Mercury Release from Cinnabar in Water and Aqueous Solutions of Hydroquinone or Ascorbic Acid

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THESIS

Submitted as partial fulfillment of the requirements
for the degree of Master of Science in Earth and Environmental Sciences
in the Graduate College of the
University of Illinois at Chicago, 2013

Chicago, Illinois

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This thesis is dedicated to Reza, my family and friends without whose support it would never have been accomplished.

AKNOWLEDGEMENTS

The work for this thesis was supported by the Geobiology and Low-Temperature Geochemistry Program of the U.S. National Science Foundation under grant EAR- 0952311 and the Subsurface Biogeochemical Research Program of the Office of Biological and Environmental Research, Office of Science, U.S. Department of Energy under grant DE-SC0001730. I would like to thank my advisor Kathryn Nagy for professional guidance and patience during the research. Also, I would like to thank my committee members D'Arcy Meyer-Dombard and Jean Bogner for encouraging words and thoughtful suggestions; my lab mates Ken Kearney, Thomas Heller and Genevieve Nano for their support; and to Gene Harris, Linnea Heraty and Abe Beloso Jr. for their technical assistance. Sulfur XANES data were obtained at the Advanced Light Source, Lawrence Berkeley National Laboratory courtesy of Alain Manceau. The ALS is supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract DE-AC02-05CH11231 at the Lawrence Berkeley National Laboratory.

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LIST OF ABBREVIATIONS

DDI	Doubly De-ionized
DOM	Dissolved Organic Matter
HCl	Hydrochloric Acid
Hg	Mercury
HgS	Cinnabar
HNO_3	Nitric Acid
HQ	Hydroquinone
$KMnO_4$	Potassium Permanganate

SUMMARY

The release of mercury from cinnabar in water and aqueous solutions of hydroquinone and ascorbic acid was investigated in batch experiments under various conditions. Experiments were conducted in a nominally anoxic or oxic state using solutions that contained different ratios of reactant to cinnabar and recycled cinnabar; variable mass of cinnabar; and variable pH. Mercury concentrations were obtained using Cold Vapor Atomic Fluorescence Spectroscopy.

The amount of mercury released in the presence of hydroquinone was about the same as that released in solutions of water under both anoxic and oxic conditions. In the presence of each of these reactants, more mercury was released than in the presence of ascorbic acid. Decreased release of mercury with increased cinnabar concentration was observed in experiments containing water or water and hydroquinone, which is likely an effect of particle aggregation and the effective decrease of the number of exposed reactive surface sites. Recycled cinnabar surfaces released less mercury than the initial surfaces. The amount of sulfate measured in selected solutions is two to three orders of magnitude greater than the amount of mercury released. Furthermore, pH over the range of ~ 3 to 8 did not measurably affect the release of mercury from cinnabar.

Altogether the results indicate a strong dependence of the release of mercury from cinnabar on the presence of oxygen. The oxidation of sulfur species at the surface of cinnabar likely weakens mercury-sulfur bonds releasing mercury to solution; or, oxidized sulfur species may remain at the surface, increase in concentration and eventually slow the reaction. Any available reductants may be able to remove the oxidized layer and promote dissolution.

I. INTRODUCTION AND BACKGROUND

1.1 *The Mercury Problem*

The significant introduction of mercury to the global budget by processes such as oceanic evasion, volcanic emissions, and natural terrestrial fluxes is dwarfed by the mercury released as air pollutants during combustion processes such as oil, gas, and coal burning (Mason et al., 1999). Moreover, the loading of mercury to the atmosphere, soils, and aquatic environment is compounded by anthropogenic contributions via products containing mercury, such as compact fluorescent lamps/light bulbs (CFLs), ballasts, and thermostats.

In aquatic systems, the pathway for magnification of mercury into higher trophic level species is direct. Mercury is methylated by microbes (Compeau and Bartha, 1987; Gilmour et al., 1998), likely adsorbed onto or into the cells of simple organisms; passed up the food chain through the consumption of contaminated species; and concentrated at toxic levels in seafood consumed by humans. For example, Hardhead catfish, Southern kingfish and Reddrum meats were determined to contain as much as 1.25 ppm Hg (Hall et al., 1978). The EPA recommends a reference dosage level of 1×10^{-4} mg kg^{-1} d^{-1} stating that one can safely consume two 8 oz fish steaks per month at concentrations of 0.37 – 0.47 ppm, and no more than one per month at concentrations ranging from 0.47 to 0.94 ppm (EPA 2000). The toxic levels of mercury in aquatic species have led to fish consumption advisories in many states (Fish Consumption Advisories, 2012).

The biomagnification of mercury can be minimized by preventing mercury release to the environment or, by sequestering the mercury(II) after it has been released. Immobilizing mercury

can be accomplished by precipitating the highly insoluble mineral, cinnabar. However, whereas mercury bound in an insoluble mineral state decreases the pool readily available for methylation, research has demonstrated that dissolved organic matter (DOM) present in aquatic environments acts to re-solubilize this mercury (Ravichandran et al., 1998; Waples et al., 2005; Kerr, 2007).

1.2 *Physical and Chemical Characteristics of Mercuric Sulfides*

In the environment mercuric sulfides exist as cinnabar (α-HgS) and metacinnabar (β-HgS) (Dryssen et al., 1991; Schuster, 1991). Under standard surface conditions, the formation of the more stable phase, cinnabar, is favored under anoxic conditions (Morel et al., 1998; Svensson et al., 2006; Wang et al., 1995), at low pH, and at relatively low sulfide concentrations (Morel et al., 1998; Dryssen et al., 1991). In addition, metacinnabar formation is kinetically controlled and metacinnabar will, over time, convert to the cinnabar structure (Paquette et al., 1997). Cinnabar is highly insoluble with $K_{sp} = 10^{-36.8}$ (Schwarzenbach and Widmer, 1963; Sillen, 1964) for the reaction,

$$\mathbf{HgS + H^{+} \rightarrow Hg^{2+} + HS^{-}} \qquad \textbf{Reaction 1}$$

at (I = 1.0 M, T = 20 °C).

The stability and low solubility of cinnabar make it a good sink for inorganic mercury(II) in anoxic environments.

The dissolution of cinnabar occurs under oxic conditions (Holley et al., 2005; Kerr 2007) and is enhanced substantially in the presence of DOM (Ravichandran et al., 1998; Waples et al., 2005). Amounts and rates of mercury released from cinnabar over 10 h in the presence of DOM samples from a wide range of natural environments were correlated with the aromaticity of the

DOM (Waples et al., 2005). These authors therefore hypothesized that redox sensitive aromatic moieties within the DOM played a role in the mechanism of mercury release from HgS. Dissolution of cinnabar may depend not only upon the redox reactivity of the DOM, but also on the type of redox environment in which both the DOM and cinnabar reside.

1.3 *Fluctuations of Redox Conditions in Natural Systems*

There is the potential for many redox reactions to occur between cinnabar and DOM during water table fluctuations (Fig. 1). During periods of rain or flooding, a rise in the water table can move the anoxic/oxic boundary toward the surface (Fig. 1: B to A), subjecting the sediments to a more reducing environment. Alternatively, during sunny periods or periods of drought, a drop in the water table moves the boundary down (Fig. 1: A to B) and the sediments experience a more oxygenated environment. Further, shifts in the anoxic/oxic boundary can result in a relatively sudden introduction of DOM into waters of different Eh where the redox state of DOM moieties may change. When the water table falls, oxidized moieties of DOM may potentially react with mercuric sulfide minerals releasing soluble mercury(II) that can be consumed by organisms. Likewise, a higher water table may result in a reaction between reduced moieties of DOM and these minerals.

1.4 *Composition of Dissolved Organic Matter*

DOM is an infinitely heterogeneous (Leenheer, 2003) macromolecular material formed early in the decay of biomatter (MacCarthy et al., 2001). The size of the organic molecules and

the distribution of oxygen functional groups within them are properties used to classify organic matter operationally into at least two groups: fulvic and humic acids (Leenheer, 2003).

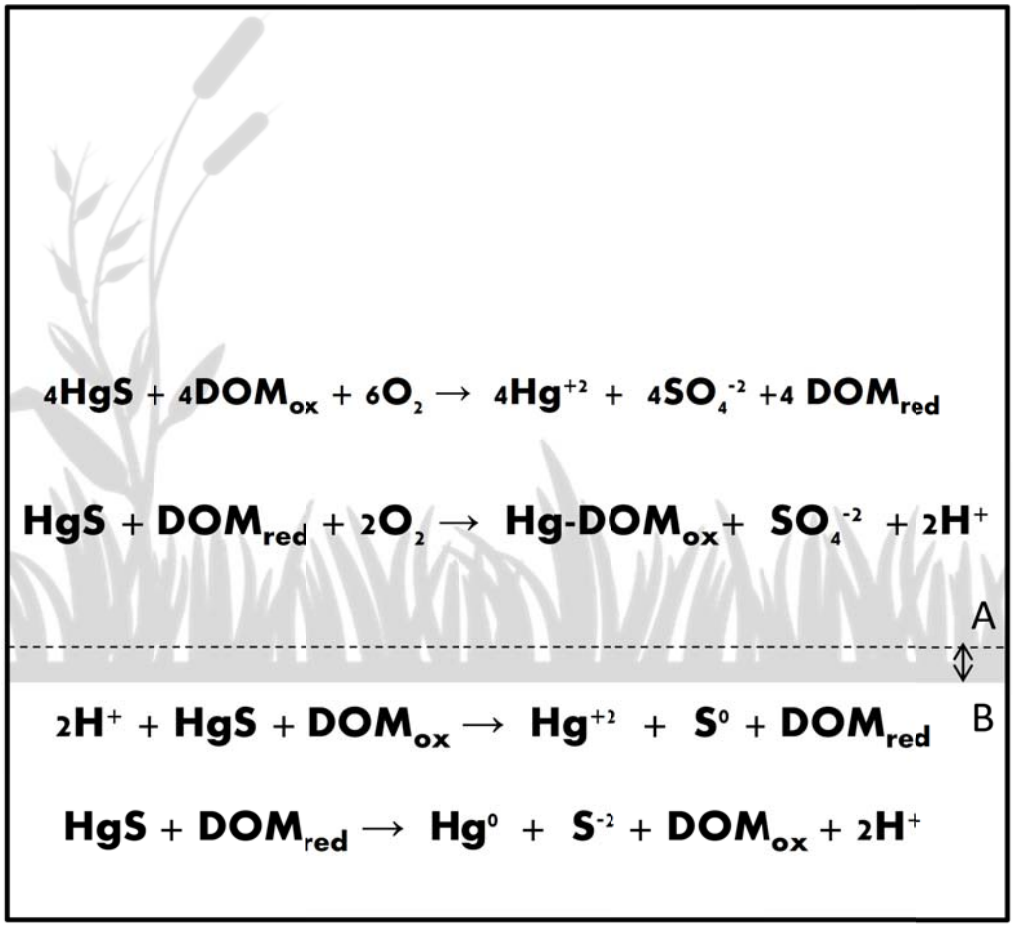

Figure 1. Schematic of mercuric sulfide and dissolved organic matter interactions under various redox conditions. The oxic/anoxic boundary (dashed line) is able to fluctuate between A (relatively higher water level due to influx of water into the system) and B (relatively lower water level due to efflux of water from the system) in response to hydrological events. Possible reactions that may occur between DOM and mercuric sulfides under different redox conditions are shown. All reactions are written assuming some DOM moiety and sulfur or mercury undergo changes in redox states.

Fulvic acids have a large percentage of oxygen functional groups, a high solubility over a wide range of pH values, and a relatively lower molecular weight. Larger molecules, referred to as humic acids, have relatively fewer oxygen functional groups than the fulvic acids and are insoluble at low pH. Further investigation into the structure of DOM fractions indicates that they contain varying proportions of redox sensitive moieties, such as quinones, ketones and aldehydes (Thorn et al., 1992) that have the potential to be aromatic.

Aromatic moieties, such as benzene, are generally comprised of carbons with parallel pi-orbitals; and the delocalization of electrons among the carbons allows the ring to accept and donate electrons from nearby molecules. For aromatic compounds that contain hydroxyl groups, such as quinones, removal of the acidic hydrogen and stabilization of the produced intermediate increases overall reactivity. Depending on the conditions of the environment in which the reaction is occurring, the quinone can exist in reduced (A), semiradical (B), and oxidized (C) forms (Fig. 2).

Further, quinone moieties may simultaneously exist in multiple redox states within the same DOM fraction; however, under reducing conditions the reduced components have a greater contribution to the overall reactivity of the quinone (Cory and McKnight, 2005). Ravichandran et al. (1998) proposed that electron-accepting groups, such as quinone moieties, may be responsible for the enhanced dissolution of mercuric sulfides by oxidizing sulfide within cinnabar; however, the direct oxidation of sulfide to sulfate in the presence of DOM was not observed. It is possible that DOM is unable to oxidize sulfide because its large and complex structure. If reducing moieties within DOM could be isolated or concentrated, potential interactions with the surface may be increased. Redox-sensitive moieties with aromatic

structures in DOM may act as electron shuttles in the mechanism that causes cinnabar to dissolve in oxic systems, as proposed by Waples et al. (2005); however, it remains to be determined if Hg(II)-sulfide bond breaks via the reduction of Hg(II) or the oxidation of S(II).

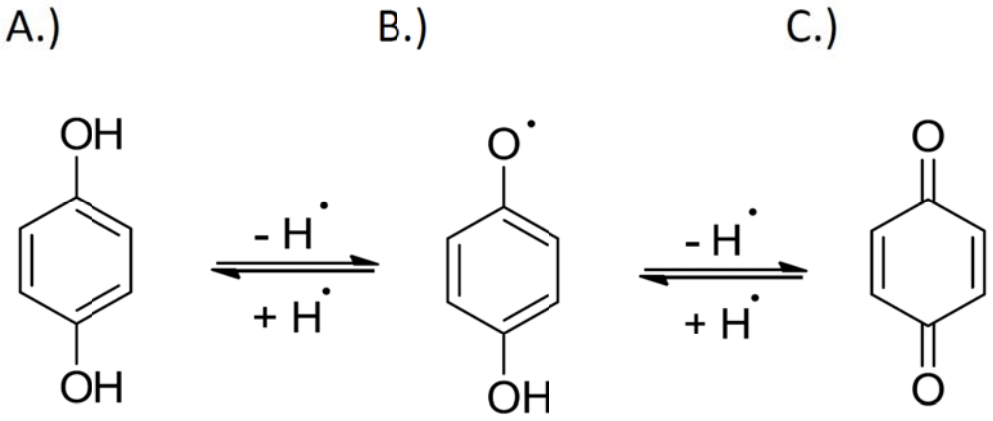

Figure 2. Oxidation states of hydroquinone**.** A.) Fully reduced compound, B.) Semiquinone state, and C.) Fully oxidized compound.

1.5 *Dissolution of Metal Oxides by Reducing Compounds*

Under anoxic conditions and at near neutral pH, various metal oxides have been shown to dissolve more rapidly in the presence of redox compounds such as hydroquinones, resorcinols, methoxy aromatics, mono-substituted benzoic acids and non-aromatics (Stone and Morgan, 1984). In particular, the dissolution of manganese (III & IV) oxides was enhanced in the presence of hydroquinone and ascorbate, although the rate was affected to a lesser extent in the presence of the latter (Stone and Morgan, 1984). Additionally, Stack et al. (2004) observed active iron reduction in hematite in the presence of hydroquinone in a solution under anoxic conditions at low pH.

In the case of the Fe-oxides, the full reduction mechanism consists of adsorption of hydroquinone to the iron-surface site, an electron transfer forming a semiquinone radical and a reduced iron, and finally desorption of the semiquinone and dissolution of the reduced iron. The initial adsorption is hypothesized to occur through an inner-sphere complex between a reduced oxygen and oxidized surface species (Stack et al., 2004). It is possible that the same type of dissolution mechanism is occurring between hydroquinone or ascorbic acid and mercury on the surface of cinnabar.

1.6 *Dissolution of Cinnabar in the Presence of Hydroquinone*

Kerr (2007) investigated the dissolution rate of cinnabar (HgS) in the presence and absence of hydroquinone (HQ); and observed an increase in rate from 3.5×10^{-10} mole Hg m^{-2} s^{-1} in the absence of quinone, to 5.5×10^{-9} mole Hg m^{-2} s^{-1} at a 2:1 mole ratio of HQ to HgS over a two- hour period. The increased release of mercury was interpreted to mean that the quinone

actively reduced mercury under anoxic conditions. Moreover, Kerr (2007) observed that an increase in the ratio of hydroquinone to cinnabar did not result in a proportional increase in the dissolution rate and hypothesized that the rate may be a function of reactive surface area. In combination with the results from Stack et al. (2004) the results indicate a series of mechanistic steps at the surface between mercury bound in cinnabar and the redox compound which may or may not include a direct bonding mechanism between the reductant and mercury on the surface.

1.7 *Natural Occurrence of Quinones and Ascorbic Acid*

Particular attention has been paid to quinones because of their predominance in natural organic matter (Thorn et al., 1992) and their ready participation in redox reactions. Quinones are actively generated by microbes during processes such as respiration (Lovely et al., 2000; Lovely et al., 2002) and are prominent in plant allelopathy (Uchimiya and Stone, 2009; Vyvyan 2002; Weston and Duke, 2003). In addition, ascorbic acid (AA), a known reducing agent, is produced by plants under oxidative stress (Bowler, 1992), during periods of drought and flood (Bowler, 1992), and in the presence of heavy metals (Singh and Sinha, 2005; Sinha et al., 1996). The two molecules used in this work were selected because of their similarity to natural components within DOM thought to be responsible for the release of Hg from cinnabar and their natural production and activity in the environment.

1.8 *Statement of Purpose*

In an attempt to continue characterizing the effects of the redox sensitive moieties commonly found in DOM on the dissolution of cinnabar, the research described in this thesis

was focused on experimental measurements in the presence of hydroquinone and ascorbic acid. Previous work by Kerr (2007) showed increased dissolution of cinnabar when in the presence of redox sensitive moieties; however, little research has been carried out to examine how parameters, such as surface area and pH, alter the release of mercury from the mineral surface. More importantly from the perspective of naturally fluctuating redox conditions, how might the subsequent release of mercury from cinnabar change after an initial reaction with hydroquinone or ascorbic acid? The results of this study are important for understanding mercury mobility in the environment and will be vital to the successful management of this toxic metal.

II. **MATERIALS AND METHODS**

2.1 *Introduction*

Thirty-two dissolution experiments were performed to quantify how the release of mercury from cinnabar changed under various redox conditions (Table I). The experiments were designed to observe effects of variations in total surface area, pH, concentration of the redox-sensitive reactants hydroquinone and ascorbic acid, and recycling of the reactant cinnabar. This chapter starts with descriptions of all materials, the preparation of experimental solutions, the experimental apparatus, and the analytical methods. Next, the procedure for the addition of reagents and sampling methods for the experiments with water, hydroquinone, and ascorbic acid are presented, followed by the procedure for experiments with recycled cinnabar. Lastly, the procedure for performing experiments in which the initial solutions were spiked with mercury or sulfate is described.

2.2 *Materials*

Certified A.C.S. or trace-metal grade reagents and doubly-deionized (DDI) water (> 18.0 Ω; DOC < 0.2 mg C L^{-1}) (Barnsted NANOPURE Infinity Model D8991) were used in all experiments. Glassware and Teflon™ containers were cleaned in an acid bath (10 % v/v (volume/volume) nitric acid (HNO_3); and 10 % v/v hydrochloric acid (HCl)) for ≥ 6 h, and rinsed at least 10 times with DDI water. The glassware was heated in a muffle furnace at 450°C for 1 h to remove any adsorbed organics.

