Evaluating the Role of Re-adsorption of Dissolved Hg²⁺ during Cinnabar Dissolution Using Isotope Tracer Technique

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ABSTRACT

Cinnabar dissolution is an important factor controlling mercury (Hg) cycling. Recent studies have suggested the co-occurrence of re-adsorption of the released Hg during the course of cinnabar dissolution. However, there is a lack of feasible techniques that can quantitatively assess the amount of Hg re-adsorbed on cinnabar when investigating cinnabar dissolution. In this study, a new method, based on isotope tracing and dilution techniques, was developed to study the role of Hg re-adsorption in cinnabar dissolution. The developed method includes two key components: 1) accurate measurement of both released and spiked Hg in aqueous phase and 2) estimation of re-adsorbed Hg on cinnabar surface via the reduction in spiked $^{202}\text{Hg}^{2+}$. By adopting the developed method, it was found that the released Hg for trials purged with oxygen could reach several hundred $\mu\text{g L}^{-1}$, while no significant cinnabar dissolution was detected under anaerobic condition. Cinnabar dissolution rate when considering Hg re-adsorption was approximately 2 times the value calculated solely with the Hg detected in the aqueous phase. These results suggest that ignoring the Hg re-adsorption process can significantly underestimate the importance of cinnabar dissolution, highlighting the necessity of applying the developed method in future cinnabar dissolution studies.

Key Words: cinnabar dissolution, Hg re-adsorption on cinnabar surface, isotope tracer technique, isotope dilution, redox condition

1. INTRODUCTION

Mercury sulfide (cinnabar and metacinnabar), a major ore mineral, is one of the largest mercury (Hg) sinks in contaminated sediments and soils [1]. It has been considered as the most insoluble and least leachable Hg species due to its low solubility product constant ($K_{sp} = 10^{-55.9}$ for the reaction $\text{HgS(s)} = \text{Hg}^{2+} + \text{S}^{2-}$) [2, 3]. The formation of mercury sulfide in the environment plays a major role in restraining Hg biogeochemical cycling. However, previous studies showed that dissolution of mercury sulfide (e.g., cinnabar) can also serve as a continuous source of inorganic Hg in natural environment due to the fact that a variety of environmental factors can facilitate its dissolution. These factors include the presence of iron(III) in acidic water [4], sulfide in water [5], and dissolved organic matter (DOM) [6-8]. The enhanced dissolution of cinnabar could be an important process controlling Hg cycling in aquatic environments as this process would make the originally stable Hg more reactive and bioavailable, increasing the possibility of Hg transport, methylation and bioaccumulation, posing a great risk to humans and wildlife. This process is particularly important at areas where soils and sediments are heavily contaminated with Hg since even the release of a small fraction of sequestered Hg would remarkably increase the amount of Hg available in aquatic environment [9].

Dissolution of cinnabar in aquatic environment is very complex and the process could be conceptually simplified in two steps, 1) elimination of dissolution products (S^{2-} and Hg^{2+}) in the aqueous phase and 2) the subsequent dissolution of cinnabar (Table S1, Figure S1) [2, 10, 11]. A variety of environmental factors are expected to enhance or inhibit cinnabar dissolution via affecting the fate of cinnabar dissolution products. These factors include pH, redox potential (Eh), and Hg binding ligands [4, 7, 12, 13]. Sulfide (S^{2-}), one of the cinnabar dissolution products, could be eliminated from the system via oxidation to SO_4^{2-} at pH 5-8 under aerobic condition [4,

10, 12, 14, 15] or conversion to HS^- and H_2S under anaerobic condition [2]. The former pathway may play a more important role as quicker dissolution of cinnabar was observed in the presence of O_2 [4, 10, 13]. Hg^{2+} , the other product, could bind with organic ligands, in particular thiol-containing moieties in dissolved organic matter (DOM) [7, 11, 16]. The binding process is expected to reduce the amount of free Hg^{2+} in aqueous phase and thus enhance cinnabar dissolution. Contrary results were sometimes observed regarding the effects of organic ligands on cinnabar dissolution. For instance, while organic ligands may enhance cinnabar dissolution, minor changes in cinnabar dissolution were observed in the presence and absence of organic ligands (salicylic acid, acetic acid, EDTA, or cysteine) [6-8, 14]. These inconsistent results were speculated to be attributed to the differences in binding strength between those ligands and Hg and the possible re-adsorption of released Hg on cinnabar [7].

Hg^{2+} ion can be adsorbed on a variety of solid phases in natural environments, e.g., particles in water [17], soil [18], sediment [19] and minerals [20]. The adsorption process may involve one or several possible mechanisms, including physisorption (Van der Waals interaction) and chemisorptions (ion exchange or surface complexation). Surface complexation was considered to be the possible mechanism of Hg^{2+} ions adsorption on HgS in most studies [10, 21]. Surface of cinnabar (with a pH_{pzc} of 3-4) is expected to be negatively charged in natural aquatic environments with a pH of 6-8 due to the deprotonation of exposed sulfhydryl groups [7, 22]. Since the dominant dissolved Hg^{2+} species in aquatic environments are often uncharged complexes, inorganic or organic complex formation, ion exchange should not be the major mechanism of Hg adsorption on cinnabar [23]. Experimental results have provided both direct and indirect evidences for the occurrence of Hg re-adsorption on cinnabar surface [7, 10, 13, 15, 24]. For instance, the amount of Hg released was found to be much lower than that of S (normally represented by SO_4^{2-}), in strong disagreement with the stoichiometric estimation,

