the standard dissolution experiments and ±0.0010 for solutions from sorption isotherm measurements using F1HpoA and WLHpoA. The difference in errors is a function of the two different instruments used for the DOC analyses.

### 2.2. Experimental Methods

#### 2.2.1. Dissolution Experiments

In batch experiments, cinnabar was reacted with one isolate (standard dissolution experiment), two isolates (mixture experiment), or prereacted with one isolate before reacting with a second isolate that was added to or replaced the first isolate (prereacted mixture and prereacted replacement experiments, respectively). Control experiments also were carried out: pure water, 0.01 M $NaNO_3$, 10 g $L^{-1}$ HgS(s) in 0.01 M $NaNO_3$, and DOM in 0.01 M $NaNO_3$.

All experiments were conducted at 22 ± 1°C in 125 mL glass