Table I
MATRIX OF GENERAL EXPERIMENTAL PARAMETERS

Experiment ID	Oxic/ Anoxic[a]	Mass HgS[b] (mg)	pH	Description[c]
CIN9711, CIN9311, CIN7111A, CIN7111B, CIN9111, CIN8911, CIN82411, CIN82711B	Anoxic	5, 25, 50	~ 5	Pure water
CIN11912	Oxic	25	~ 6	Pure water
CIN9911, CIN62311, CIN81911, CIN71411, CIN71611A	Anoxic	5, 25, 50, 100	~ 5	HQ in water
CIN102411-2	Oxic	25	~ 4	HQ in water
CIN10511, CIN10311, CIN4312, CIN101211-1, CIN33012	Anoxic	25	~ 2 – 6	AA in water
CIN101211-2, CIN101211-3, CIN102411-1	Oxic	25	~ 2- 5	AA in water
CIN82711A	Anoxic	25	~ 5	Recycled[d] HgS in water
CIN71611B, CIN7111	Anoxic	5, 25	~ 4 - 8	Recycled HgS with HQ
CIN3812, CIN22412, CIN31412, CIN32312	Oxic	25	~ 5	Mercury Spike
CIN111611-1	Anoxic	25	~ 6	Sulfate Spike
CIN111611-2	Oxic	25	~ 6	Sulfate Spike

[a]Anoxic = Water sparged with Ar(g) ≥ 6 h; Oxic = Sparged with compressed air.
[b]For exact masses used in each experiment see Appendix A.
[c] HQ = Hydroquinone; AA = Ascorbic Acid.
[d] Recycled = Cinnabar solid previously used in a dissolution experiment, filtered, stored in a dessicator and reused.

The powdered cinnabar (HgS_{red}) (99.5 +% Acros Organics) had been washed and characterized previously by Kerr (2007). Briefly; the cinnabar was cleaned by soaking the mineral in 10% HNO_3 for 4 d and then dried at 60°C for 4 d. After the cinnabar was dry, it was sieved to obtain the 20-53 μm size fraction. The specific surface area, as measured by the BET method (Brunauer, Emmett and Teller, 1938), was equal to 0.23 $m^2\ g^{-1}$. The cinnabar was stored in contact with air in a closed amber glass bottle covered with aluminum foil. Hydroquinone and ascorbic acid (99 +% Acros Organics) were obtained from Sigma Aldrich and used without further purification.

2.3 *Experimental Apparatus*

The experimental apparatus consisted of two connected 100 mL volumetric flasks made of amber glass and covered in foil to prevent any photolytic reactions of Hg(II) (Fig. 3). The reactor flask contained cinnabar and the reacting aqueous solution and the trap flask contained an oxidizing solution (100 mL of 0.1 M potassium permanganate ($KMnO_4$) in 10% w/v (weight/volume) HNO_3). Each flask was capped with a silicone plug fitted with 1/16″ ID Teflon™ inlet and outlet tubing. The inlet tubing for the reactor was connected to a gas flow meter (Cole Parmer 65 mm polytetrafluoroethylene (PTFE) flow meter) (Fig. 3A) before entering the reactor (Fig. 3B), where it extended to the bottom of the flask into the solution. The outlet tube sampled only the headspace above the reactor solution before exiting the reactor (Fig. 3C) and entering the trap (Fig. 3D), where it was submerged in the oxidizing solution. The outlet tube in the trap flask was used to vent gas from the headspace into the hood (Fig. 3E). All experiments were conducted for 4 h at room temperature. The trap solution flask was replaced

every hour, i.e., at the beginning of hours 2, 3, and 4, with fresh oxidizing solution in a fresh flask.

For experiments under anoxic conditions, fresh DDI water was sparged with high purity Ar(g) for ≥ 6 h in a clean 1.0 L Teflon™ bottle. After sparging, the headspace was filled with Ar(g) and then the container was capped until the water was needed for an experiment (< 24 h from sparging to use). Sparged water older than 24 h was not used. For oxic conditions the DDI water was not pre-treated, but taken fresh from the NANOPURE Infinity unit as needed.

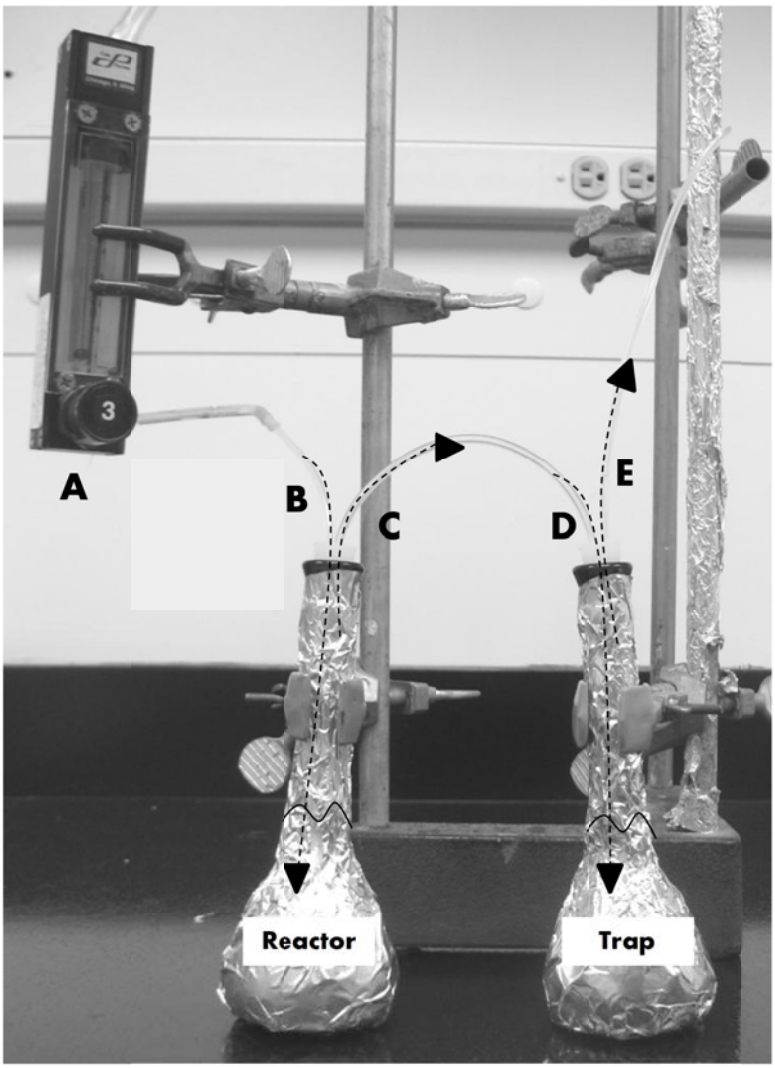

Figure 3. Experimental apparatus**.** The reactor flask contains cinnabar and solutions of variable composition. The trap contains 0.1 M $KMnO_4$. The two flasks are made of amber glass, stoppered with silicone plugs, and wrapped in aluminum foil. Gas flow is regulated by a Teflon™ flow meter (A). Argon (anoxic experiments) or compressed air (oxic experiments) flows into the reactor solution via a 1/16″ ID Teflon™ tube (B). The gas bubbles through the reactor solution and passes into a small headspace (< 5 mL) from which it continues through a Teflon™ tube (C) into the trap solution (D). The gas above the trap solution is then vented out into the hood through another Teflon™ tube (E) that connects with the headspace.

2.4 *Analytical Methods*

2.4.1 *Mercury*

Mercury in all experimental solutions was analyzed by Cold Vapor Atomic Fluorescence Spectrophotometry (CVAFS; Hydra AF Gold+, Teledyne-Leeman) using the Environmental Protection Agency (EPA) method 245.7 as a template (EPA, 2005). Upon completion of an experiment, 10 mL of sample was immediately transferred to a glass test tube containing 250 μL concentrated HCl (Optima Grade) and 100 μL 0.1 M bromide/ bromated (Br^-/BrO_3^-; Teledyne Leeman Labs) to form bromine (Br_2). Mercury (Hg^0) is oxidized by Br_2 according to (Rxn. 2), which maintains the mercury in a stable form in solution:

$$\mathbf{Br_2 + Hg^0 \rightarrow Hg^{2+} + 2Br^-} \qquad \textbf{Reaction 2}$$

The sample was allowed to oxidize (confirmed by a persistent yellow color) for at least 30 min (maximum digestion time of 4 h), after which 400 μL of 10% (w/v) hydroxylamine (NH_2OH) was added to expel any un-reacted bromine. Some solutions, particularly those with $KMnO_4$, required excess NH_2OH (400 – 1600 μL). The concentration for these solutions was adjusted for the dilution. The test tube containing a 10 mL sample and ~ 0.75 – 1.55 mL of digestion reagents was placed in an autosampler rack. The instrument extracted an aliquot from the sample tube into a Teflon™ tube and subsequently mixed in tin(II) chloride ($SnCl_2$) solution, which reduces aqueous Hg(II) to Hg(0) gas according to (Rxn. 3):

$$\mathbf{Hg^{2+} + Sn^{2+} \rightarrow Hg^0 + Sn^{4+}} \qquad \textbf{Reaction 3}$$

The vapor, a mixture of water and mercury, was carried by high purity argon (Ar) gas flow through a soda lime drier where excess water vapor was removed. The dried gas was then passed into an optical cell, where a mercury lamp delivered an emission beam at 254 nm. After

the absorption of energy from the emission beam the fluorescence of the mercury gas was measured using a solid state detector.

Calibration standards were prepared daily according to EPA 245.7 protocols. A mercury reference standard solution of known concentration (10 ppm ± 1% in 1.8% HNO_3) was diluted by mass to produce a secondary standard (~ 0.5 ppm). A set of working standards was prepared from the secondary standard in the concentration range of 0.5 to 500 ppb. Check standards, also prepared from the secondary standard, were analyzed at the beginning of, and periodically during, the analyses to confirm the validity of the calibration line. Typically, any check standard solution with a > 20% deviation from the calibration line was rejected and the calibration line was reassessed for accuracy. The method detection limit was 1.0 μg L^{-1}. The error associated with dissolved Hg concentrations, as measured by CVAFS, was determined by least squares analysis of the individual calibration output on a given day.

For solutions that received excess mercury, the spike solution was prepared by dissolving $HgCl_2$ (99.999 +% Acros Organics) in oxic or anoxic DDI water. Spike solutions were prepared in 100 mL amber glass volumetric flasks and used in experiments within 1 h of preparation.

2.4.2 *Sulfate*

Nine reactor solutions (CIN9711, CIN7111A, CIN7111B, CIN9111, CIN8911, CIN82711B, CIN9911, CIN71611B, CIN10311) were selected for sulfate analysis using Ion Chromatography (IC) (Dionex IC 2500). Prior to IC analysis the solutions were mixed with an Ambersep GT74 weak acid cation exchange resin (1.30 eq/L Ion Exchange Capacity) to remove any free mercury(II). The solution was mixed by placing 10 mL of the reactor solution into a clean 50 mL beaker containing a magnetic stir bar and 2 mL of resin. The mixture was stirred

for at least 2 h. The solution was decanted into a 10 mL amber glass vial and stored for < 48 h prior to analysis. Instrument calibration was performed prior to each run with 5 to 450 ppb sulfate standards mixed by serial dilutions from a stock DIONEX standard.

For experiments where excess sulfate was to be added, sulfate reactant solutions were prepared by dissolving Na_2SO_4 (99 +% Acros Organics) in oxic or anoxic DDI water. At the end of the experiment, the reactor sample was filtered and a portion of the filtrate set aside for complexometric titration with $BaCl_2$ (99 +%, Acros Organics).

2.4.3 *Changes in pH*

Adjustments of pH were carried out using (1:1) HCl (Optima grade) and (1:1) sodium hydroxide (NaOH) in DDI water. When adjustments were made, the solutions typically received both HCl and NaOH. The final pH of the reactor solution was measured at the end of the experiment after the solid cinnabar had been filtered from the solution. Measurements were made using standard pH buffers (4.0 and 7.0), an Orion pH meter (model 720A), and a PerpHecT ROSS Combination electrode.

2.5 *Experiments*

2.5.1 *Cinnabar Reactivity in Water and Solutions of Hydroquinone or Ascorbic Acid*

The release of mercury from cinnabar was measured in solutions of pure water, hydroquinone, or ascorbic acid. In all cases solid cinnabar was added to the reactor flask prior to the addition of a solution. After the addition of the solution, the reactor was sealed, connected in sequence with the trap flask, and the experiment was allowed to proceed.

For experiments in pure water, a reactor flask containing either no or a fixed initial mass of cinnabar (5, 25 or 50 mg) was connected to a trap flask. Water (100 mL) was added to the reactor, after which the flask was stoppered, and the gas (argon or compressed air) pressure adjusted to 10 - 20 psi. For solutions containing hydroquinone or ascorbic acid, 50 mL of pre-treated DDI water was added to a reactor flask containing cinnabar before the addition of reducing solutions. Prior to the beginning of an experiment, the solution of water and cinnabar in the reactor flask was purged for 5 min: experiments under anoxic conditions were purged with high purity argon (99.998 %), and experiments under oxic conditions were purged using compressed air from the laboratory's house line. After 5 min, the gas was turned off and 50 mL of the solution containing the designated reagents (at twice the desired concentration) was added to the reactor flask using a 50 mL volumetric pipette. After the stopper was removed to add the reagent, the flask was re-stoppered in less than 5 s. Once the reactor was re-stoppered it was not opened again until the end of the 4 h experiment.

In each experiment the trap solution was changed every 1 h according to the following procedure: the gas was turned off; the used trap flask was removed and replaced with a 100 mL volumetric flask containing a fresh solution of 0.1 $KMnO_4$; the silicone stopper was replaced; and, the gas flow was restarted. The duration of time during which there was no gas flow was less than 5 s. The flasks containing the first three used trap solutions were capped with glass stoppers and were stored under the hood until the end of the experiment. The reactor and all trap solutions were analyzed immediately after the end of the experiment.

The gas was turned off after 4 h and the reactor flask was removed from the experimental apparatus. For some reactor solutions, the reacted cinnabar was saved for subsequent dissolution experiments. The filtration method for recycled cinnabar will be discussed in the following

section. However, when the cinnabar solid was not going to be reused, the reactor solution was drawn into a polypropylene syringe fitted with a Teflon™ tube extension and extruded directly through a Whatman Puradisc 0.45 μm filter into a glass test tube containing the digestion reagents. A portion of the reactor filtrate was set aside for pH testing, while another portion of the filtrate solution was transferred to a 10 mL amber glass vial with a PTFE cap and placed in a plastic bin for storage.

In all experiments, released mercury concentrations were normalized to the specific surface area (0.23 $m^2\ g^{-1}$) using the total mass of cinnabar and total volume of solution contained in each flask according to (Eq. 1):

$$\mathbf{Hg_T\ (\mu mol\ Hg\ m^{-2})} = \frac{\mathbf{Hg_{Reactor}\ (\mu mol\ Hg) + \Sigma\ Hg_{Traps}\ (\mu mol\ Hg)}}{\mathbf{Cinnabar\ (g) * 0.23\ (m^2\ g^{-1})}} \qquad \textbf{Equation 1}$$

In addition, the moles of reactant (i.e., HQ and/or AA) were compared to the number of moles exposed at the surface of mercury for each experiment (see Appendix B for conversion factors). The error in Hg_T was calculated by combining the standard error of a surface area measurement (± 10%), and uncertainty in the detection of Hg as determined by quality control checks during CVAFS measurements. In general, the uncertainty within the calibration curve was less than 10%; and typically, the deviation of the calibration curve from the reference standard was less than 20%.

2.5.2 *Reactivity of Recycled Cinnabar*

Cinnabar undergoing an experiment under the conditions described in the previous section will furthermore be referred to as initial cinnabar when compared to experiments

involving recycled cinnabar. Reacted cinnabar from six experiments (CIN7111A, CIN7111B, CIN81911, CIN71411, CIN6711, and CIN62311) was collected to reuse in subsequent dissolution experiments. Three experiments were performed to measure mercury release from recycled cinnabar in anoxic water: one experiment combined cinnabar from experiments CIN7111A- anoxic water, CIN7111B- anoxic water, and CIN81911- anoxic HQ; one used cinnabar from CIN71411-anoxic HQ; and one combined cinnabar from CIN6711-anoxic HQ and CIN62311-anoxic HQ.

When the cinnabar solid was to be saved and stored for later use in a recycled experiment, the reactor solution was poured through a Nalgene filter funnel fitted with a 0.45 μm Millipore Durapore® HVLP membrane into a clean Erlenmeyer flask connected to a vacuum pump. The cinnabar collected on the filter was immediately rinsed three times with DDI water by squirting water from a wash bottle directly onto the filter. The filter with cinnabar was transferred into a clean glass 100 mL beaker. The beaker was covered in Parafilm® and placed in a vacuum sealed desiccator covered in foil. Dried cinnabar was scraped off of the filter and transferred directly into a clean and tared amber glass volumetric flask. The mass of the cinnabar was recorded and the experiment proceeded as previously described.

2.6 *Reactivity of Cinnabar in the Presence of Excess Sulfate or Mercury*

2.6.1 *Sulfate Spike Experiments*

Two spike experiments (CIN111611_1 under anoxic conditions and CIN111611_2 under oxic conditions) were performed to test the effect of high sulfate concentrations on the amount of mercury released from cinnabar. Sulfate solutions (193 and 184 moles sulfate (SO_4) L^{-1}) were added to the reactor flask after 5 min of sparging. After the completion of the experiment the

reactor solution was filtered through a Nalgene filter funnel fitted with a 0.45 μm Millipore Durapore HVLP membrane. Ten (10) mL of the filtrate were collected and set aside for determination of sulfate concentration by titration with barium (II) chloride $BaCl_2$.

The titrant was prepared by dissolving $BaCl_2$ in DDI water (0.576 and 0.703 M). During the titration barium sulfate ($BaSO_4$) precipitated according to (Rxn 5):

$$\mathbf{Ba^{+2} + SO_4^{2-} \rightarrow BaSO_4} \qquad \textbf{Reaction 5}$$

The precipitated $BaSO_4$ was collected on a 0.7 μm Whatman glass microfiber filter by vacuum filtration and the filter with precipitate was placed on a watch glass covered in Parafilm® and stored in a dessicator. A qualitative method (Brush and Penfield, 1898) was used to confirm the presence of barium and sulfate. A platinum wire loop was coated with precipitate and held over an open flame from a Bunsen burner. The production of a green flame verified the presence of barium. Sulfate was confirmed in the precipitate by wiping a heated slurry of charcoal, sodium bicarbonate, and the precipitate onto a solid silver plate and observing the presence of a dark black precipitate.

2.6.2 *Mercury Spike Experiments*

Four experiments (CIN22412, CIN3812, CIN31412, CIN32312) with mercury(II)-spiked reactor solutions were performed to test for possible adsorption of mercury(II) to the surface of cinnabar during dissolution. The spike solution concentration was analyzed separately.

The experimental apparatus, analytical procedure, and reagent addition were the same as previously described. Fifty mL of the spike solution was added to the reactor flask after the initial 5 min of sparging. After completion of the experiment, the reactor solution was filtered

through a 0.45 μm Millipore Durapore® HVLP membrane on a Nalgene filter funnel. Ten mL of the filtrate was collected and set aside for mercury analysis.

The minimum amount of adsorbed mercury, if any, was determined by subtracting the sum of the moles of mercury in the reactor and trap flasks from the moles of mercury added to the reactor solution. This estimate of the minimum amount assumes there was no release of mercury from cinnabar and that any mercury moved to the traps was from the initial spike. A positive value represents the net minimum adsorbed mercury. A negative value represents net mercury release from cinnabar. An adsorption isotherm was generated by plotting the minimum number of moles adsorbed vs. the concentration of mercury remaining in the reactor for each experiment.