indicating the adsorption of released Hg back on cinnabar particles [7, 10, 13, 15]. Hg^{2+} added into cinnabar suspension was observed to decrease quickly, further proving the occurrence of this process [10]. Nevertheless, this process has not yet been taken into account when measuring cinnabar dissolution rate in previous studies [7, 8, 10, 13, 14], mainly due to the lack of a feasible technique that can differentiate the dissolution and re-adsorption processes. It is almost impossible to determine the re-adsorption rate of released Hg on cinnabar using traditional Hg addition method due to the simultaneous dissolution of Hg from cinnabar. The Hg re-adsorbed on cinnabar surface is expected to behavior differently in the environment than HgS itself, and therefore measuring cinnabar dissolution without considering Hg re-adsorption could result in underestimation of the importance of cinnabar dissolution in the environment.

Mercury isotope tracer technique has been widely applied in studying transport and transformation of Hg, e.g., methylation/demethylation and oxidation/reduction [25-28] in recent years mainly due to its high precision and ability of simultaneously determining the rates of multiple processes. It has also been successfully used to quantify the adsorption and desorption of Hg in sediments and particles [19, 29]. The objective of this study was to decipher the role of re-adsorption of the released Hg in cinnabar dissolution. It is expected that the application of isotope tracer technique would make it feasible to simultaneously differentiate the dissolution and re-adsorption processes. An experimental approach, using both isotope tracing and isotope dilution techniques, was developed to monitor Hg released into the solution as well as Hg re-adsorbed on cinnabar during the course of cinnabar dissolution. Equations were then derived to calculate the rates of cinnabar dissolution and Hg re-adsorption. The major virtue of the developed method is its ability to quantify the re-adsorption of released Hg on cinnabar during cinnabar dissolution. This method was then applied to investigate the dissolution of cinnabar and re-adsorption of released Hg under both aerobic and anaerobic conditions.

2. EXPERIMENTAL METHODS

2.1 Pretreatment of cinnabar and selection of filters

The surface of cinnabar was cleaned prior to use by soaking and shaking the cinnabar powder (0.02 g) in 1 mol L⁻¹ HNO₃ at 150 rpm (Orbital shaker, Henry Troemner LLC) for 3 days and subsequently filtering through a 0.45 µm PVDF membrane (Millipore) [8]. Cinnabar on the filter membrane was washed until the filtrate reaching neutral using approximately 2.5 L DI (de-ionized) water (>18.2 MΩ) and then transferred to a 250 mL Teflon bottle containing 200 mL NaNO₃/NaOH solution (pH 8.0). The final concentration of cinnabar in the suspension was approximately 100 mg L⁻¹ as HgS. The average size of cinnabar was approximately 3,272 nm determined by dynamic light scattering (DLS) (Malvern Zetasizer Nano-ZS, Westborough, MA) (Supplementary Data Fig. S2). DI water and NaNO₃/NaOH solution used were purged overnight with N₂ to eliminate O₂. All procedures were performed in a N₂ glove box to avoid the exposure to air. Experiments were conducted to examine the adsorption of Hg on four types of filters (0.22 µm PTFE, 0.45 µm PTFE, 0.22 µm PVDF, and 0.45 µm PVDF), and 0.22 µm PTFE filter was chosen in this study since it had the best recovery for Hg with minimum adsorption on the filter (Supplementary Data, Table S2).

2.2 Simultaneous determination of cinnabar dissolution and Hg²⁺ re-adsorption in the presence of N₂ and O₂

Experiments using isotope tracer were designed to monitor the adsorption of Hg²⁺ on cinnabar during the course of cinnabar dissolution experiments. ²⁰²HgNO₃ (215 µL, 46.6 mg L⁻¹ as Hg) was spiked into a 250 mL Teflon bottle with 180 mL NaNO₃/NaOH solution. Pretreated cinnabar (0.02 g wt.) was then added into the solution. The volume of the suspension solution

was adjusted to 200 mL by adding NaNO₃/NaOH solution. The final concentrations of ²⁰²Hg²⁺ and cinnabar were 50 µg L⁻¹ as Hg and 100 mg L⁻¹ as HgS, respectively. After shaking vigorously, 2.5 mL suspension was immediately sampled from each bottle using a 2.5 mL syringe and filtered through a 0.22 µm PTFE membrane (representing time 0). Bottles with the remaining suspensions were then shaken at 125 rpm with the purging of N₂ (~55 mL min⁻¹, treatment 1) or O₂ (~55 mL min⁻¹, treatment 2). Triplicates (three independent Teflon bottles) were prepared for each treatment. An aliquot of suspension (2.5 mL) was sampled from each bottle at 1, 2, 4, 6, 8, 10, 23, 30, 47, and 54 h, respectively, then filtered and preserved in a 4 °C refrigerator prior to analysis. Dissolved ²⁰¹Hg and ²⁰²Hg in the filtrates were analyzed using an isotope dilution method. Upon analysis, 44.2 µL ¹⁹⁹HgCl₂ (453 µg L⁻¹ as Hg) was spiked into 2 mL filtrate, mixed thoroughly, diluted to 20 mL and then stabilized for 1 hour. ¹⁹⁹Hg²⁺, ²⁰¹Hg²⁺ and ²⁰²Hg²⁺ in the solutions were detected by a flow injection mercury analysis system (FIAS, from PerkinElmer) coupled with inductively coupled plasma mass spectrometry (ICP-MS, Elan DRC-e from PerkinElmer) following the method of isotope dilution technique [30]. Details can be found in the Supplementary Data. Concentrations of spiked ²⁰²Hg²⁺ and Hg²⁺ released from the HgS in the aqueous phase were calculated, as detailed below in Results section.