III. **RESULTS**

3.1 *Introduction*

Results from this work for the reactivity of cinnabar under various experimental conditions are reported in Tables II-V. The data for mercury release are presented in detail below by type of experiment: cinnabar in pure water, cinnabar in hydroquinone solutions, and cinnabar in ascorbic acid solutions. These results include effects of variable pH, cinnabar mass, and concentration of hydroquinone and ascorbic acid where relevant. Next, sulfate concentrations in reactor solutions for selected experiments are reported and compared to the amount of mercury released. Lastly, the results from the experiments with added mercury are presented.

3.2 *Mercury Released from Cinnabar in Water*

In anoxic experiments, the concentration of mercury in trap solutions increased initially and then assumed a constant value after ~ 2-3 h with the exception of experiment CIN9711 in which the mercury concentration continued to rise over the 4 h reaction period (Fig. 4). Data from Kerr (2007) are included in Figure 4 for comparison. The cumulative concentration of mercury in the trap solutions was greater than that in the reactor solution and on average decreased with increasing mass of cinnabar (Fig. 5). In the reactor solutions, there was little difference in mercury concentration in experiments with 5 or 25 mg HgS (2.98 ± 4.15 and 2.91 ± 4.64 μmol Hg m^{-2}, respectively), and these values were near the detection limit (1 ppb). The concentration of mercury in the reactor solution from the experiment with 50 mg HgS was below the detection limit. Under oxic conditions with 25 mg HgS, the trap solutions contained more mercury than in the corresponding anoxic trap solutions (Fig. 5).

TABLE II

EXPERIMENTAL PARAMETERS AND RESULTS FOR MERCURY RELEASE

ID	Oxic/ Anoxic[a]	HgS[b] (mg)	Reductant[c]	Mole Ratio Reductant: $Hg_{surface}$[d]	$Hg_{Reactor}$ (μmol Hg)	Σ Hg_{Traps} (μmol Hg)	Released Mercury (μmol Hg m^{-2})	$pH_{initial}$	pH_{final}	$pH_{adjusted}$
CIN9711	Anoxic	5	-	-	7.68×10^{-3}	6.08×10^{-3}	10.7 ± 3.03	nm[e]	4.6	No
CIN9311	Anoxic	5	-	-	bdl[f]	1.64×10^{-2}	12.3 ± 1.24	nm	4.7	No
CIN11912	Oxic	25	-	-	2.79×10^{-3}	5.78×10^{-2}	9.28 ± 0.97	nm	5.6	No
CIN7111A	Anoxic	25	-	-	2.96×10^{-3}	2.78×10^{-2}	6.71 ± 0.69	3.7	5.5	Yes
CIN7111B	Anoxic	25	-	-	5.83×10^{-3}	3.34×10^{-2}	7.26 ± 0.74	6.5	5.6	Yes
CIN9111	Anoxic	25	-	-	1.36×10^{-1}	4.99×10^{-4}	4.60 ± 0.48	4.9	4.5	No
CIN8911	Anoxic	25	-	-	6.48×10^{-2}	4.34×10^{-3}	10.1 ± 1.02	5.7	nm	No
CIN82411	Anoxic	50	-	-	6.33×10^{-3}	2.25×10^{-2}	2.02 ± 0.21	nm	4.5	No
CIN82711B	Anoxic	50	-	-	bdl	1.17×10^{-2}	0.99 ± 0.11	nm	3.8	No
CIN9911	Anoxic	5	HQ	11×10^{3}	bdl	bdl	bdl	4.8	4.7	No
CIN102411-2	Oxic	25	HQ	8.5×10^{3}	3.80×10^{-2}	bdl	6.05 ± 0.70	4.1	3.5	No
CIN62311	Anoxic	25	HQ	21×10^{3}	8.54×10^{-4}	7.28×10^{-2}	9.09 ± 1.00	6.8	5.0	Yes
CIN81911	Anoxic	50	HQ	8.4×10^{3}	bdl	7.88×10^{-3}	0.65 ± 0.066	nm	nm	No
CIN71411	Anoxic	50	HQ	163×10^{3}	bdl	4.42×10^{-2}	4.45 ± 0.82	7.5	6.4	Yes
CIN71611A	Anoxic	100	HQ	2.3×10^{3}	bdl	1.03×10^{-2}	0.44 ± 0.050	6.8	nm	Yes
CIN6711[j]	Anoxic	100	HQ	62.4×10^{3}	nm	nm	nm	nm	nm	na[h]
CIN101211-2	Oxic	25	AA	9.0×10^{3}	bdl	bdl	bdl	5.2	4.7	Yes
CIN101211-3	Oxic	25	AA	883×10^{3}	bdl	6.58×10^{-3}	1.02± 0.14	2.3	2.4	No
CIN102411-1	Oxic	25	AA	750×10^{3}	8.38×10^{-3}	bdl	1.24 ± 0.26	2.4	2.4	No
CIN10511	Anoxic	25	AA	9.8×10^{3}	bdl	bdl	bdl	5.9	5.2	No
CIN10311	Anoxic	25	AA	9.0×10^{3}	6.18×10^{-4}	2.49×10^{-3}	0.40 ± 0.064	6.1	5.5	No
CIN4312	Anoxic	25	AA	12×10^{3}	1.15×10^{-3}	7.98×10^{-4}	3.38 ± 0.039	3.7	3.7	No

TABLE II (Con't)
EXPERIMENTAL PARAMETERS AND RESULTS FOR MERCURY RELEASE

ID	Oxic/ Anoxic[a]	HgS[b] (mg)	Reductant[c]	Mole Ratio Reductant: $Hg_{surface}$[d]	$Hg_{Reactor}$ (μmol Hg)	Σ Hg_{Traps} (μmol Hg)	Released Mercury (μmol Hg m^{-2})	$pH_{initial}$	pH_{final}	$pH_{adjusted}$
CIN101211-1	Anoxic	25	AA	911 x 10^3	bdl	bdl	bdl	2.5	3.4	Yes
CIN33012	Anoxic	25	AA	900 x 10^3	bdl	2.3	0.20 ±0.020	2.5	2.3	No
CIN82711A	Anoxic	25	R CIN7111A, CIN7111B, CIN81911	-	bdl	8.23×10^{-3}	0.13 ± 0.014	4.8	4.5	No
CIN71611B	Anoxic	5	R/HQ CIN71411	15×10^3	bdl	2.45×10^{-3}	3.14 ± 0.71	7.1	8.1	Yes
CIN71111	Anoxic	25	R/HQ CIN6711[g], CIN62311	17×10^3	bdl	1.45×10^{-2}	3.42 ± 0.54	3.7	4.1	Yes

[a] Anoxic = Water sparged with Ar(g) ≥ 6 h; Oxic = Water sparged with compressed air.
[b] For exact masses used in each experiment see Appendix A.
[c] HQ = Hydroquinone; AA = Ascorbic Acid; R = Recycled
[d] Moles of surface Hg based on estimated density of 1 atom Hg per 39 $Å^2$ of cinnabar surface. See Appendix B for calculation used to obtain this value.
[e] nm= not measured
[f] bdl = below detection limit.
[g] CIN6711 is excluded from Table 1 because of errors in the mercury analysis. The solid, however, was stored and used in a recycled dissolution experiment.
[h] Value not available.

TABLE III

EXPERIMENTAL PARAMETERS AND RESULTS FOR SULFUR RELEASE (AS SULFATE)

Experiment ID	Oxic/ Anoxic[a]	HgS[b] (mg)	Reductant[c]	Ratio Reductant: $Hg_{surface}$[d]	Hg_{Total}[e] (μmol Hg m^{-2})	$SO_{4,Reactor}$ (μmol SO_4 m^{-2})	Ratio SO_4^{2-}: Hg_{Total}[f]	pH adj.
CIN9711	Anoxic	5	-	-	10.7	10,454	977	No
CIN7111A	Anoxic	25	-	-	6.71	bdl[g]	na[h]	Yes
CIN7111B	Anoxic	25	-	-	7.27	bdl	na	Yes
CIN9111	Anoxic	25	-	-	23.0	2,241	97	No
CIN8911	Anoxic	25	-	-	10.5	2,257	215	No
CIN82711B	Anoxic	50	-	-	bdl	1,681	na	No
CIN9911	Anoxic	5	HQ	11×10^3	bdl	12,229	na	No
CIN71611B	Anoxic	5	R/HQ	15×10^3	3.14	bdl	na	Yes
CIN10311	Anoxic	25	AA	9.0×10^3	0.475	1,675	3,526	No

[a] Anoxic = Water sparged with Ar(g) ≥ 6 h; Oxic = Water sparged with compressed air.

[b] Masses of cinnabar are grouped into four categories: 5, 25, 50, and 100 mg. For specific masses used in experiments see Appendix A.

[c] HQ = Hydroquinone; AA = Ascorbic Acid; R = Recycled.

[d] Moles of surface Hg based on estimated density of 1 atom Hg per 39 Å of cinnabar surface. See Appendix B for calculations used to obtain this value.

[e] Hg_{Total} represents the sum of the mercury concentration of four trap solutions and the corresponding reactor solution.

[f] Ratio calculated by dividing SO_4 (μmol SO_4 m^{-2}) by Hg_{Total} (μmol Hg m^{-2}).

[g] bdl = below detection limit.

[h] Value not available.

Table IV

REACTIVITY OF CINNABAR UNDER ANOXIC AND OXIC CONDITIONS IN THE PRESENCE OF ADDED SULFATE

ID	Oxic/Anoxic[a]	HgS (mg)	SO_{4Spike}	Ratio Sulfate: $Hg_{Surface}$[c]	$Hg_{Reactor}$ (μmol Hg)	Σ Hg_{Traps} (μmol Hg m^{-2})	$Hg_{Released}$[d] (μmol Hg m^{-2})
CIN111611_1	Anoxic	25	192	650×10^{3}	3.56×10^{-3}	3.41×10^{-2}	2.67 ± 0.27
CIN111611_2	Oxic	25	152	669×10^{3}		8.80×10^{-2}	6.57 ± 0.66

[a] Anoxic = Water sparged with Ar(g) ≥ 6 h; Oxic = Water sparged with compressed air.

[b] For specific masses used in experiments see Appendix A.

[c] Moles of surface Hg based on estimated density of 1 atom Hg per 39 Å of cinnabar surface. See Appendix B for calculations used to obtain this value.

[d] $Hg_{Released}$ represents the difference between the amount of mercury measured in the reactor solution at the beginning of an experiment minus the concentrations of mercury in four trap solutions and the corresponding reactor solution.

[e] bdl = below detection limit.

TABLE V

REACIVITY OF CINNABAR UNDER ANOXIC CONDITIONS
IN THE PRESENCE OF ADDED MERCURY(II)

ID	Oxic/ Anoxic[a]	HgS[b] (mg)	Hg_{Spike}[c] (mole Hg)	$Hg_{Reactor}$ (mol Hg)	ΣHg_{Traps} (mol Hg)	$C_{Reactor}$[d] (mg L^{-1})	X[e] (μg g^{-1})	$pH_{initial}$	pH_{final}
CIN3812	Oxic	25	0.30×10^{-8}	5.47×10^{-10}	6.18×10^{-10}	1.87×10^{-9}	0.624	5.9	5.70
CIN22412	Oxic	25	1.34×10^{-8}	5.60×10^{-9}	8.92×10^{-10}	6.86×10^{-9}	0.946	5.9	5.4
CIN31412	Oxic	25	2.23×10^{-8}	1.04×10^{-8}	5.11×10^{-10}	1.14×10^{-8}	0.951	5.7	3.9
CIN32312	Oxic	25	3.51×10^{-8}	2.33×10^{-8}	bdl[f]	1.17×10^{-8}	1.99	5.7	3.7
CIN4612	Anoxic	25	1.38×10^{-8}	2.02×10^{-9}	1.96×10^{-8}	4.05×10^{-3}	na	5.7	5.3
CIN41012	Anoxic	25	4.25×10^{-8}	4.00×10^{-8}	1.17×10^{-7}	8.02×10^{-2}	na	5.4	5.2

[a] Anoxic = Water sparged with Ar(g) ≥ 6 h; Oxic = Water sparged with compressed air.
[b] Masses of cinnabar are grouped into the same category. For specific masses used in experiments see Appendix A.
[c] Moles of mercury added to reactor solution at the beginning of the experiment.
[d] $C_{Reactor}$ = amount of mercury (mg L^{-1}) in the reactor solution at the end of 4 h period.
[e] X = (reactor + Σ traps (μg)) • (Mass HgS (mg))$^{-1}$
[f] bdl = below detection limit.

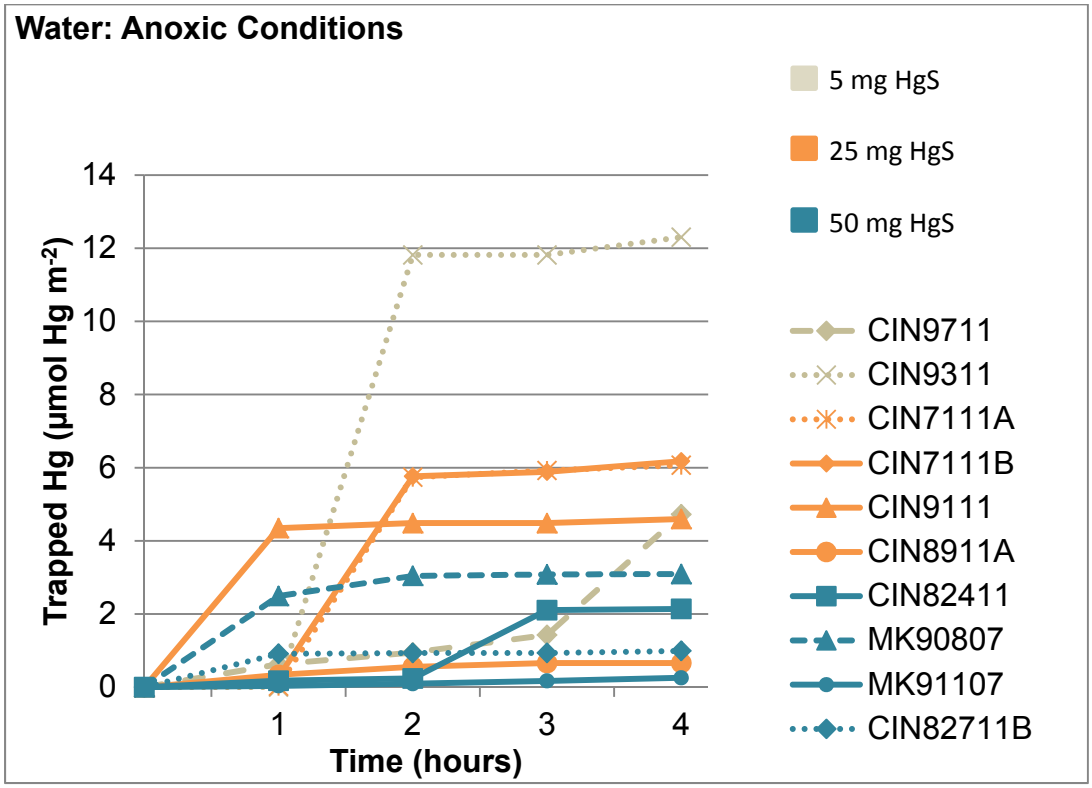

Figure 4. Release of mercury from various initial amounts of cinnabar with time. The cumulative amount of mercury released to trap solutions normalized to the total surface area of cinnabar, as a function of time is compared for experiments carried out under anoxic conditions in water with various starting masses of cinnabar. Data from Kerr (2007) (Table 6) are included for comparison.

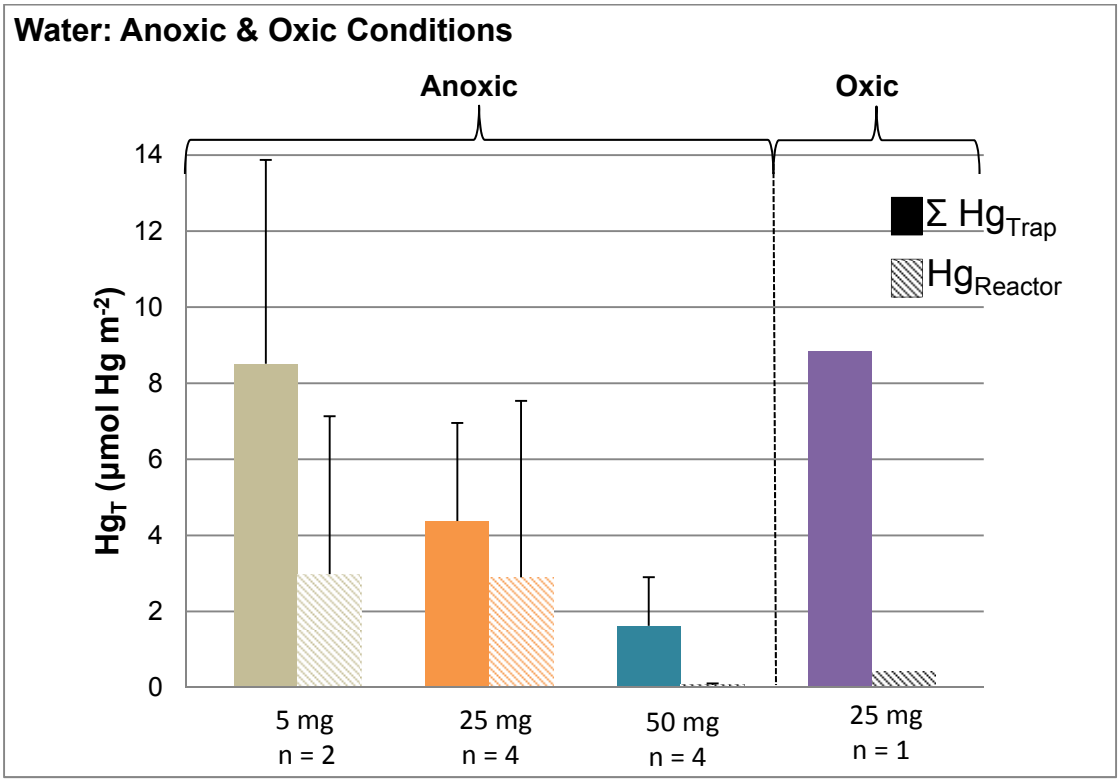

Figure 5. Total release of mercury in water. The average and standard deviation of the amount of Hg in trap (solid) and reactor (striped) solutions in experiments carried out under anoxic conditions on left separated by initial mass of cinnabar (5, 25, and 50 mg). The four experiments with 50 mg cinnabar include two from Kerr (2007). The amount of Hg released in an experiment carried out under oxic conditions with 25 mg HgS is shown at right. Mercury in both reactor solutions for experiments with 25 mg HgS (anoxic and oxic) were near or below the detection limit. The pH varied from 3.8 to 6.0.

The mercury concentration in the oxic reactor solution was also below the detection limit. The amount of mercury released from cinnabar (Hg_T) in units of moles Hg m^{-2} cinnabar is correlated inversely ($R^2 = 0.75$) to the total initial surface area of cinnabar (SA_T) (Fig. 6) according to (Eq. 2):

$$\mathbf{Hg_T\ \mu mol\ Hg\ m^{-2} = -903\ \mu mol\ Hg^{2+}\ m^{-4} \bullet SA_T + 12.1\ \mu mol\ Hg^{2+}\ m^{-2}} \qquad \textbf{Equation 2}$$

The total amount of mercury released decreases by two orders of magnitude with a one order of magnitude increase in surface area.

In an experiment with recycled cinnabar, the amount of mercury released in both the reactor and traps (Fig. 7) was nearly two orders of magnitude less than in solutions that contained initial cinnabar. Over the pH range of 4 to 6, the release of mercury may be a slight positive function of pH for constant initial mass of cinnabar, based on the data for the 25 and 50 mg samples (Fig. 8). However, the sparseness of the data more likely indicates little to no pH-dependence.

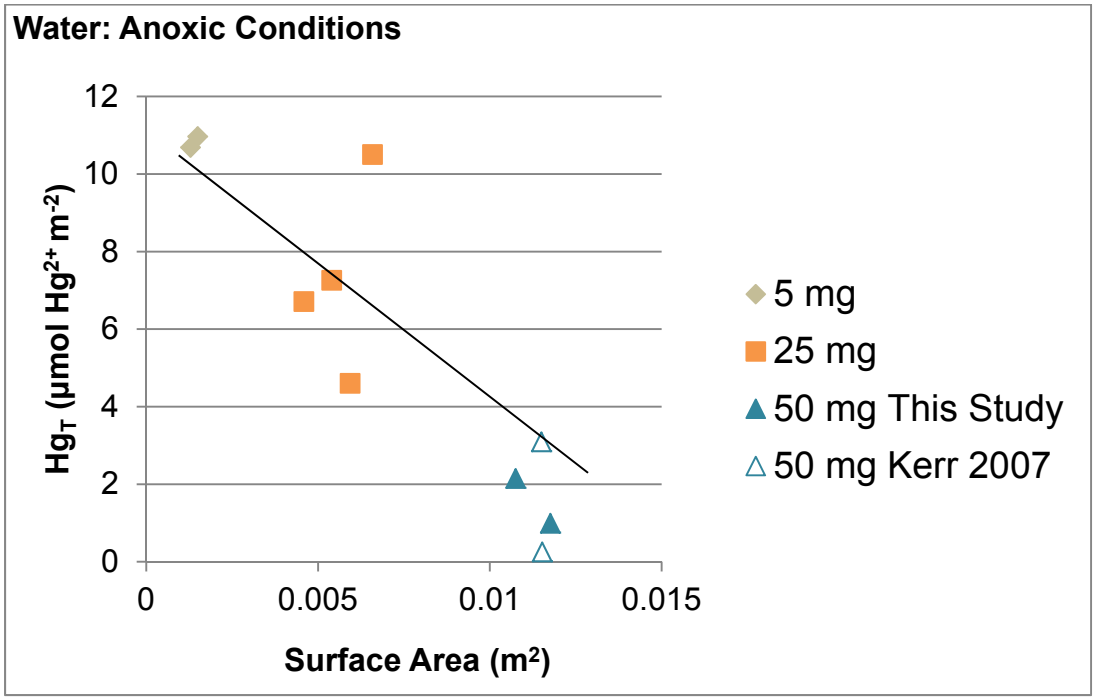

Figure 6. Release of mercury as a function of surface area. The total Hg (Hg_T) released in experiments carried out in water under anoxic conditions with different starting masses of HgS (5, 25, and 50 mg) as a function of the total surface area (0.23 m^2 g^{-1} HgS x mass of cinnabar). Two data points from Kerr (2007) are represented by open triangles (Δ). The data were fit to a straight line Hg_T = -903 µmol Hg^{2+} m^{-4}• SA_T + 12.1 µmol Hg^{2+} m^{-2} (R^2 = 0.8077). The pH varied from 3.8 to 6.0.

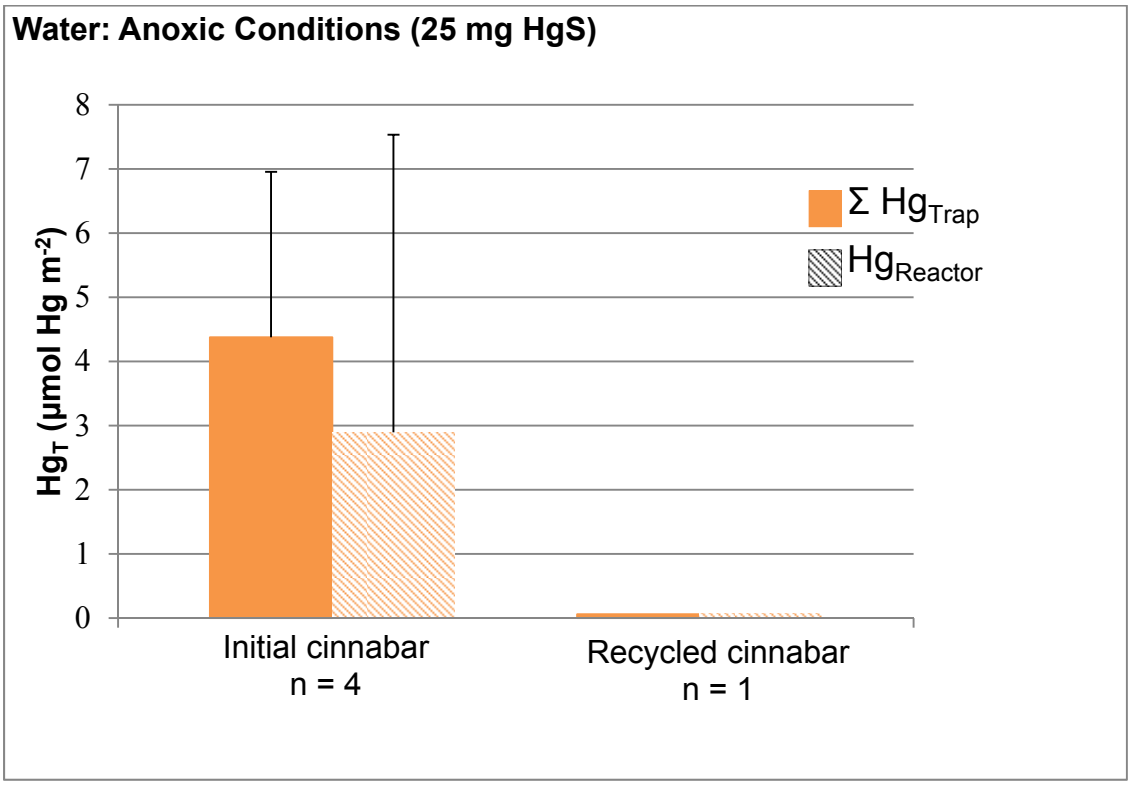

Figure 7. Release of mercury in solutions with initial versus recycled cinnabar. The amount of mercury measured in reactor (striped) and trap (solid) solutions in experiments carried out in water under anoxic conditions with 25 mg initial cinnabar is compared to the amount of mercury measured in a similar experiment with recycled cinnabar. The initial cinnabar experiment is the average of results from four experiments (CIN7111A, 7111B, 9111, and 8911) and the recycled cinnabar experiment used the dried cinnabar from three of those experiments (CIN7111A, 7111B, and 8911).

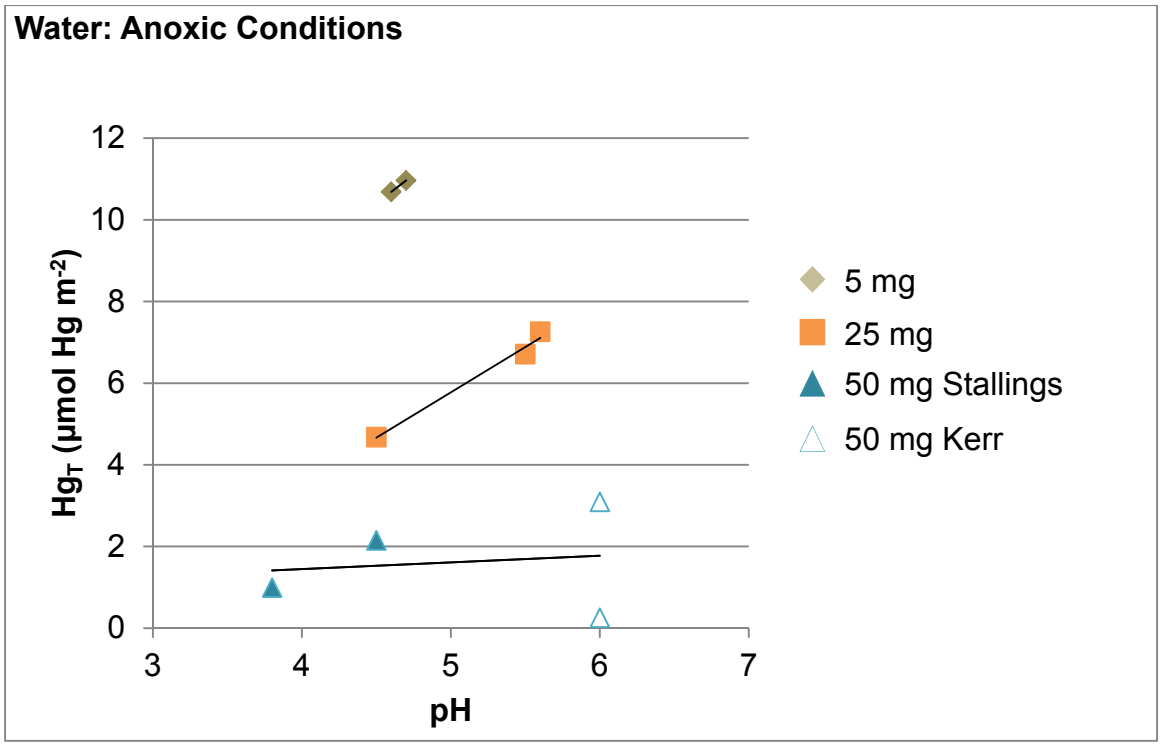

Figure 8. Release of mercury in water as a function of pH. The final pH of the reactor solutions is compared to the total amount of mercury released in nine anoxic dissolution experiments with different initial masses of cinnabar (5, 25, and 50 mg HgS). Two data points from Kerr (2007) are included and are represented by open triangles (Δ). Linear trends were fit to each mass group; however, the slopes are likely insignificant because the number of data points is low.

3.3 *Mercury Released from Cinnabar in Hydroquinone Solutions*

In anoxic experiments, the concentration of mercury in the trap solutions also decreased with increasing cinnabar mass (Fig. 9), similarly to the release of mercury in water. However, the amount of mercury released was about twice that in pure water for the same initial mass of cinnabar. The amount of mercury in the reactor solution was highest in the experiment carried out with 25 mg HgS and undetectable for all other experiments. The concentration of mercury in

the trap solutions for the experiment performed under oxic conditions with 25 mg HgS is 40% less than that in the corresponding trap solutions under anoxic conditions.

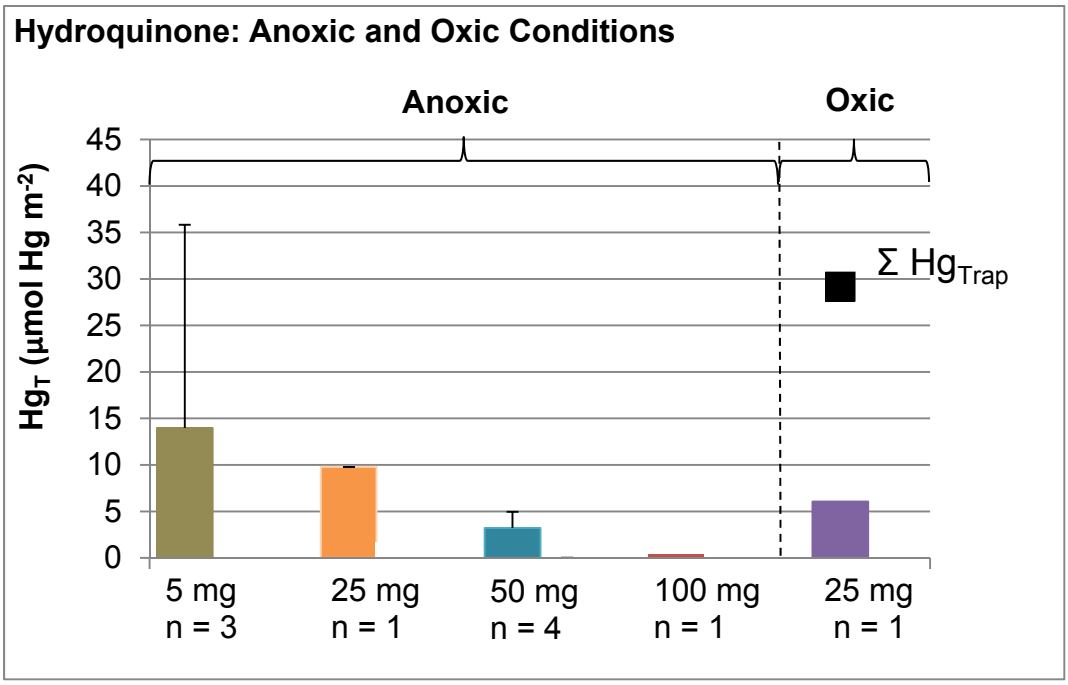

Figure 9. Release of mercury in the presence of hydroquinone. The amount of Hg in trap (solid) solutions in experiments carried out under anoxic conditions in the presence of HQ with different masses of cinnabar and various ratios of moles of HQ to moles of surface mercury (9.66, 9.29 and 10.7 × 10^3 for 5 mg; 21.2 for 25 mg; 0.968, 0.980, 8.36 and 16.3 × 10^3 for 50 mg; and 2.23 × 10^3 for 100 mg). For comparison, the amount of Hg dissolved in an experiment carried out under oxic conditions with 25 mg HgS is included for the ratio 8.54 × 10^3 moles of HQ per mole of surface Hg. The concentration of Hg in anoxic reactor solutions for experiments with 5, 50, and 100 mg cinnabar and the oxic experiment with 25 mg HgS were below the detection limit; therefore, not present on this figure. Error bars represent the standard deviation of the average of more than one experiment. See Appendix B for a list of conversions used to calculate the ratios.

The amount of mercury released from 25 mg of recycled cinnabar in the presence of a ratio of 17.3 moles HQ per mole of $Hg_{Surface}$ is 68% less than the amount of mercury released from fresh cinnabar (Fig. 10). At a constant mass of cinnabar of 50 mg, including one data set from Kerr (2007) (MK81707 and MK82807) for the ratio 0.974×10^3 HQ to $Hg_{Surface}$, there was no obvious trend in the total amount of mercury released as a function of the concentration of hydroquinone (Fig. 11). All of the released mercury was transferred to the trap solutions in both experiments; neither reactor solution had detectable concentrations of mercury. The data from experiments performed with 50 mg HgS suggest there is no pH-dependence to the amount of mercury released (Fig. 12).

Compared to the experiment in pure water under anoxic conditions, the amount of released mercury increased by approximately a factor of 2.5 to 2.7 with hydroquinone concentrations of 0.974×10^3 and 163×10^3. However, a hydroquinone concentration of 8.36×10^3 resulted in the same amount of released mercury within experimental uncertainty as that in pure water.

3.4 *Mercury Released from Cinnabar in Ascorbic Acid Solutions*

The release of mercury from cinnabar decreased by as much as two orders of magnitude with the addition of ascorbic acid to water in anoxic experiments (Fig. 13 A). Increasing the amount of ascorbic acid by almost two orders of magnitude from 10×10^3 to 906×10^3 decreased the release of mercury by approximately 75%. Under oxic conditions the amount of mercury released in solution also decreased with added ascorbic acid (Fig. 13 B).

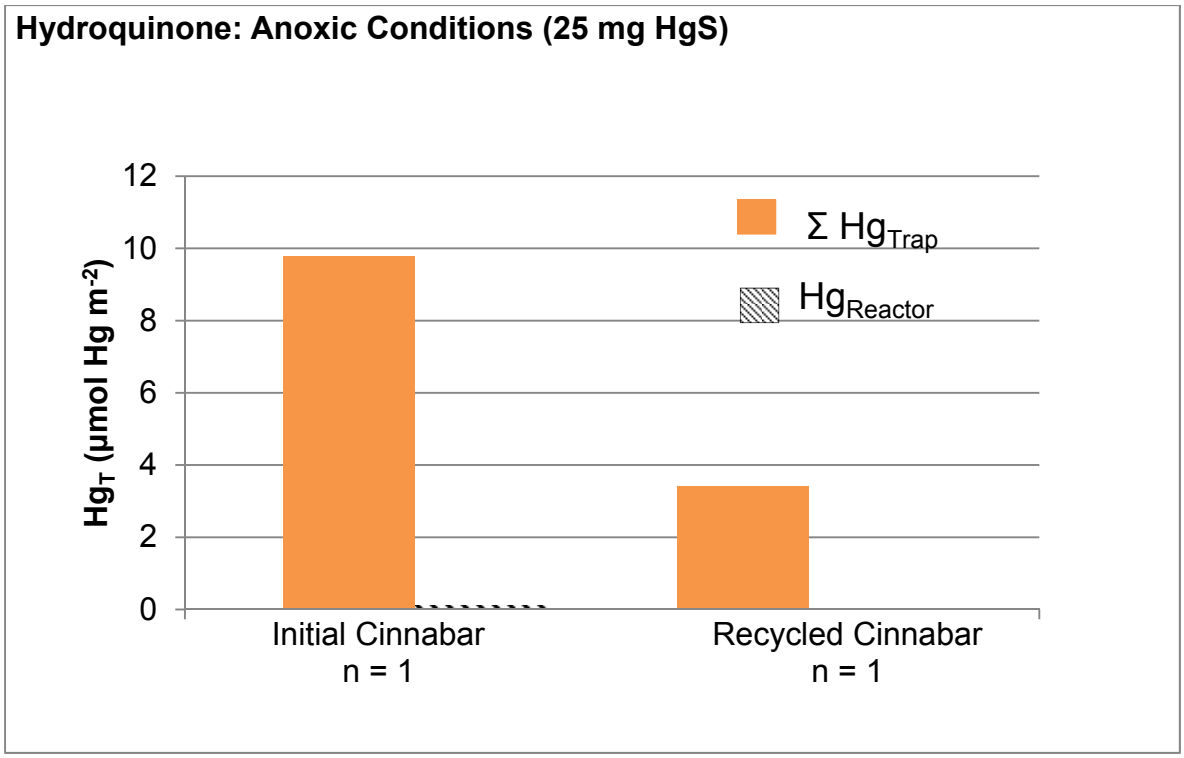

Figure 10. Comparison of experiments containing initial versus recycled cinnabar. Comparison of the amount of mercury measured in the presence of initial and recycled cinnabar in reactor (striped) and trap (solid) solutions for experiments carried out in water with hydroquinone under anoxic conditions. The recycled cinnabar combined dried cinnabar from the experiments with 25 and 100 mg unreacted material (CIN62311 and CIN6711, respectively) at a ratio of 17.3 moles of HQ per mole of $Hg_{Surface}$.