2.3 Thermodynamics of Hg adsorption on cinnabar

Thermodynamic experiments were further conducted to evaluate the adsorption capacity of Hg²⁺ on cinnabar. Adsorption of spiked ²⁰²Hg²⁺ on cinnabar was observed to achieve equilibrium after 6 hours according to the results of preliminary experiments. The procedures for the adsorption experiments used here were identical to treatment 1 of the above experiment (purging with N₂). ²⁰²Hg²⁺ was spiked into the cinnabar suspension at the final concentrations of 0, 10, 20, 50, 100, 200, and 400 µg L⁻¹. After shaking the bottles at 125 rpm for 6 hours, 2.5 mL sample

was collected from each bottle, filtered through a 0.22 μm PTFE membrane, and stored at 4°C for analysis. Concentrations of the spiked $^{202}\text{Hg}^{2+}$ were then analyzed using the aforementioned isotope dilution method.

2.4 Data analysis

Two most commonly used adsorption isotherm equations [31-37], Langmuir and Freundlich isotherms, were adopted here to calculate the thermodynamic parameters of Hg adsorption on cinnabar. The kinetic adsorption of Hg^{2+} on cinnabar can be described as a pseudo-second order reaction [38] while first order reaction [39] was used to describe cinnabar dissolution. Details about these models can be found in the Supplementary Data (Eqs. (S1-S6)).

3. RESULTS AND DISCUSSION

3.1 Developing a method for simultaneously monitoring Hg adsorption and dissolution using isotope dilution and isotope tracer technique

A portion of the released Hg can be re-adsorbed on cinnabar surface after dissolving from cinnabar particles, resulting in the coexistence of two forms of Hg in the cinnabar suspension, the released Hg present in the aqueous phase and the released Hg re-adsorbed on cinnabar surface (Fig. 1). Concentration of the released Hg present in the aqueous phase can be determined readily, whereas it is still a challenge to directly measure the fraction of released Hg that is re-adsorbed on cinnabar surface. Without considering Hg re-adsorption, the direct measurement of solution Hg can only account for the portion of released Hg from HgS dissolution that is present in the aqueous phase, leaving out the fraction re-adsorbed on cinnabar surface, and thus resulting in underestimation of Hg dissolution rate. To quantify the sum of Hg released from cinnabar (in the aqueous phase and re-adsorbed on cinnabar surface), a new method based on isotope tracer

technique was developed. The rationale is that re-adsorbed Hg on cinnabar surface ($^N\text{Hg}^{2+}(\text{ads})$) (N represents Hg natural isotopic numbers) can be estimated by the decrease in the spiked isotope-enriched Hg ($^{202}\text{Hg}^{2+}(\text{aq})$) in aqueous phase. Developing such a method includes two key steps: 1) measuring both released Hg in the aqueous phase ($^N\text{Hg}^{2+}(\text{aq})$) and the residual $^{202}\text{Hg}^{2+}$ in the aqueous phase ($^{202}\text{Hg}^{2+}(\text{aq})$), and 2) developing a method that can be used to estimate re-adsorbed Hg on cinnabar surface ($^N\text{Hg}^{2+}(\text{ads})$) by the reducing amount of spiked $^{202}\text{Hg}^{2+}$ in the aqueous phase ($^{202}\text{Hg}^{2+}(\text{aq})$).

Hg isotopes in the filtrate were analyzed using an isotope dilution technique. Prior to sample analysis, a known amount of $^{199}\text{Hg}^{2+}$ was spiked into the filtrate to serve as an internal standard. Abundances of $^{202}\text{Hg}^{2+}$, $^{199}\text{Hg}^{2+}$, and $^{201}\text{Hg}^{2+}$ (N_{202} , N_{199} , N_{201}) in the solution were analyzed and the ratios of $^{201}\text{Hg}/^{199}\text{Hg}$ (≈ 199201) and $^{202}\text{Hg}/^{199}\text{Hg}$ (≈ 199202) were determined. Hg isotope ratios in the filtrates were different from the natural abundance of Hg because of the addition of $^{202}\text{Hg}^{2+}$ at time zero. These isotope ratios also changed over time accompanying with Hg dissolution from cinnabar and adsorption of the spiked $^{202}\text{Hg}^{2+}$. Therefore, the traditional isotope dilution method for analyzing samples with the natural abundance of Hg isotopes [40-44] is not applicable here for calculating Hg concentrations in the filtrates. A new method was developed in order to simultaneously calculate Hg originated from cinnabar dissolution and residual spiked $^{202}\text{Hg}^{2+}$ in the filtrates.