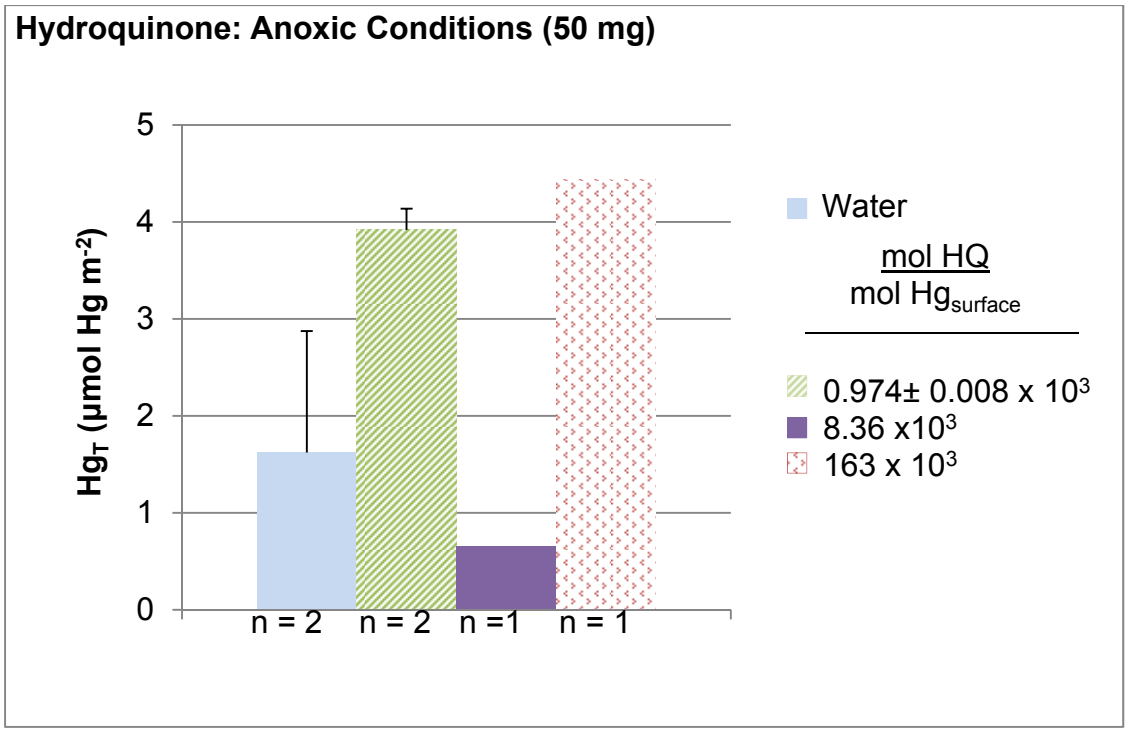

Figure 11. Release of mercury in the presence of hydroquinone at various concentrations. The total amount of mercury (reactor + Σ trap solutions) is plotted for three different concentrations of hydroquinone in solutions containing 50 mg HgS and carried out under anoxic conditions. Two data points from Kerr 2007 are included (MK81707 and MK82807) at the ratio 0.974 x 10^3. See Appendix B for conversion factors used to calculate the ratios.

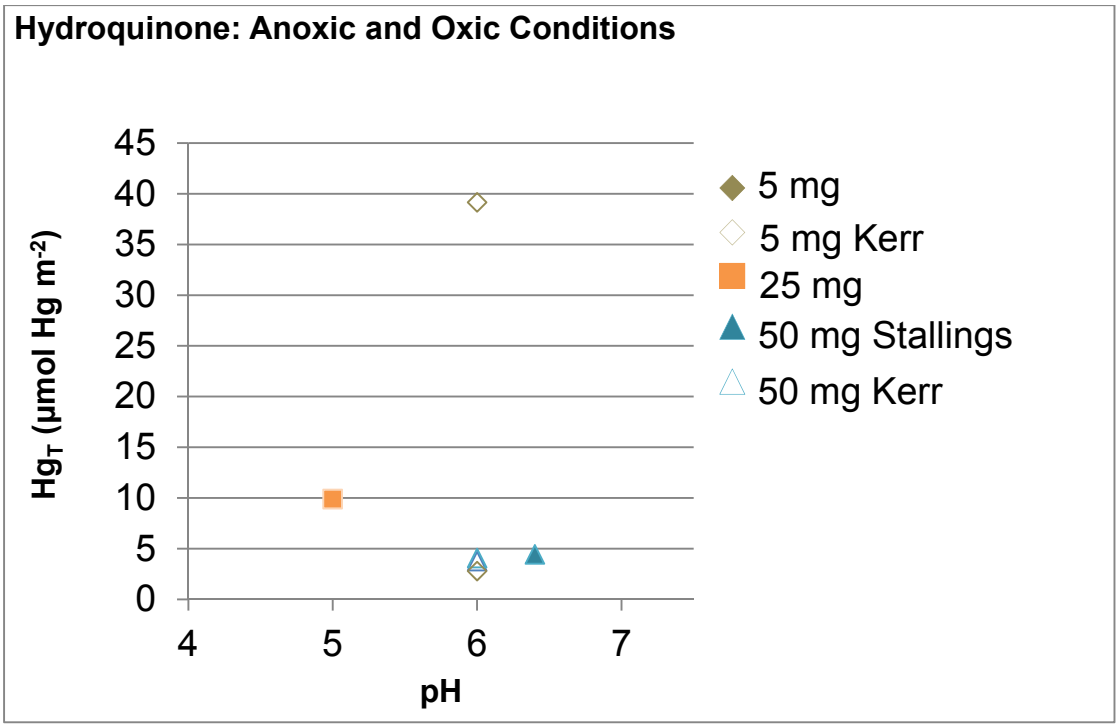

Figure 12. Total release of mercury with pH. The final pH values of reactor solutions are compared to the total amount of mercury released for seven anoxic dissolution experiments. Four data points are from Kerr (2007).

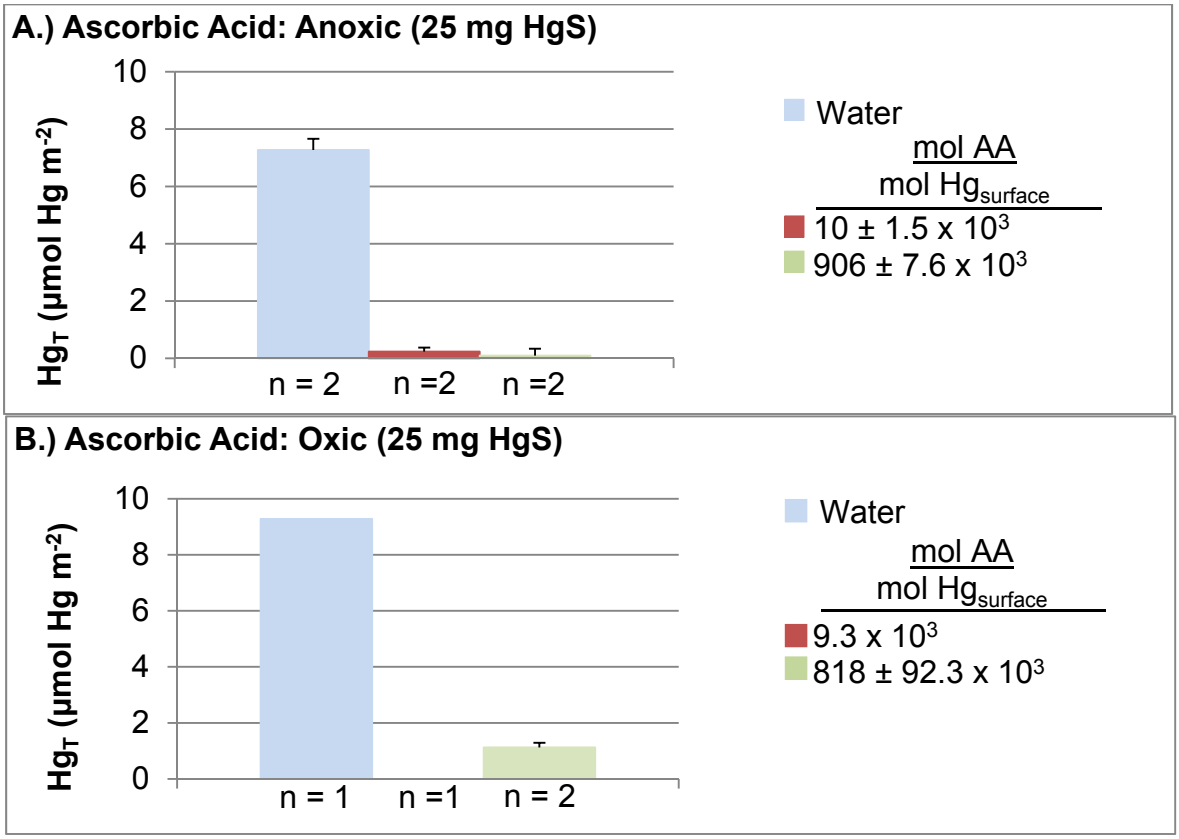

Figure 13. Release of mercury in the presence of ascorbic acid at various concentrations under anoxic conditions. The concentration of total mercury released (reactor + Σ trap solutions) for experiments carried out under anoxic A.) and oxic B.) conditions with 25 mg HgS are compared for solutions containing various concentrations of ascorbic acid. The concentration of ascorbic acid is represented in three cases by the average ratios from several experiments. See Appendix B for a list of the conversions used to obtain the ratio.

3.5 *Sulfate Concentrations in Reactor Solutions*

For experiments with cinnabar in water under anoxic conditions, the sulfate concentrations measured in the reactor solutions at the end of the experiments were 60 to 340 times higher than the corresponding total mercury concentrations. The concentration of sulfate generally decreased as the mass of cinnabar increased from 5 to 25 mg (Fig. 14). The release of mercury followed a similar trend, but the decrease occurred between experiments with 25 and 50 mg cinnabar. The sulfate

concentration was highest in the solution with 5 mg HgS and the mercury concentration was highest in the solution that contained 25 mg HgS.

In the presence of hydroquinone (11 x 10^3 mol HQ: mole $Hg_{Surface}$) and 5 mg cinnabar, the amount of released sulfate displayed a slight increase over the amount released in pure water (Fig. 15). On the other hand, the released mercury decreased to below the detection limit. The amount of sulfate released in water is significantly greater than the amount of mercury released.

The relative amounts of released mercury and sulfate in anoxic experiments using 5 mg initial vs. recycled cinnabar in the presence of 11 x 10^3 moles HQ per mole $Hg_{Surface}$ are in stark contrast. Only sulfate is measurable in the experiment with initial cinnabar; whereas only mercury is measurable in the experiment with recycled cinnabar (Fig. 16). In addition, the amount of released sulfate in the non-recycled cinnabar experiment is almost 4,000 times the released mercury in the recycled cinnabar experiment.

In the presence of a ratio of 9 x 10^3 moles of ascorbic acid per mole $Hg_{Surface}$ under anoxic conditions, the concentration of sulfate released into the reactor solution in the presence of 25 mg cinnabar increased by 33% (Fig. 17) over that in pure water. In contrast, the total amount of mercury released decreased by 96%. The mole ratio of sulfate to mercury in water is approximately 100; whereas, the ratio in the ascorbic acid solution is approximately 2,000.

For experiments in which sulfate was added to the reactor solutions, more mercury was released under oxic conditions by a factor of two than under anoxic conditions (Fig. 18). However, in both cases, the amount of mercury released was less than in pure water.

3.6 *The Addition of Mercury to Water Containing Cinnabar*

Under oxic conditions, the sum of the amount of mercury measured in trap and reactor solutions at the end of the experiments was less than the amount of mercury added in the beginning of

the experiment as a spike, evidenced by positive values of X, where ($X = (Hg_{spike} - Hg_T)\ g^{-1}$ HgS). The mercury present in the beginning of the experiment and not measured in the final reactor solutions is interpreted to have been adsorbed to the surface of cinnabar. As the amount of mercury added to reactor solutions increased the amount of mercury adsorbed to the surface increased (Fig. 19). In contrast, experiments carried out under anoxic conditions resulted in dissolution in the presence of excess mercury (Fig. 20). Moreover, doubling the concentration of mercury added to anoxic solutions containing cinnabar, resulted in more than nine times the amount of mercury released.

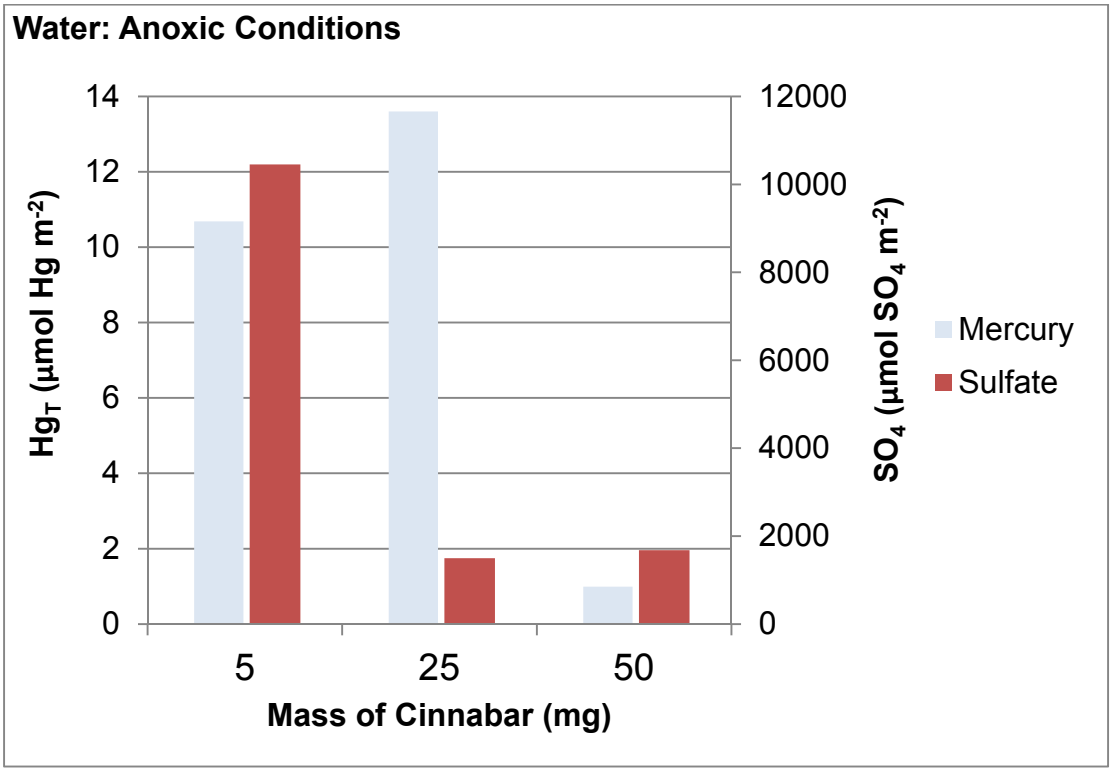

Figure 14. Release of sulfate and mercury in water. The concentration of total mercury (reactor + Σ traps; left axis) and sulfate (right axis) released during anoxic experiments in pure water using different initial masses of cinnabar (5, 25, and 50 mg HgS). Only results from selected dissolution experiments are plotted (See Table 3).

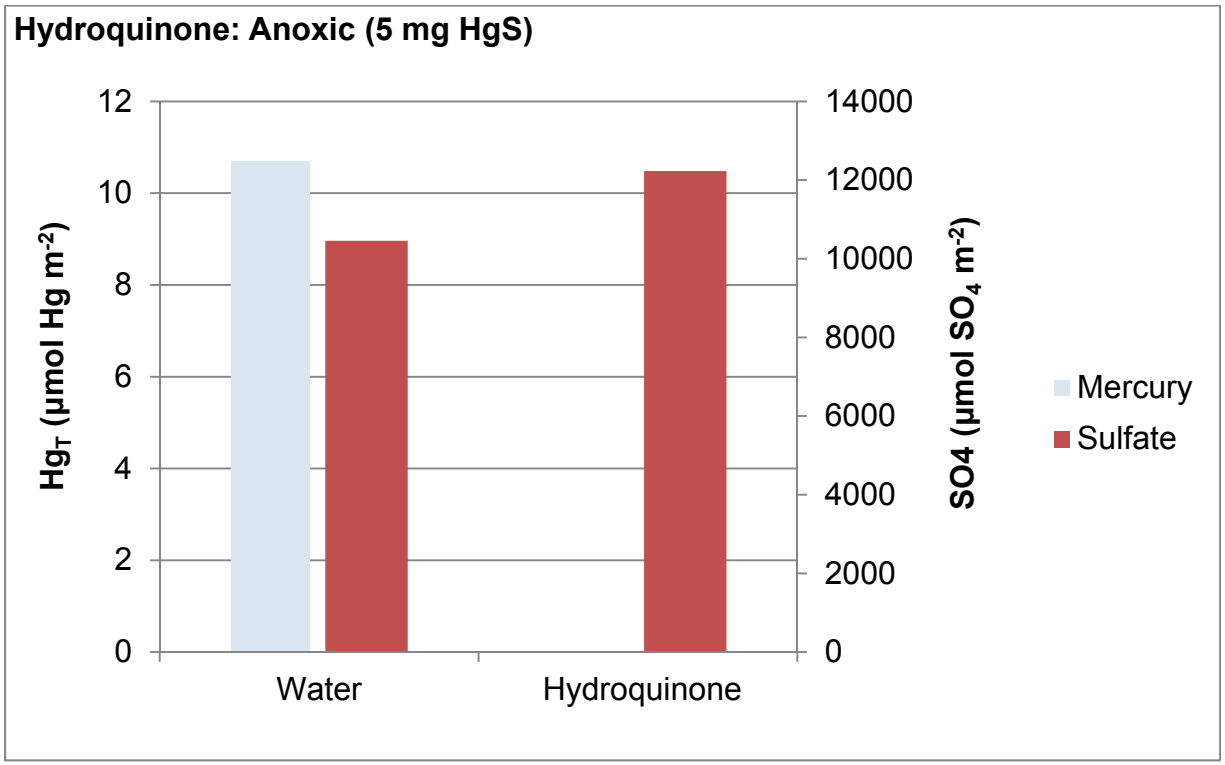

Figure 15. Release of sulfate and mercury in the presence of hydroquinone. The amount of total mercury (reactor + Σ traps; left axis) measured in the reactor solution and the concentration of sulfate (right axis) for an experiment carried out in water with 5 mg HgS is compared to a comparable experiment with hydroquinone (mol [HQ]: mol $Hg_{surface}$ = 11 x 10^3). Refer to Table 3 for specifics on which experimental solutions were selected for sulfate analysis.

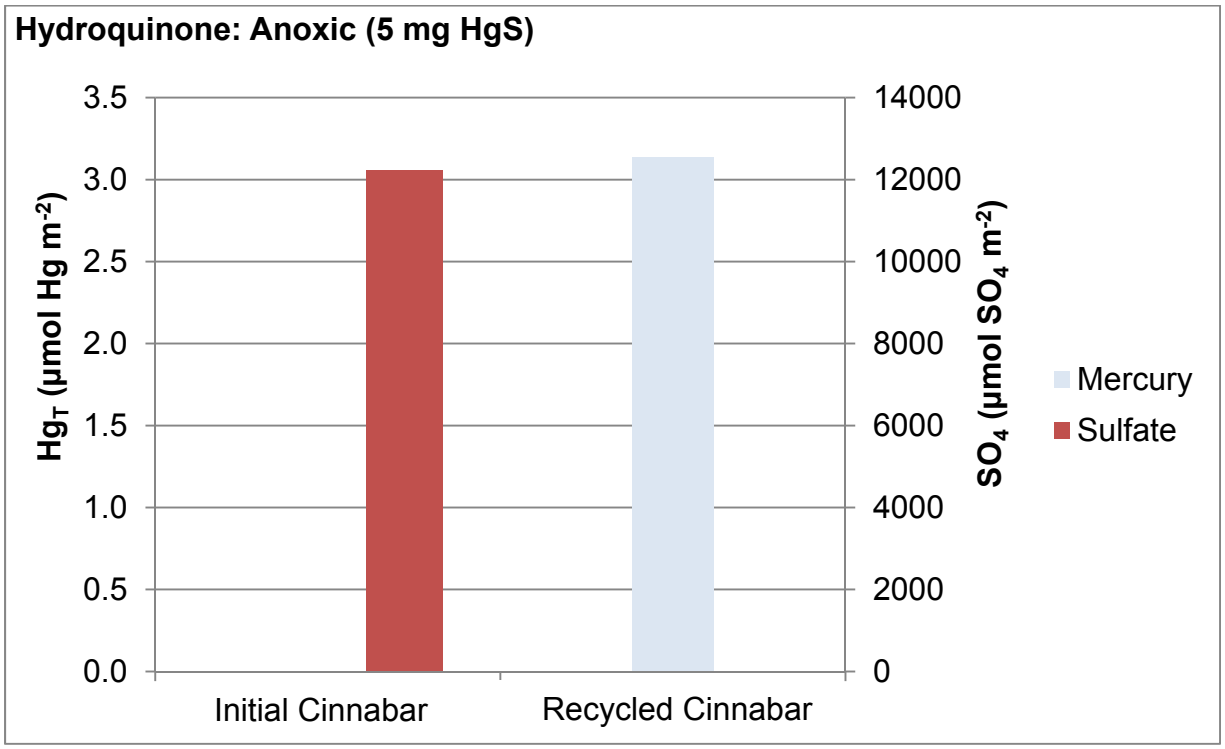

Figure 16. Release of sulfate and mercury in solutions with initial versus recycled cinnabar. The amount of total mercury (reactor +Σ traps; left axis) and sulfate (right axis) measured in the reactor solution and for an experiment carried out under anoxic conditions with 5 mg initial cinnabar and containing hydroquinone (mol HQ: mol $Hg_{surface}$ = 11 x 10^3) is compared to an experiment under similar conditions with 5 mg recycled HgS (mol HQ: mol $Hg_{surface}$ = 15 x 10^3). Refer to Table 3 for specifics on which experimental solutions were selected for sulfate analysis.

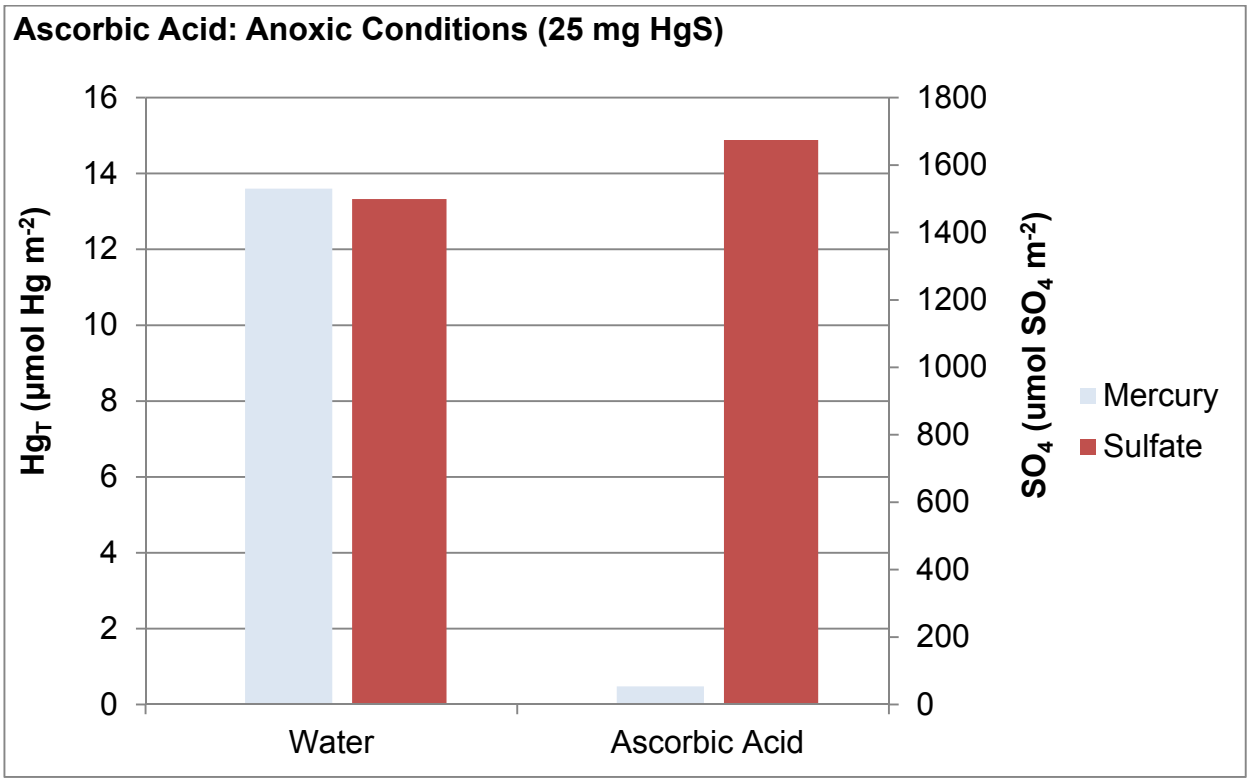

Figure 17. Sulfate and mercury concentrations in solutions containing ascorbic acid. The amount of total mercury (reactor + Σ traps; left axis) and sulfate (reactor solution; right axis) released in solutions of water with 25 mg HgS and carried out under anoxic conditions are compared to amounts released in a solution containing 25 mg HgS in the presence of ascorbic acid (mol AA: mol $Hg_{surface}$ = 9 x 10^3). Refer to Table 4 for specifics on which experimental solutions were selected for sulfate analysis.

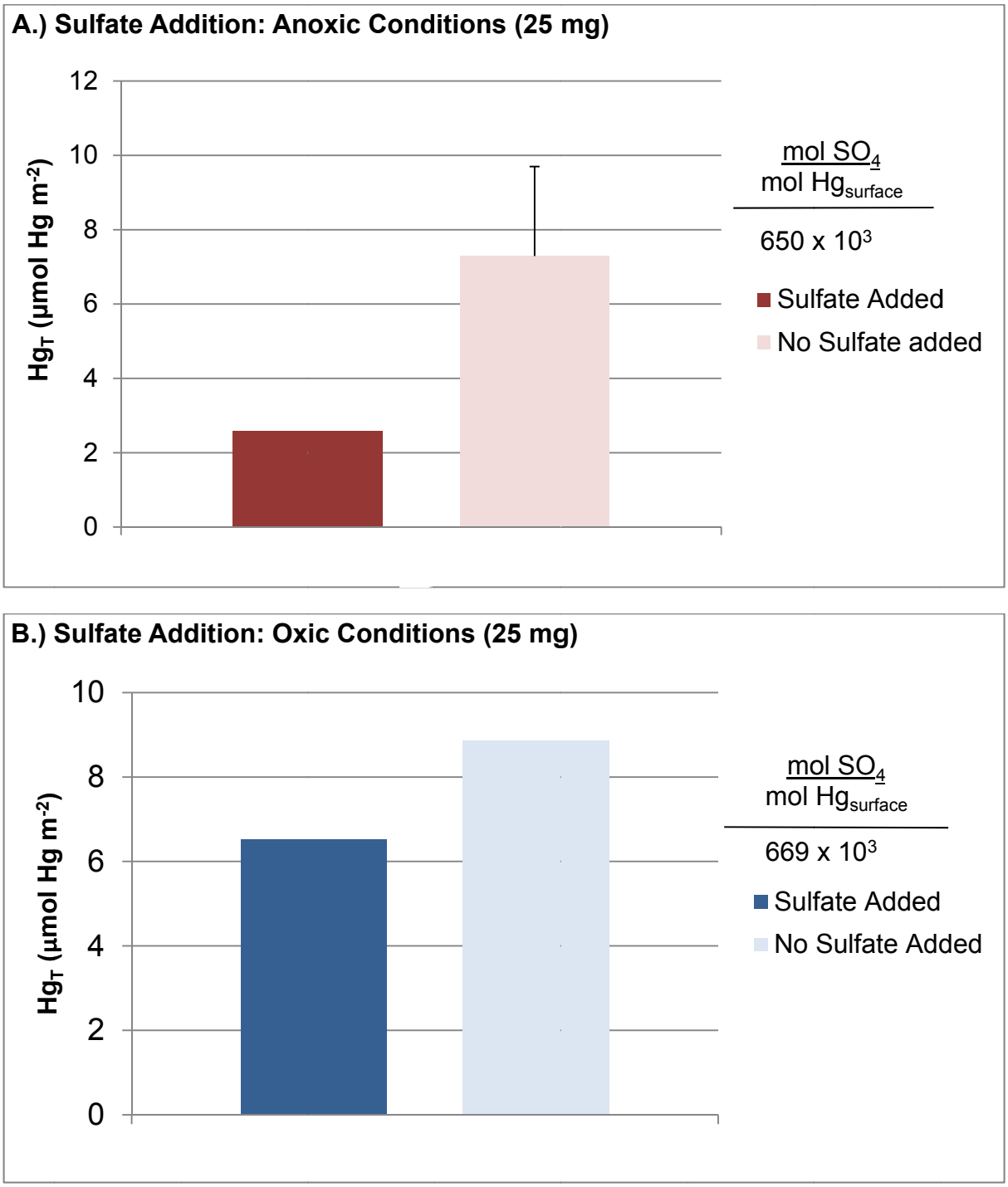

Figure 18. Mercury released in solutions with added sulfate. The concentration of total mercury released in reactor and trap solutions for experiments carried out under A.) anoxic and B.) oxic conditions with 25 mg HgS are compared for solutions containing no sulfate and a relatively high concentration of sulfate. The concentration of sulfate is represented by the ratio: mol SO_4 / mol $Hg_{surface}$.

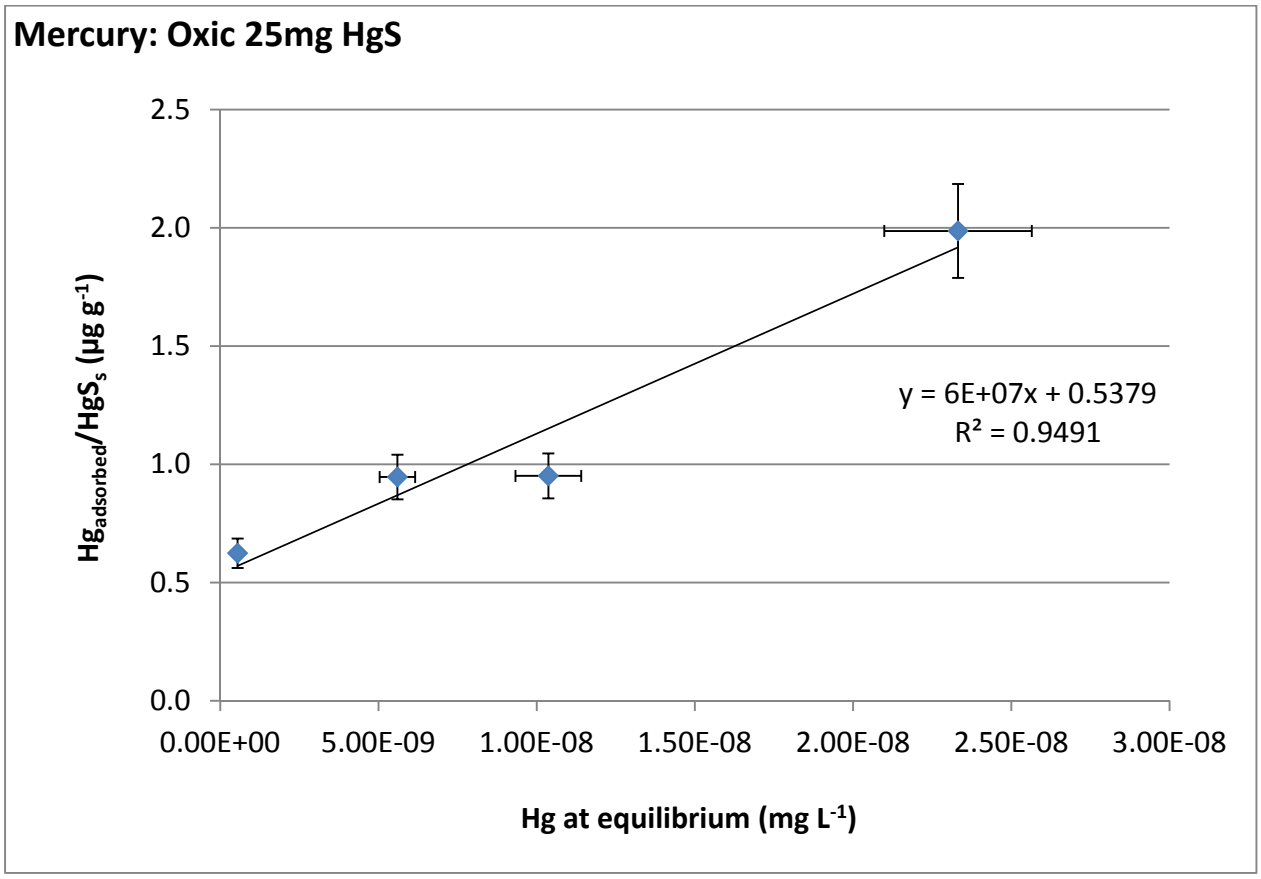

Figure 19. Adsorption isotherm for mercury uptake on the cinnabar surface. The minimum amount of mercury adsorbed per unit mass of cinnabar ($X = Hg_{adsorbed} = (Hg_T - Hg_{Spike})$ g^{-1} HgS versus total moles of mercury remaining in the reactor (C = Hg at equilibrium) in a series of experiments carried out under oxic conditions. 10% deviation in X is included for error associated with surface area measurements; and 20% error is included in C to account for error associated with CVAFS measurements.

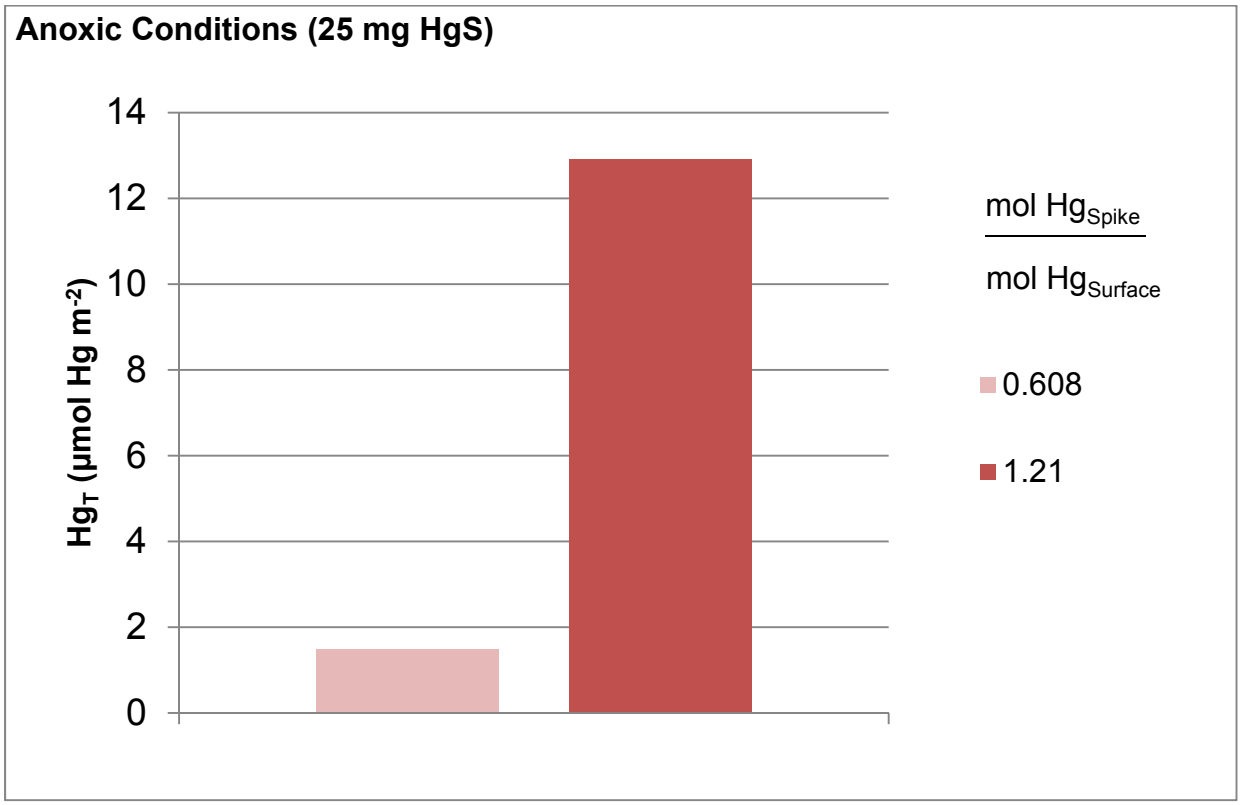

Figure 20. Mercury release in solutions with added mercury. The concentration of total mercury released in reactor and trap solutions for experiments carried out under anoxic conditions with 25 mg HgS are compared in solutions containing various concentrations of added mercury (Hg_{spike}).

IV. DISCUSSION

4.1 Introduction

The scope of this thesis was limited to quantifying the release of mercury from cinnabar under selected experimental conditions relevant to oxic/anoxic interfaces in the environment. The data were used to characterize the types of surface reaction mechanisms that likely controlled the release. These include mechanisms that are sensitive to redox conditions, the extent of cinnabar particle aggregation, the presence of hydroquinone or ascorbic acid, and whether or not the cinnabar was used in initial form or recycled after reacting for a 4 h period. The discussion topics will begin with the release of mercury from cinnabar under anoxic and oxic conditions; followed by surface reaction mechanisms, including, how changes in surface area affect mercury and sulfur release; and, lastly, the implications of recycling the cinnabar surface.

4.2 Reduction of Mercury

4.2.1 Anoxic Conditions

It was expected that cinnabar in the presence of hydroquinone (HQ) and ascorbic acid (AA) would release a significant amount of mercury into solution (Kerr 2007; Waples et al., 2005). The dissolution of mercury from the surface may occur through one of two possible mechanisms: the reduction of mercury or the oxidation of sulfide and subsequent weakening of the Hg-S bond. According to one set of redox reactions pertinent to certain environmental conditions (Fig. 21), the dissolution of cinnabar should not be possible through the reduction of mercury by hydroquinone or ascorbic acid. However, the presence of similar aromatic and conjugated moieties in DOM, and the correlation of the aromaticity of DOM with

enhanced cinnabar dissolution (Waples et al., 2005; Ravichandran et al., 1998) suggested that these moieties are contributing significantly to the dissolution of mercury.