Since all 7 natural Hg isotopes were present in the used isotope-enriched Hg ($^{202}\text{Hg}^{2+}$ and $^{199}\text{Hg}^{2+}$) because of the impurities in the standards, Hg isotopes in the filtrates originated from three sources, including cinnabar dissolution (with natural abundance of Hg isotopes, $C_{\text{d}}\text{aq}$), spiked $^{202}\text{Hg}^{2+}$ ($C_{\text{x}}\text{aq}$), and added $^{199}\text{Hg}^{2+}$ ($C_{\text{y}}\text{aq}$). In consideration of all these sources, the ratios

of $^{201}\text{Hg}/^{199}\text{Hg}$ (Eq. (1)) and $^{202}\text{Hg}/^{199}\text{Hg}$ (Eq. (2)) can be described using the following functions (Eq. (1)-(2)):

$$\begin{aligned} R_1 = \frac{^{201}\text{Hg}}{^{199}\text{Hg}} = \frac{^{201}\text{Hg}}{^{199}\text{Hg}} = \frac{C_d(aq) \cdot V_n \cdot 201 + C_x(aq) \cdot V_n \cdot 202}{C_d(aq) \cdot V_n \cdot 199 + C_x(aq) \cdot V_n \cdot 199} \\ + \frac{C_y(aq) \cdot V_n \cdot 199}{C_d(aq) \cdot V_n \cdot 199 + C_x(aq) \cdot V_n \cdot 199} \end{aligned} \quad (1)$$

$$\begin{aligned} R_2 = \frac{^{202}\text{Hg}}{^{199}\text{Hg}} = \frac{^{202}\text{Hg}}{^{199}\text{Hg}} = \frac{C_d(aq) \cdot V_n \cdot 202 + C_x(aq) \cdot V_n \cdot 202}{C_d(aq) \cdot V_n \cdot 199 + C_x(aq) \cdot V_n \cdot 199} \\ + \frac{C_y(aq) \cdot V_n \cdot 199}{C_d(aq) \cdot V_n \cdot 199 + C_x(aq) \cdot V_n \cdot 199} \end{aligned} \quad (2)$$

where R_1 represents the ratio of ^{201}Hg to ^{199}Hg in the filtrates; R_2 represents the ratio of ^{202}Hg to ^{199}Hg in the filtrates; $C_d(aq)$ ($\mu\text{g L}^{-1}$) represents the concentration of natural Hg (from cinnabar dissolution) in the filtrates; $C_x(aq)$ ($\mu\text{g L}^{-1}$) represents the residual concentration of spiked ^{202}Hg in the filtrates; $C_y(aq)$ ($\mu\text{g L}^{-1}$) represents the concentration of added ^{199}Hg in the filtrates; 201 represents the abundance of Hg isotope i in natural Hg; 202 represents the abundance of Hg isotope i in the spiked ^{202}Hg -enriched Hg; 199 represents the abundance of Hg isotope i in the used ^{199}Hg -enriched Hg; $V(L)$ represents the volume of filtrates.

By solving Eq. (1) and Eq. (2), the concentrations of released Hg present in the aqueous phase $C_d(aq)$ and residual spiked ^{202}Hg $C_x(aq)$ in the solution can be calculated by Eqs. (3) and (4), respectively. This isotope dilution method provides a precise tool to determine the concentrations of both released Hg and residual spiked $^{202}\text{Hg}^{2+}$ in the filtrates ($C_d(aq)$ and $C_x(aq)$) at each sampling time of the dissolution experiment. Both $C_d(aq)$ and $C_x(aq)$ are necessary for the later calculation of cinnabar dissolution rate and re-adsorption rate of the released Hg.

$$C_x = \frac{R_1 \cdot C_y(aq) \cdot 199}{R_1 \cdot 199 - R_2 \cdot 199 + R_2 \cdot 201 - R_1 \cdot 202}$$

$$R_2 = \frac{R_1 \cdot 202 - R_1 \cdot 201 + R_1 \cdot 199 - R_1 \cdot 199}{R_1 \cdot 202 - R_1 \cdot 201 + R_1 \cdot 199 - R_1 \cdot 199}$$

$$n_{201}^{202} - n_{201}^{199} = \frac{n_{201}^{202} - n_{201}^{199}}{n_{201}^{202} + n_{201}^{199}} \times \frac{n_{201}^{202} - n_{201}^{199}}{n_{201}^{202} - n_{201}^{199}} \quad (3)$$

$$d = \frac{n_{201}^{202} - n_{201}^{199}}{n_{201}^{202} + n_{201}^{199}} \times \frac{n_{201}^{202} - n_{201}^{199}}{n_{201}^{202} - n_{201}^{199}} \quad (4)$$

is known and it can be calculated as follows:

$$(5)$$

where $(\mu\text{g L}^{-1})$ is the concentration of ^{199}Hg spiked into the filtrates as internal standard; V_1 (L) is the volume of $^{199}\text{HgCl}_2$ spiked into the filtrates.

The second key step of the proposed method is to calculate the amount of released Hg re-adsorbed on cinnabar (C_{dads}). Since the total amount of spiked ^{202}Hg (represented by M_{xtot}) is known (Eq. (6)), the amount of spiked ^{202}Hg adsorbed on cinnabar (M_{xads}) at each sampling time can be obtained by subtracting M_{xaq} from M_{xtot} . If M_{dads} can be related to M_{xads} , it would be feasible to calculate M_{dads} by M_{xads} and C_{daq} . Isotope ratios of Hg adsorbed on cinnabar surface are controlled by the adsorption/desorption process, while both adsorption/desorption and dissolution processes determine the ratios of Hg in the aqueous phase. As adsorption/desorption of Hg on cinnabar is expected to be much faster than cinnabar dissolution [18], it is reasonable to assume that the isotope ratios of Hg in the aqueous phase approximately equal to those of adsorbed Hg on cinnabar (Eq. (7)) due to the quick exchange of Hg isotopes between the aqueous and the particulate phases. This assumption was verified by the experiments described later.

$$(6)$$

$$d_{\text{ads}}/x_{\text{ads}} = d_{\text{aq}}/x_{\text{aq}} \quad (7)$$

where $(\mu\text{g L}^{-1})$ is the concentration of ^{202}Hg spiked into the cinnabar suspension solution; V_2 (L) is the volume of ^{202}Hg spiked; (μg) is the amount of ^{202}Hg spiked into the cinnabar suspension; (μg) represent the amount of natural Hg (from cinnabar dissolution) adsorbed on cinnabar surface and in the solution, and the amount of spiked ^{202}Hg adsorbed on cinnabar surface and in the solution, respectively.

By resolving Eq. (7), the amount of released Hg^{2+} that was re-adsorbed on cinnabar surface can be calculated from the released Hg in the aqueous phase and the distribution of spiked ^{202}Hg between the aqueous phase and cinnabar adsorbed phase using Eq. (8).

where V_3 (L) is the volume of the cinnabar suspension solution.

Accordingly, the total amount of Hg released from cinnabar ($M_{\text{d tot}}$) can be calculated by summing the measured dissolved Hg in the aqueous phase ($C_{\text{d aq}}$) and the estimated Hg adsorbed on cinnabar surface ($M_{\text{d ads}}$).

(9)

Then, the total concentration of Hg released from cinnabar (C_{d}) can be calculated by the division of M_{d} by V_3 (Eq. 10).

(10)

The equation can be simplified to Eq. (11) by defining as .

$$C_{\text{d tot}} = C_{\text{d aq}} + \frac{M_{\text{d ads}}}{V_3} = C_{\text{d aq}} + \frac{C_{\text{d aq}} \cdot V_3}{V_3} = 2 \cdot C_{\text{d aq}} \quad (11)$$

where C_{d} and $(\mu\text{g L}^{-1})$ represent the total concentrations of natural Hg (from cinnabar dissolution) and spiked ^{202}Hg in the suspension solution (referring to the volume of cinnabar suspension solution).

3.2 Applying the developed technique to study cinnabar dissolution and Hg^{2+} re-adsorption

The developed technique was applied to determine the concentrations of Hg re-adsorbed on cinnabar surface (C_{ads}) and the total amount of Hg released from cinnabar (C_{tot}). The results showed that the spiked $^{202}\text{Hg}^{2+}$ adsorbed on the cinnabar surface quickly under both oxic and anoxic conditions, as illustrated by the rapid decrease in the dissolved $^{202}\text{Hg}^{2+}$ concentrations in the first 6 hours (Fig. 2A and 2B). For the treatment purged with N_2 , the variations in both the released Hg present in the aqueous phase and the total amount of released Hg were observed to be insignificant ($p>0.1$, one-way ANOVA) during the course of experiment (54 hours), indicating that dissolution of Hg from cinnabar was negligible under anaerobic condition. In the presence of O_2 , detectable amount of Hg was dissolved from cinnabar, indicated by the continuous increase of both C_{aq} and C_{tot} with time (Fig. 2D). The concentration of total released Hg was estimated to be more than $300 \mu\text{g L}^{-1}$ after 54 hours. The results suggest that O_2 can enhance the dissolution of cinnabar, in agreement with most previous studies [10, 12, 13, 15]. Oxygen is expected to oxidize S^{2-} (one product of cinnabar dissolution) to SO_4^{2-} , and thus facilitating the dissolution of cinnabar. The dissolution product, S^{2-} , could also be converted to HS^- and H_2S under anaerobic condition and subsequently facilitate cinnabar dissolution [2]. Results of this study support the notion that oxidization of S^{2-} to SO_4^{2-} may play a more important role in cinnabar dissolution.

The importance of Hg re-adsorption in assessing cinnabar dissolution was evaluated by comparing the amount of released Hg from cinnabar with and without the consideration of the re-adsorption of the released Hg on cinnabar. As shown in Fig. 2D, the concentrations of total released Hg were found to be much higher than that in the solution (~ 2 times), suggesting that a large proportion of the released Hg from cinnabar was re-adsorbed on cinnabar surface. To further evaluate the importance of Hg re-adsorption on cinnabar dissolution, parameters relevant to the adsorption of Hg and the dissolution of cinnabar were calculated using Eq. (S5) and Eq.

(S6). Variations of the spiked ^{202}Hg fitted well with the pseudo-second order model, as indicated by the high value of R^2 (0.9999) (Fig. 3A). Dissolution of cinnabar could be well predicted by the first order reaction equation ($R^2 = 0.9898$, Fig. 3B). Cinnabar dissolution rate constant was estimated to be 0.0208 h^{-1} when considering the re-adsorption of Hg on cinnabar surface by using the new method developed in this study (Table 1). If only the released Hg in the aqueous phase ($C_{\text{d}aq}$) was taken into account, this rate constant would decrease to 0.0109 h^{-1} (Fig. 3C), indicating that ignoring the re-adsorption of Hg on cinnabar surface would significantly underestimate the dissolution rate of cinnabar.