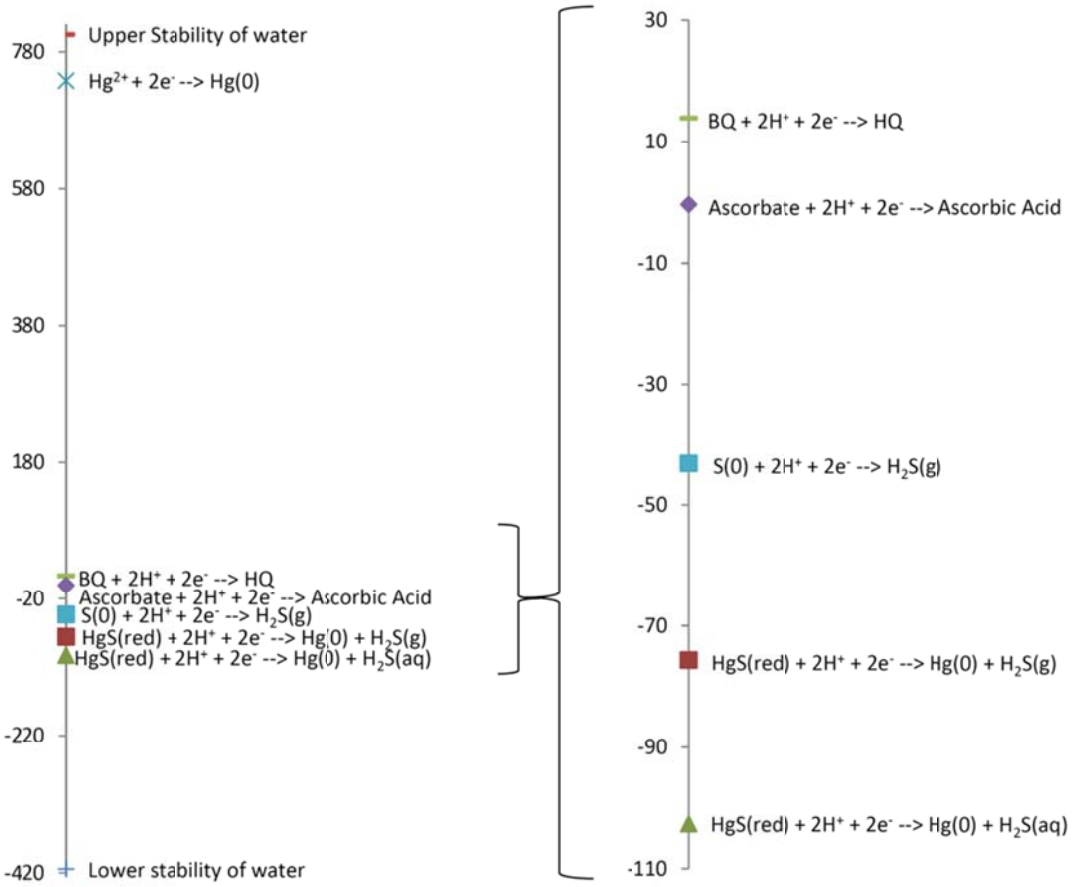

Figure 21. Redox ladder for various reactions involving cinnabar (HgS_{red}), sulfur, hydroquinone/benzoquinone and ascorbic acid/ascorbate. Redox ladder for half reactions (in E_h (mV)) involving hydroquinone (HQ) (and its oxidized form benzoquinone BQ), ascorbic acid (and its oxidized form ascorbate), cinnabar (HgS_{red}); and metacinnabar (HgS_{black}) under conditions representative of those measured for sites in the Florida Everglades: $[Hg^{+2}]$ = 13 pM, $[SO_4^{-2}]$ = 470 µM, $[H_2S]$ = 0.22 µM, pH = 7, 25°C (Drexel et al., 2002); $P_{[Hg0]} = 2.47 \times 10^{-13}$ (Valente et al. 2007). Natural waters typically have an E_h range of 0 to 700 mV.

Hydroquinone and ascorbic acid, the two model compounds for aromatic/conjugated moieties investigated in this study, behave differently under redox conditions. Hydroquinone is resistant to oxidation at the pH conditions of this experiment (pH = 2 to 8) because of the high value of the equilibrium constant for its first acid dissociation (pK_{a1} = 10.1). Conversely, it is generally accepted that ascorbic acid prevents oxidation by reducing dissolved oxygen, which implies that AA itself is highly susceptible to being oxidized. By comparing results of cinnabar dissolution in the presence of these two different molecules it is possible to make some assessment of the sensitivity of the cinnabar surface to oxidation state of the solution. If the dissolution of cinnabar occurs through the oxidation of sulfide, we should observe decreased release of mercury in the presence of AA compared to pure water because the primary oxidant in solution, dissolved oxygen, should be consumed by the AA and not the sulfide. There should be no effect on the release of mercury in the presence of HQ compared to pure water, because HQ does not react with dissolved oxygen under these conditions.

Stack et al. (2004) provided a general description of the reaction mechanism between an oxidized iron site in hematite and HQ: adsorption of HQ to the iron surface site; electron transfer (forming a semiquinone radical and reduced iron); desorption of the semiquinone; and dissolution of the reduced iron. If the dissolution of cinnabar were to occur through the reduction of mercury, we would expect to observe increased dissolution of cinnabar in the presence of HQ and AA since they are both reductants. Moreover, as the amount of reducing agent is increased the amount of mercury released from the surface of the mineral should also increase. Also, because the reducing power of the reductant should be depleted over time, the dissolution of mercury from the surface should cease.

In general, the same amount of mercury was released from cinnabar in the presence of HQ as in the presence of only water (Table VI). Furthermore, in solutions of HQ and AA as the concentration of the reductant increased, the amount of mercury measured in solution did not increase proportionally. Kerr (2007) observed comparable results with cinnabar in the presence of HQ under anoxic conditions (pH ~ 6, I = 0.01) as those in water; and her results are within the statistical uncertainties of our observations. In addition, she measured a 16% increase in the amount of released mercury with only a 10% increase in HQ concentration. The negligible difference between the amount of mercury measured in HQ solutions versus water and the lack of a correlation between mercury and increasing concentrations of reductant indicates that the release of mercury from the surface of cinnabar is not driven simply by a direct reduction of mercury by either HQ or AA.

TABLE VI
RELEASE OF MERCURY IN THE PRESENCE OF WATER COMPARED TO HYDROQUINONE + WATER

Mass (mg)	Water (μmol Hg m^{-2})	HQ (μmol Hg m^{-2})
5	11.4± 6.82	15.0± 20.9
25	7.29± 2.42	11.5
50	1.62± 1.25	3.22± 1.74
25 (oxic)	8.85	6.05

Further, high concentrations of mercury in reactor solutions containing water versus an HQ solution suggest that HQ does not reduce mercury even after it has been released from cinnabar. It may be possible that HQ prevents mercury from being reduced and transported to the trap solution by forming an aqueous complex; therefore, resulting in less mercury in the trap solution and more soluble mercury measured in the reactor, while maintaining the same overall concentrations of mercury for experiments containing water versus HQ.

The release of mercury from cinnabar significantly decreased in the presence of AA for experiments carried out under both oxic and anoxic conditions. Significant decreases in the amount of mercury released in the presence of increasing concentrations of AA indicate the importance of oxygen in the dissolution mechanism and further support that the idea that the mechanism is not controlled by a direct interaction between AA and the surface of cinnabar. If oxygen is a major limiting factor, then the amount of mercury released during dissolution of cinnabar may be limited by the oxidation of sulfide within the mineral structure.

Banwart et al. (1989) observed increased reductive dissolution of hematite in the presence of increasing concentrations of ascorbate (ascorbic acid at pH 3) ($I = 0.01$ M $NaNO_3$, pH = 3, 25°C, SA = 17.5 $m^2 g^{-1}$). Moreover, the addition of oxalate and ascorbate together resulted in an amount of dissolved iron that was greater than the sum of the amounts produced by the two reactants individually. These authors hypothesized that oxalate acted as a chelating agent and aided in the reduction and release of iron. These results indicate that HQ and AA cannot directly bind with the surface and may only indirectly affect dissolution; or that HQ and AA bind to the surface for an electron transfer reaction, but do not bind with the Hg once it is released from the surface.

The release of mercury decreased significantly after typically two hours of reaction time for all experiments (Fig. 22) in agreement with Kerr's (2007) observations. Together, the results indicate that the dissolution of cinnabar depends on the amount of reactive surface sites exposed and how the number of reactive surface sites is altered over time. Echigo et al. (2012) observed steady-state reaction rates of two different sized hematite nanoparticles (6.8 nm and 30.5 nm) after 210 minutes of reaction time during batch experiments carried out under dark, anoxic conditions (2 g L^{-1} hematite, I = 10 mM, pH = 3.35, T = 23.0± 0.03). They observed increased aggregation between particles as time passed; and significant changes in particle morphology over time, including rounding of the grains. It is possible that the reaction of HQ and AA with mercury and/or sulfur at the cinnabar surface diminishes with time either because molecules bind to the surface and decrease the amount of reactive surface available for subsequent reduction/oxidation; or physical changes in the surface decrease the amount of exposed reactive surface sites.

Altogether, the results indicate that hydroquinone and ascorbic acid are indirectly participating in the surface mechanism that controls dissolution. It seems more likely that the mechanism for dissolution is controlled by the oxidation of sulfur, and any species that interferes with the oxidation of sulfur, also inhibits the dissolution of cinnabar. Protons (H^+) are also able to bind to reduced sulfur sites on the surface of cinnabar and can compete with oxidants in solution for reduced sulfur sites. If H^+ reacts with surface reduced sulfur, then this sulfur becomes less likely to react with other species in solution, such as the oxidized like benzoquinone and ascorbate. However, when comparing the concentration of mercury released from cinnabar in solutions that received pH adjustments to those that did not (Fig. 23) the effect

on the overall dissolution trends produced by changes in pH is minimal and suggests that H^+ is neither inhibiting nor enhancing dissolution.

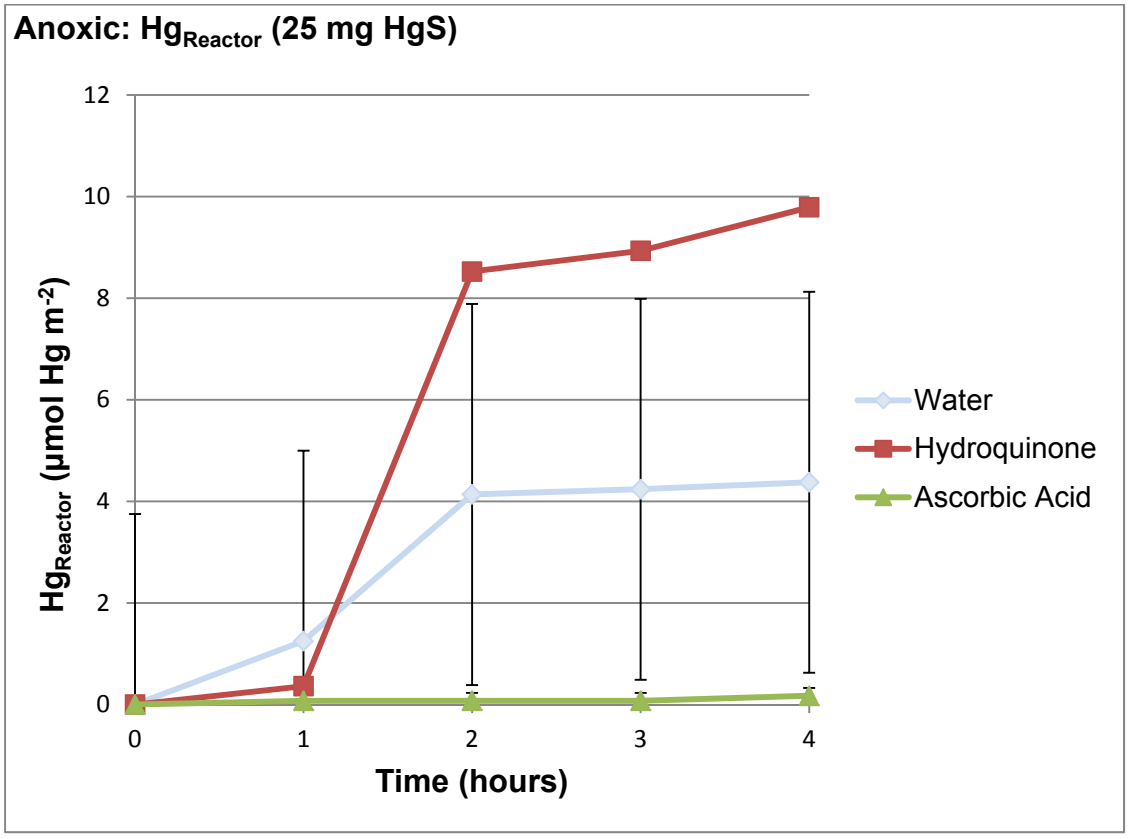

Figure 22. The release of mercury over time. The release of mercury to reactor solutions containing hydroquinone (21 x 10^3) and ascorbic acid (9 x 10^3) in the presence of 25 mg HgS and carried out under anoxic conditions over a 4 h period.

4.2.2 Oxic Conditions

The results from the anoxic experiments indicated that increased amounts of mercury would be released in oxygenated environments because sulfur is highly reactive with dissolved oxygen. Assuming that the dominant reaction controlling dissolution is that between an oxidant and reduced sulfur on the surface, the presence of HQ (in the most reduced state; $pH < pKa_1 < 10.16$) should not have affected the amount of mercury released to solution, as observed. If oxygen mediates the dissolution reaction, and ascorbic acid scavenges the oxygen in solution, then decreased release of mercury in the presence of AA is expected and as also observed. Overall, oxidizing species are expected to react with reduced sulfur to a greater degree than the reductant with mercury thereby controlling the dissolution mechanism.

The same amount of mercury was released from 25 mg HgS in water under anoxic conditions as in water under oxic conditions (7.27± 2.44 μmol Hg m^{-2} and 9.28 μmol Hg m^{-2}, respectively); and approximately the same amount of mercury was released in solutions containing hydroquinone in anoxic compared to oxic conditions (9.90 μmol Hg m^{-2} at a ratio of 8.85 x 10^3 moles HQ: moles $Hg_{Surface}$ and 6.05 μmol Hg m^{-2} at a ratio of 21 x 10^3 moles HQ: moles $Hg_{Surface}$ respectively). However, significantly less mercury was released in ascorbic acid solutions under anoxic conditions when compared to oxic conditions (0.098± 0.14 μmol Hg m^{-2} and 1.13± 0.16 μmol Hg m^{-2}, respectively). These comparisons further support the interpretation that ascorbic acid scavenges oxygen and prevents the oxidation of reduced sulfur on the cinnabar surface, thereby, decreasing the amount of mercury released.

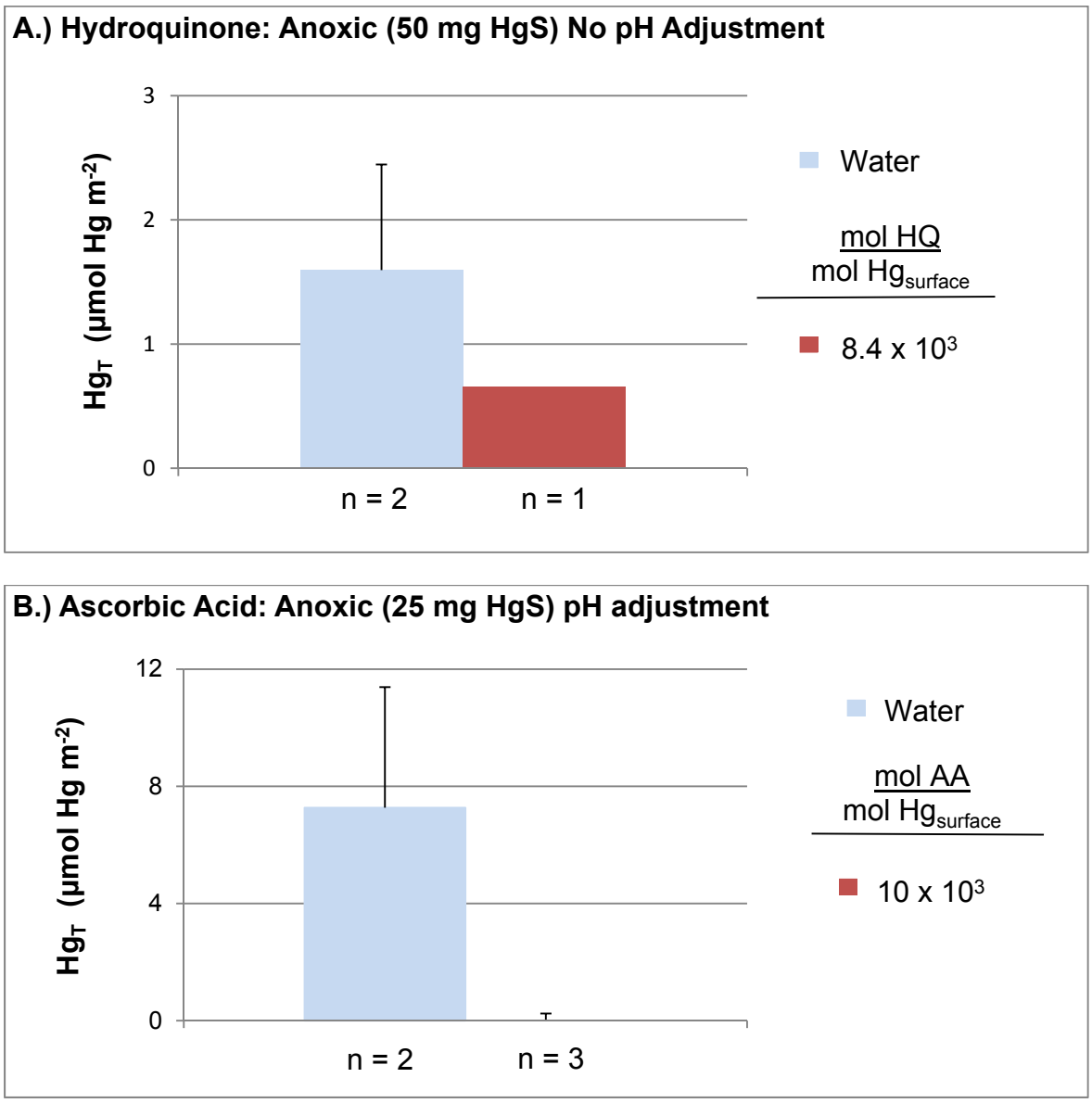

Figure 23. Comparison of mercury released in non-pH adjusted solutions of water, hydroquinone and ascorbic acid. The concentrations of total mercury (reactor + Σ traps) released in solutions containing a ratio of approximately 9.2 x 10^3 moles reductant to moles Hg exposed at the surface are compared for solutions containing hydroquinone A.) and ascorbic acid B.) with 50 and 25 mg HgS, respectively. Data are shown only for solutions that did not receive a pH adjustment.

Dissolved organic matter contains aromatic and ketone moieties similar to hydroquinone and ascorbic acid. If HQ and AA are representative of the DOM moieties responsible for dissolution of cinnabar, then little mercury should be released in the presence of DOM in contrast to previous work (Ravichandran et al., 1998; Waples et al., 2005). Aromatic structural units within DOM molecules may stabilize negative charge by evenly distributing it throughout the structure of the molecule. As the amount of aromatic units increase in a particular sample of DOM, the more negative charge (e.g., electrons pulled from reductants such as sulfide) can be efficiently distributed. In turn, the DOM more readily continues to react with reduced moieties, such as sulfur on the surface of cinnabar. In this way, the DOM structures with more aromatic moieties are likely more reactive with reduced species. The correlation between the amounts of mercury released in the presence of increasingly aromatic structures indicates that the process likely occurs through a single or double electron transfer mechanism.

It is possible that the reactivity of the model compounds HQ and AA with cinnabar do not represent the overall reactivity of large DOM structures with cinnabar. These particular moieties likely are not entirely representative of the more complex molecules responsible for the enhanced dissolution as observed by Waples et al., 2005. Further, Kerr (2007) observed increased dissolution of mercury in the presence of benzoquinone (the oxidized form of hydroquinone) when compared to hydroquinone (1.54×10^{-9} vs. $< 1.80 \times 10^{-11}$, respectively) for experiments carried out under oxic conditions. It seems evident that oxidants promote mercury release through reaction with reduced sulfur on the surface of cinnabar even in environments where oxygen is limited.

4.3 Surface Reaction Mechanisms

4.3.1Surface Area

It was expected that as the mass of cinnabar, and therefore the total surface area, increased, the amount of dissolved mercury measured in the experimental solution should also have increased. However, this was not observed for cinnabar dissolution under anoxic conditions in solutions containing water. Furthermore, decreased release of mercury with increased cinnabar concentration was also observed in experiments containing hydroquinone.

As the amount of cinnabar particles in solution become more concentrated the probability of particle-particle interactions becomes more probable, especially because cinnabar is hydrophobic. Aggregation appears to decrease the amount of reactive surface sites and limits the extent of dissolution of surface species. Turbulent hydrodynamic conditions may be necessary to disturb aggregation and promote dissolution (Barnett et al., 2001). Mercury may be less in solutions containing higher masses of cinnabar because the aggregates are larger in size, effectively burying entire particles within the center of the aggregate.