As shown in Fig. 2A, natural Hg^{2+} in the solution was approximately $6 \mu\text{g L}^{-1}$ at the beginning of the experiment (0 h), while the concentration for the control treatment (without the addition of $^{202}\text{Hg}^{2+}$) was less than $1 \mu\text{g L}^{-1}$. The high concentration of natural Hg occurred in the solution after the addition of $^{202}\text{Hg}^{2+}$ could be caused by the instant adsorption of spiked $^{202}\text{Hg}^{2+}$ on cinnabar and the subsequent replacement of natural Hg from cinnabar surface. Although cinnabar particles were cleaned for several times with 1 mol L^{-1} nitric acid and DI water prior to the experiment, there could be still some Hg ions adsorbed loosely on the surface. This assumption was further tested by measuring the amount of replaced Hg with different initial concentrations of $^{201}\text{Hg}^{2+}$ spiked (Fig. S3). As shown in Fig. S3, the concentrations of Hg were less than $1 \mu\text{g L}^{-1}$ before $^{201}\text{Hg}^{2+}$ was spiked. An instant increase in Hg^{2+} was observed after spiking $^{201}\text{Hg}^{2+}$ for all treatments. In addition, the concentrations of natural Hg^{2+} increased gradually with the increasing concentration of spiked $^{201}\text{Hg}^{2+}$ (more $^{201}\text{Hg}^{2+}$ was instantly adsorbed on cinnabar). These results indicate that the initial increase in Hg concentration may be due to the isotopic replacement of the residual adsorbed Hg on cinnabar with the spiked isotope-

enriched Hg, rather than the cinnabar dissolution. Therefore, this Hg was deducted from the measured ΣHg when calculating the total released Hg from cinnabar dissolution ($\Sigma \text{Hg}_{\text{tot}}$).

For traditional isotope dilution methods, Hg isotope ratios in the solution are expected to be a known constant (natural abundance of Hg in most cases) [40-44]. However, Hg isotope ratios would change with time when investigating dynamic processes in which isotope tracers were spiked. For example, isotope ratios in the filtrates changed over time (Fig. 2) accompanying Hg dissolution from cinnabar and adsorption of the spiked $^{202}\text{Hg}^{2+}$ in this study. If traditional isotope dilution approaches are adopted, Hg isotope ratios in the filtrates before the addition of $^{199}\text{Hg}^{2+}$ should also be analyzed as well as that in the filtrates after spiking $^{199}\text{Hg}^{2+}$. However, this would make the analysis more tedious and may introduce extra errors. In this study, we developed a new isotope dilution method to determine both Hg released from cinnabar and residual spiked enriched Hg in the aqueous phase according to the detected Hg ratios in only the filtrates after spiking $^{199}\text{Hg}^{2+}$ at each sampling time. This method may also be applicable in studying other dynamic processes of Hg using isotope tracer techniques.

3.3 Thermodynamics of Hg adsorption on cinnabar and validation of the developed method

Thermodynamics of Hg adsorption on cinnabar were investigated by using the isotope-tracer method. As shown in Fig. 4A, percentage of ^{202}Hg adsorbed on cinnabar decreased from 94 to 48% with the increase of initial $^{202}\text{Hg}^{2+}$ concentration from 0 to 400 $\mu\text{g L}^{-1}$, while the equilibrium adsorption capacity increased from 94 to 1930 $\mu\text{g g}^{-1}$. At higher concentrations of initial Hg, adsorption sites on cinnabar may be over occupied which could explain the negative relation of Hg removal efficiency with initial Hg concentration [45]. The increasing equilibrium adsorption capacity at higher Hg concentrations could be attributed to higher adsorption rate at higher concentration and occupation of more available active sites [37]. Nonlinear regression of the equilibrium adsorption capacity q_e ($\mu\text{g g}^{-1}$) against the equilibrium concentration of $^{202}\text{Hg}^{2+}$ C_e

($\mu\text{g L}^{-1}$) using both Langmuir and Freundlich models was performed to estimate parameters of isotherms. Langmuir model predicted the experimental data better than Freundlich model, indicated by its higher R^2 (Table 1, and Fig. 4B).

In order to derive the equation for calculating the total released Hg (Σdtot), it was assumed that the isotope ratios of Hg in the solution were identical with that adsorbed on cinnabar (Eq. (7)). This assumption was formulated based partially on that the rates of Hg adsorption/desorption were much higher than cinnabar dissolution. As shown in Fig. 2B and 2D, the dissolution of cinnabar has not achieved equilibrium at the end of the experiments (54 hours), while the equilibrium time for Hg adsorption was determined to be less than 6 hours, supporting this assumption. In order to further verify the hypothesis, the concentrations of dissolved Hg in the solution tot were also calculated based on the thermodynamic model (Langmuir model). Total Hg detected at t time can be considered as C_e (i.e. $C_d(\text{aq}) + C_x(\text{aq})$). Parameters (K_L and q_m) obtained from the thermodynamic experiments in the presence of N_2 were adopted. By using Langmuir model, total adsorbed Hg on cinnabar can be calculated (Eq. (S1)) as ads. Then, the total amount of dissolved Hg can be estimated as:

$$\text{tot} = \text{aq} + \text{ads} = \text{aq} + (\text{ads} - \Sigma x \text{ads}) \quad (8)$$

The comparisons of total released Hg calculated by both methods (Eqs 7 and 8) were shown in Fig. 5. In the present of O_2 , the total dissolved Hg estimated by Langmuir model (Eq. (8)) was observed to be higher than that estimated using the newly developed method for the first 6 hours, and then became very close with time (Fig. 5B). This is reasonable since the adsorption of spiked Hg had not achieved equilibrium at the beginning of the experiment, which was expected to result in the overestimation of Hg adsorbed on cinnabar if Langmuir model was adopted. Dissolved Hg estimated using both methods were observed to be similar ($p > 0.05$, two-way

ANOVA), especially after 6 hours ($p>0.1$, two-way ANOVA, with an average RSD of 9.9% (2.4-16.6%) when Hg in the aqueous phase and cinnabar surface was expected to be equilibrated. These results further support the hypothesis that the isotope ratio of Hg in the solution is approximately identical with that adsorbed on cinnabar, suggesting the reliability of the proposed method in estimating the real dissolution of cinnabar. On the basis of these validations, the proposed method is expected to be a reliable technique in studying the dissolution of cinnabar.

Isotope tracers have been already used for determining adsorption and desorption processes [19, 29]. It has also been applied in investigating the methylation rates of geochemically relevant inorganic Hg(II) species, including isotopically labeled cinnabar, metacinnabar, adsorbed Hg(II), and complexed Hg(II) [46]. The application of the newly developed isotope tracer techniques in this study provides new insights on how Hg dissolution occurs, evidencing the importance of re-adsorption process. The estimated dissolution rate without considering the re-adsorption is much lower than that with the consideration of re-adsorption on cinnabar surface. The cinnabar dissolution rates with the consideration of the Hg adsorbed on cinnabar surface have been previously estimated using an indirect method, from the increase in the concentration of SO_4^{2-} in the solution. However, it should be noted that the calculation of Hg dissolution rates from changes in SO_4^{2-} concentration could underestimate the dissolution rate since sulfide oxidation intermediates (e.g., $\text{S}_2\text{O}_3^{2-}$) also exist in the solution or on the cinnabar surface [13]. In addition, this method cannot be applied in quantitatively measuring cinnabar dissolution rates under natural conditions, where a variety of factors (e.g., Eh, DOM, pH) can affect the transformations of sulfur, resulting in a large variation in the ratio of released Hg to SO_4^{2-} . In de-ionized water, the dissolution rates within 48h were determined to be 0.71 to 0.82 $\mu\text{mol} (\text{SO}_4^{2-}) \text{ m}^{-2} \text{ day}^{-1}$ for cinnabar.[13]. This rate (within 48h) was calculated to be 3.63 $\mu\text{mol m}^{-2} \text{ day}^{-1}$ using the new method developed in this study, larger than that determined by the generated SO_4^{2-} , which is

supposed to underestimate the dissolution rate. The thermodynamic parameters of Hg^{2+} adsorption on cinnabar, i.e., q_m (the maximum monolayer adsorption capacity) and K_L (the Langmuir constant) were also estimated using isotope tracer techniques. The estimated q_m of Hg^{2+} adsorption on cinnabar ($2137.1 \mu\text{g g}^{-1}$) was only one order of magnitude less than the values on some clays, illustrating the high affinity of Hg^{2+} toward Hg (e.g., Sepiolite, $q_m = 34.1 \text{ mg g}^{-1}$ and Montmorillonite, $q_m = 50.2 \text{ mg g}^{-1}$). These clays have already been proposed to have the capability of removing Hg from polluted environmental water [47].

Dissolution of cinnabar can serve as a continuous source for bioavailable Hg^{2+} in the environment, and subsequently enhances the methylation process and increasing the amount of more toxic methylmercury. Due to the lack of a feasible technique for measuring Hg adsorbed on cinnabar, only the Hg detected in the aqueous phase was considered to be dissolved from cinnabar in previous studies [12, 13], although several of which have speculated that dissolved Hg from cinnabar surface could be re-adsorbed back onto cinnabar surface [10, 12, 13]. The developed isotope tracer method makes it possible to simultaneously monitor both the dissolution and re-adsorption of Hg. A variety of environmental factors, including pH, redox potential (Eh), and Hg binding ligands [4, 7, 12, 13], are expected to enhance or inhibit cinnabar dissolution via affecting the fate of cinnabar dissolution products and Hg adsorption/desorption. It should be noted that experiments in this study were conducted in a dilute NaNO_3 solution system without the addition of any inorganic or organic ligands. Future work of applying the developed method in determining cinnabar dissolution in natural waters would be helpful for better understanding the importance of cinnabar dissolution in Hg cycling.