Alternatively or simultaneously, mercury dissolved from the surface of cinnabar may be removed from solution by re-adsorption to the surface (Burkstaller et al., 1975; Holley et al., 2007). As the surface area of cinnabar increases, the amount of reactive surface sites increases, and the opportunity for mercury to re-adsorb to the surface increases. Burkstaller et al. (1975) observed decreased concentrations of soluble mercury as the mass of New Almaden cinnabar mass was increased from (0.3 to 3 to 33 g L^{-1}) at pH 1.5 in solutions containing 10 mM Fe(III) and 3 mM Cl. Whereas the conditions for experiments conducted for this thesis were carried out at near neutral pH and contained considerably lower cinnabar concentrations (0.05, 0.25, and 0.50 g L^{-1}), our observations also support the possibility of the re-adsorption mechanism.

An additional hypothesis was proposed by Holley et al. (2007) who also observed decreased dissolution of cinnabar in experiments performed under oxic conditions as the concentration of cinnabar increased from 25 to 100 g L^{-1}. They suggested that as the concentration of cinnabar increased the solution became saturated with respect to soluble mercury and the dissolution eventually stopped. The amount of mercury in the reactor solutions under anoxic conditions that was needed to reach equilibrium with respect to cinnabar was estimated using the solubility constant for Rxn. 1 ($K_{sp} = 10^{-36.8}$). It was assumed that the measured sulfate concentrations were simply equivalent to the concentration of HS^- in the reactor during the experiment and the pH corresponded to that measured at the end of the experiment (Table III). In most cases, the amounts of mercury estimated, (on the order of 10^{-38}) assuming equilibrium was achieved, were orders of magnitude lower than measured amounts. In these cases dissolution does not appear to have been limited by attainment of equilibrium with dissolved mercury and hydrogen sulfide. In three cases (CIN9911, CIN71611, and CIN10311) mercury was below detection in the reactor, and thus could have been as low as the estimated amount. Notably, the reactor solutions with no measureable mercury, also contained HQ or AA; and experimental solutions that were adjusted for pH had sulfate concentrations below detection limits (CIN7111A, CIN7111B and CIN71611B). The observations indicate that aqueous mercury and sulfate concentrations are not limiting the dissolution of mercury from the surface. Moreover, in general, the release of mercury plateaus after ~2 h, further supporting aggregation and re-adsorption as limiting factors involved in dissolution.

4.3.2 Recycled Cinnabar

If there had been no significant changes to the cinnabar surface after the end of the initial dissolution reaction, we would have expected the recycled cinnabar surfaces to release the same amount of mercury as the initial cinnabar surfaces. In addition, based on results described above, the amount of released mercury is expected to be equivalent between recycled surfaces and the initial surfaces in the presence of hydroquinone under both anoxic and oxic conditions. However, less mercury was released from recycled compared to initial surfaces (0.061 and 7.27± 2.44 μmol Hg m^{-2}), and significantly less mercury was released from recycled vs. initial surfaces in solutions containing hydroquinone (3.42± 0.54 and 9.09± 1.00 μmol Hg m^{-2}, respectively). Interestingly, 99% more mercury was released from recycled surfaces of cinnabar in the presence of hydroquinone than in water (3.42± 0.54 and 0.061 μmol Hg m^{-2}). Based on these results, hydroquinone reactivates the surface of cinnabar and promotes dissolution.

Other researchers have observed a layer of oxidized sulfur on the surface of iron-sulfide minerals under oxic conditions (McGuire and Hamers, 2000); and exploratory X-ray Absorption Near-Edge Structure (XANES) spectroscopy suggests that a coating of oxidized sulfur species also exists on the surface of cinnabar exposed to water under anoxic conditions (Fig. 24). The presence of oxidized sulfur may block the interaction of other species with the surface of cinnabar. Further, the introduction of reduced species such as HQ could reduce the oxidized sulfur coating and allow dissolution to proceed. If an excess amount of oxidized sulfur exists on the surface of cinnabar after the initial dissolution experiment, it would be expected that a large amount of sulfate would be released from recycled cinnabar surfaces, resulting in higher concentrations of measured sulfate. It is possible that residual sulfate remained on the surface from cleaning methods performed on the cinnabar by Kerr 2007; however, the high amounts of

sulfate measured by other groups suggest that sulfur in cinnabar, rather than residual sulfur from cleaning, is the source of the sulfate.

Measured sulfate concentrations ranged from 1,500 – 12,230 ppm in experimental solutions of water, hydroquinone and ascorbic acid. However, no sulfate was measured in solutions in contact with recycled cinnabar. In this and other studies significantly higher sulfate concentrations relative to mercury concentrations were observed in solutions contacting cinnabar under anoxic conditions (3.82 μmol Hg and 26.3 μmol SO_4 m^{-2}; $Ratio_{Hg/SO4}$ = 6.88; Ravichandran et al. (1998)) and (10.7 μmol Hg m^{-2} and 10,454 μmol SO_4 m^{-2}; $Ratio_{Hg/SO4}$ = 977; this study). Under oxic conditions the concentrations of mercury and sulfate are lower relative to those measured in anoxic conditions, but the ratio of sulfate released per μmol Hg is much greater (0.004 μmol Hg m^{-2} and 13.1 μmol SO_4 m^{-2}; $Ratio_{Hg/SO4}$ = 3,275; Holley et al., (2007)). The results indicate that sulfur oxidation on the surface of cinnabar is rate-limiting even under conditions where oxygen is limited.

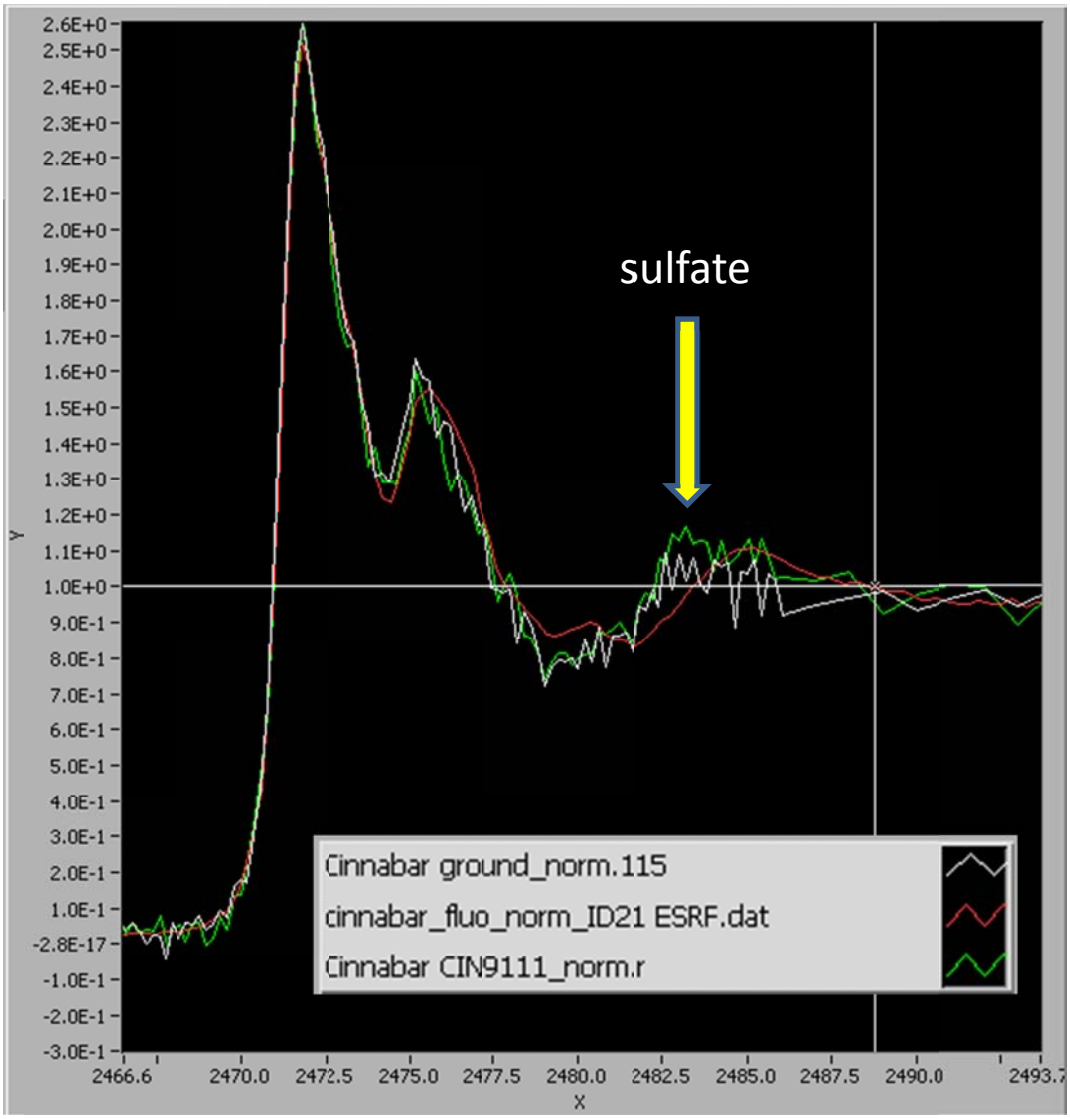

Figure 24: X-ray Absorption Near Edge Structure spectroscopy for an experiment. The raw spectra for an experiment with 25 mg HgS in water (Cinnabar CIN9111_norm.r) carried out under anoxic conditions is compared to freshly ground cinnabar (Cinnabar ground_norm.115) taken directly from the cinnabar storage bottle; and reference spectra (cinnabar_fluo_norm_ID21 ESRF.dat).

V. CONCLUSIONS AND FUTURE WORK

The release of mercury remains largely unaffected in the presence of hydroquinone; and significantly decreases in the presence of ascorbic acid. The results from this study indicate that hydroquinone and ascorbic acid are indirectly participating in the surface mechanism that controls dissolution; and more likely that the mechanism for dissolution is controlled by the oxidation of sulfur. Increasing the surface area decreases the amount of mercury released and less mercury is released from recycled surfaces, indicating that physical surface characteristics such as the number of exposed reactive surface sites may be important factors controlling dissolution. Moreover, pH appears to have minimal control on the release of mercury under the conditions specific to this study (pH = ~2-8).

As the water table fluctuates in the near-surface environment, the position of the oxic/anoxic boundary will fluctuate as well. The constantly fluctuating exposure of cinnabar to oxidized and reduced moieties in DOM creates an ever-changing potential for dissolution and release of mercury to solution where it can be methylated. Reductants such as quinones comprise a large number of moieties in DOM and they are able to easily transfer and/or lose electrons; however, environmental oxidants are likely the limiting factor in the dissolution of cinnabar at the oxic/anoxic boundary. Cinnabar that has formed in the sediments becomes exposed to more oxidizing conditions during periods of drought, as the fall of the oxic/anoxic boundary introduces more oxidized species to the sediments; resulting in the formation of oxidized complexes on the surface of cinnabar. As the boundary moves up, such as during

periods of flooding, cinnabar is exposed to a more reducing environment and reductants can remove the oxidized surface layer, leaving behind an exposed and "clean" cinnabar surface layer. During a subsequent cyclic drop in the oxic/anoxic boundary layer the "clean" surface is exposed to oxidizing conditions in which the sulfur is easily oxidized; the Hg-S bond weakens; and mercury is released. Furthermore, reductants, such as hydroquinone and ascorbic acid could enhance the release of mercury.

The mechanism of mercury release from cinnabar may occur through the adsorption of an oxidant to a reduced sulfur site where an initial oxidizing reaction converts sulfide to higher oxidation states; an electron transfer from the oxidant forming a semiquinone, or some other comparable radical species; desorption of the semiquinone or radical species; and dissolution of the oxidized surface species. The oxidation of sulfur species at the surface of cinnabar likely weakens mercury-sulfur bonds releasing mercury to solution; or, oxidized sulfur species may remain at the surface and build up. Available reductants may be able to remove the oxidized layer and promote dissolution.

To better determine the direct role that oxidized species play in inhibiting dissolution, Transmission Electron Microscopy (TEM) imaging of the cinnabar surface should be conducted to determine the condition of the surface (i.e., shape and size of the particles); and XANES spectroscopy could be used to monitor changes in the speciation of sulfur on the surface. Furthermore, Fourier Transform Infrared (FT-IR) spectroscopy would be useful in determining the change in the simple organic reactants, such as quinones; and spectrofluorometry for measuring the change in complex organic reactants, such as DOM after interaction with the cinnabar surface, especially for measuring the relatively low concentrations

required to model concentrations found in nature. In order to maintain realistic concentrations of reagents, sensitive methods must be employed.

Limited investigation has been carried out on the aggregative properties of cinnabar despite the fact that exposed reactive surface sites have been identified as a major limiting factor controlling dissolution. The changes in morphology and reactivity over time evoke the need for a detailed study on the structure and interaction of cinnabar particles. In addition, isotope analysis may provide answers to questions regarding re-adsorption of mercury(II).

It is not clear why some reactions produced no sulfate and others produced a large concentration of sulfate in the final solution. Finally, the possible formation of surface complexes of hydroquinone and ascorbic acid with cinnabar needs to be explored. Their formation coupled with subsequent transfer of released mercury to other complexants (e.g., sulfhydryl or carboxyl sites in DOM in the natural world) would be mechanistic steps in an overall dissolution reaction to examine in future work. Clearly, cinnabar surface reactivity is complicated by the oxidation-reduction reactions that both the cation and anion in the solid may experience in an aquatic system. Results from the lines of investigation posed above should produce a clearer picture as to the mechanisms that control cinnabar dissolution.

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APPENDIX A

Table VII
Raw Data for Dissolution Experiments

Environment	Experiment	Mass of Cinnabar (mg)	Trap 1	Trap 2	Trap 3	Trap 4	Reactor
Anoxic	9711	5.6	1.62	0.826	1.24	8.52	15.4
Anoxic	CIN9311	6.5	bdl	35.43	bdl	1.46	bdl
Anoxic	CIN7111A	19.9	0.25	52.5	1.71	1.32	5.94
Anoxic	CIN7111B	23.4	3.05	59.3	1.31	3.2	11.7
Anoxic	CIN9111	25.8	51.7	1.65	bdl	1.32	0.067
Anoxic	CIN8911A	28.6	4.5	2.87	1.37	bdl	130
Anoxic	CIN82711A	29.6	0.84	bdl	bdl	bdl	1.00
Anoxic	CIN82411	46.7	3.79	1.32	40.3	0.72	1.27
Anoxic	CIN82711B	51.1	21.5	0.54	bdl	1.36	bdl
Oxic	CIN11912	28.4	bdl	bdl	bdl	116	5.6
Anoxic	CIN71611B	3.4	4.92	bdl	bdl	bdl	bdl
Anoxic	CIN9911	5.8	bdl	bdl	bdl	bdl	bdl
Anoxic	CIN71111	18.5	14.6	14.5	bdl	bdl	bdl
Anoxic	CIN62311	32.4	5.43	122	6.1	12.8	1.72
Anoxic	CIN71411	43.4	87.7	1	bdl	bdl	bdl
Anoxic	CIN81911	52.5	bdl	15.8	bdl	bdl	bdl
Anoxic	CIN71611A	102	20.6	bdl	bdl	bdl	bdl
Oxic	CN102411-2	27.3	63.1	6.66	5.98	0.51	bdl
Anoxic	CIN10511	25.2	bdl	bdl	bdl	bdl	bdl
Anoxic	CIN101211-1	25.3	bdl	bdl	bdl	bdl	bdl
Anoxic	CIN10311	28.4	1.09	bdl	bdl	3.87	bdl
Anoxic	CIN4312	24.8	1.56	bdl	bdl	bdl	2.31

Table VII (Con't)
Raw Data for Cinnabar Experiments

Environment	Experiment	Mass (mg)	Trap 1	Trap 2	Trap 3	Trap 4	Reactor
Anoxic	CIN33012	24.9	2.26	bdl	bdl	bdl	bdl
Oxic	101211-2	26.5	bdl	bdl	bdl	bdl	bdl
Oxic	CIN101211-3	28.4	bdl	2.75	2.53	7.95	bdl
Oxic	CIN102411-1	29.3	13.2	2.21	bdl	1.37	bdl
Anoxic	CIN11611-1	30.3	13	bdl	bdl	19.8	3.42
Oxic	CIN11611_2	28.1	bdl	70.7	1.91	11.9	bdl
Anoxic	CIN4612	23.1	0.98	3.38	2.06	32.8	4.05
Anoxic	CIN41012	38.7	96.8	133	1.14	4.61	80.2
Oxic	CIN22412	21.9	bdl	bdl	bdl	1.79	11.2
Oxic	CIN3812	29	1.24	bdl	bdl	bdl	1.10
Oxic	CIN31412	24.9	1.02	bdl	bdl	bdl	1.00
Oxic	CIN32312	26.5	bdl	bdl	bdl	bdl	bdl

Data include results for 4 different trap measurements over a period of 4 h and reactor measurements for mercury concentrations from cinnabar dissolution in the presence of water, hydroquinone, ascorbic acid, mercury spike and sulfate spike experiments. bdl = below detection limit.

APPENDIX B

Sample Calculations for Redox Ladder:

All parameter values are taken from Drexel et al. (2002). E_h^0 values are taken from several sources: Harris' Exploring Chemical Analysis, CRC Handbook of Chemistry and Physics and Uchimiya and Stone (2006).

STP, pH 7

$[SO_4^{2-}]$= 470 μM;
$[H_2S]_{Total}$ = 0.22 μM
$[Hg^{2+}]$ = 13 pM
$[Hg^0]$ = 0.247 pM

1. $Hg^{2+} + 2e^- \rightarrow Hg^0_{(g)}$
   $E_h = 0.688V + (0.05916/2)*\log [Hg^{2+}] / [Hg^0]$
   = 738 mV
1. Benzoquinone + $2H^+ + 2e^- \rightarrow$ Hydroquinone
   $E_h = 0.428V + (0.05916/2)*\log [H^+]^2 [BQ] / [HQ]$ if, ([BQ] = [HQ] = 1)
   = 13.88 mV
2. Ascorbate + $2H^+ + 2e^- \rightarrow$ Ascorbic Acid
   $E_h = 0.06 + (0.05916/2)*\log [H^+]^2$ [Ascorbate] / [Ascorbic acid]
   = -0.354 mV
3. $S(0) + 2H^+ + 2e^- \rightarrow H_2S_{(g)}$
   $E_h = 0.174V + (0.05916/2)*\log[H^+]^2/[H_2S]$
   = -43.1 mV
4. $HgS_{red} + 2e^- + 2H^+ \rightarrow Hg^0 + H_2S_{(g)}$
   $E_h = -0.2314V + (0.05916/2)*\log [H^+]^2 / [H_2S_{(g)}][Hg^0]$
   = -75.66 mV
5. $2e^- + 2H^+ + HgS_{red} \rightarrow Hg^0 + H_2S_{(aq)}$
   $E_h = -0.261\ V + (0.05916/2)*\log [H^+]^2 / [H_2S_{(aq)}][Hg^0]$
   = -102.6 mV

Number of exposed mercury atoms per unit area. (from Kerr (2007)):

$A = 1x\ 10^{-10}$ m

$A^2 = 1x\ 10^{-20}\ m^2$

1 mol = 6.02214×10^{23} atoms

20 – 53 μm HgS = 0.23 m^2 per g

53 – 105 μm HgS = 0.14 m^2 per g

Assume 1 atom per 39 A^2 HgS = 1 atom Hg per $3.9 \times 10^{-19}\ m^2$

$1\ m^2 / 3.9 \times 10^{-19}\ m^2 = 2.564 \times 10^{-18}$

2.564×10^{18} *(1 atom Hg per $3.9 \times 10^{-19}\ m^2$) = 2.564e18 atom Hg per $1m^2$

2.564×10^{18} atom Hg per 1 m^2 / (6.02214×10^{23} atom Hg per mol Hg) =

4.2578×10^{-6} mol Hg per 1 m^2 of HgS

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