4. CONCLUSIONS

In this study, an isotope tracer based method was developed to investigate both dissolution and re-adsorption of Hg during the course of cinnabar dissolution. The rationale of the proposed method is that re-adsorbed Hg on cinnabar surface can be estimated from decreasing in the amount of spiked isotope-enriched Hg ($^{202}\text{Hg}^{2+}$) in aqueous phase. A modified isotope dilution method ($^{199}\text{Hg}^{2+}$) was developed to simultaneously calculate Hg originated from cinnabar dissolution and residual spiked $^{202}\text{Hg}^{2+}$ in the filtrates. The amount of re-adsorbed Hg was calculated from the adsorption of spiked $^{202}\text{Hg}^{2+}$ on cinnabar based on the validated assumption that the isotope ratios of Hg in the aqueous phase are approximately equal to that adsorbed on cinnabar. By using the developed method, cinnabar dissolution rate with the consideration of Hg re-adsorption using the newly developed method (0.0208 h^{-1}) was approximately 2 times the value calculated solely from the Hg detected in the aqueous phase (0.0109 h^{-1}). The results suggest that re-adsorption of Hg on cinnabar surface play an important role in accurately evaluating cinnabar dissolution, and omission of the Hg re-adsorbed on cinnabar surface would significantly underestimate the importance of cinnabar dissolution in Hg cycling. Experiments in this study were conducted in a simulated system without the addition of any inorganic or organic ligands. Future work of applying the developed method in determining cinnabar dissolution in natural waters with different water chemical characteristics is necessary for better understanding the importance of cinnabar dissolution in Hg cycling.

APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at XXX.

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Figure legends

Figure 1. A schematic showing the procedure of simultaneously monitoring the dissolution of cinnabar and re-adsorption of released Hg using isotope tracer and isotope dilution techniques.

Figure 2. Variations of spiked $^{202}\text{Hg}^{2+}$ in aqueous phase (Σdaq), Hg dissolved from cinnabar in aqueous phase (Σdaq), and the total Hg dissolved from cinnabar (Σdtot). A and C, purged with N_2 ; B and D, purged with O_2 . Since Σdaq at time 0 was likely resulted from the isotopic replacement of natural Hg adsorbed on cinnabar by the spiked $^{202}\text{Hg}^{2+}$, rather than the cinnabar dissolution, this Hg was deducted from the measured Σdaq when calculating the total released Hg from cinnabar (Σdtot).

Figure 3. Nonlinear regressions of spiked ^{202}Hg (A), total dissolved Hg (B), and dissolved Hg in the aqueous phase (C) against time.

Figure 4. The thermodynamic of $^{202}\text{Hg}^{2+}$ adsorption on cinnabar. A, variation of equilibrium concentrations of ^{202}Hg ($\mu\text{g L}^{-1}$) at 24 h with different initial $^{202}\text{Hg}^{2+}$ concentrations (0, 10, 20, 50, 100, 200, 400 $\mu\text{g L}^{-1}$). B, non-linear regression of q_e against C_e using Langmuir and Freundlich models ($T = 20\text{ }^\circ\text{C}$).

Figure 5. Comparisons of total dissolved Hg estimated by the thermodynamic equilibrium using Langmuir model (Eq.8) and by the new method developed in this study (Eq.7). A, without O_2 (purging with N_2); B, with O_2 (purging with O_2).

Figure 1

$^N\text{Hg}^{2+}(\text{aq})$ is the released Hg from cinnabar present in the aqueous phase.
 $^N\text{Hg}^{2+}(\text{ads})$ is the released Hg re-adsorbed on cinnabar surface.
 $^{202}\text{Hg}^{2+}(\text{aq})$ is spiked $^{202}\text{Hg}^{2+}$ present in the aqueous phase.
 $^{202}\text{Hg}^{2+}(\text{ads})$ is spiked $^{202}\text{Hg}^{2+}$ adsorbed on cinnabar surface.

Figure 2

Figure 3

Figure 4

Figure 5

Table 1 Parameters of adsorption kinetics and isotherms of Hg on cinnabar using different models (in the absence of O₂) and dissolution (in the present of O₂)

Kinetic models	Parameters	Values	R ²
The pseudo-second order rate equation $\frac{q}{t} = \frac{k_2 q_e^2}{1 + k_2 q_e t}$	q_e (μg g ⁻¹) K_2 (g μg ⁻¹ h ⁻¹)	485.4 0.00663	0.9999
Dissolution kinetic model $q = q_0(1 - e^{-kt})$	C_0 (tot)(μg L ⁻¹) K (tot)(hour ⁻¹)	430.26 0.0208	0.9898
	C_0 (aq)(μg L ⁻¹) K (aq) (hour ⁻¹)	217.55 0.0109	0.9851
Langmuir model $q = \frac{q_m K_L C}{1 + K_L C}$	q_m (μg g ⁻¹) K_L (L μg ⁻¹)	2137.1 0.0450	0.9952
Freundlich model $q = F C^{1/n}$	K_F 1/n	275.89 0.375	0.9390

Cinnabar Dissolution and Re-adsorption of Hg^{2+}

$^{\text{N}}\text{Hg}^{2+}(\text{aq})$ is the released Hg from cinnabar present in the aqueous phase.

$^{\text{N}}\text{Hg}^{2+}(\text{ads})$ is the released Hg re-adsorbed on cinnabar surface.

$^{202}\text{Hg}^{2+}(\text{aq})$ is spiked $^{202}\text{Hg}^{2+}$ present in the aqueous phase.

$^{202}\text{Hg}^{2+}(\text{ads})$ is spiked $^{202}\text{Hg}^{2+}$ adsorbed on cinnabar surface.