Analytical methods, formation, and dissolution of cinnabar and its impact on environmental cycle of mercury

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\textbf{ABSTRACT}

Mercury sulfide (HgS, cinnabar, and metacinnabar) is a major Hg sink, widely available in various environmental compartments. The formation and dissolution of HgS play a crucial role in the geochemical cycle of Hg, including its transport, reduction, methylation, and toxicity. Unlike other Hg species (e.g., methylmercury, Hg\textsubscript{0}), environmental HgS occurs in the form of different sized particles, leading to various challenges regarding its quantification and the evaluation of potential environmental impacts. This review summarizes the current analytical methods for the identification, characterization, and quantification of HgS, including sequential chemical extraction, X-ray absorption spectroscopy, programmed thermal desorption, and selective vapor generation, among other methods. In addition, the chemical/biological pathways and mechanisms involved in the formation and dissolution of HgS are reviewed, as are the analytical and environmental perspectives of HgS. This review furthers our understanding and encourages the study of the environmental formation and dissolution of HgS and its role in the geochemical cycle of Hg.

\textbf{KEYWORDS}

Cinnabar; mercury; sulfidation

1. Introduction

The study of the natural and anthropogenic environmental emissions of mercury (Hg) is of particular importance due to its effects on human and ecosystem health. The volatility of elemental Hg and its long atmospheric half-life facilitate its distribution at the global scale (Driscoll et al., 2013). Methylmercury, a potent neurotoxin, can be produced in natural environments from

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inorganic Hg through various Hg methylating microbes (Parks et al., 2013), in particular sulfate-reducing bacteria (Gilmour et al., 1992), iron (Fe)-reducing bacteria (Fleming et al., 2006; Kerin et al., 2006), and methanogenic bacteria (Yu et al., 2013). Thus, the bioaccumulation and biomagnification of methylmercury through the food chain result in elevated human exposure to methylmercury. Indeed, it is well known that the general population is primarily exposed to methylmercury through the consumption of fish and marine mammals, as well as Hg-contaminated rice (Li et al., 2010). New input Hg in lakes (Harris et al., 2007) and rice paddies (Zhao et al., 2016a, 2016b) is methylated in sediments and rapidly accumulated in fish and rice, demonstrating that newly deposited Hg is the major contributor to Hg methylation and bioaccumulation. Comparably, the mobility and methylation rate of ambient Hg are significantly lower than that of new input Hg (Hintelmann et al., 2002; Li et al., 2012), suggesting the occurrence of an “aging” process of Hg following its sedimentation. Many studies have revealed that sulfidation of Hg (i.e., formation of HgS) is an important pathway in the Hg aging process, and can decrease the transport (Gai et al., 2016), bio-reduction (Kelly et al., 2007), and methylation (Zhang et al., 2014) of Hg. The latter is also one of the important mechanisms in the biological detoxification of Hg (Wu and Wang, 2014b). Therefore, the formation and dissolution of HgS play a critical role in the environmental bioavailability, reduction, methylation, toxicity, and bioaccumulation of Hg.

Unlike other Hg species (e.g., methylmercury, Hg\(^0\)), environmental HgS occurs in the form of different sized particles, leading to various challenges in its extraction, speciation, characterization, and quantification. In recent decades, scientists have developed a variety of methods to identify HgS particles and track their environmental fate. Despite the importance of HgS species in controlling the biogeochemical cycle of Hg, to date, there are no comprehensive reviews on the analytical methods available for its characterization or its environmental formation and dissolution. In this review, we summarize the environmental occurrence, characterization methods, and formation and dissolution of HgS, highlighting its role in the geochemical cycle, bioaccumulation, and toxicity of Hg, and discussing the future analytical and environmental perspectives of HgS. This review will enrich our understanding and further the study on the environmental formation and dissolution of HgS and its role in the geochemical cycle of Hg.

2. Cinnabar as an environmental Hg sink

HgS minerals represent the most abundant form of Hg in the lithosphere, with their mining initiating the anthropogenic cycling of Hg (Smith et al., 2015). HgS is dimorphic in nature, available in the two crystal forms of cinnabar (hexagonal \(\alpha\)-HgS, red) and metacinnabar (cubic \(\beta\)-HgS, black). Figure 1 gives the
photography of cinnabar and metacinnabar mineral ores and pure $\alpha$-HgS and $\beta$-HgS chemicals. Generally, $\alpha$-HgS is the primary ore HgS species in most Hg mineral belts, while $\beta$-HgS is comparably less common (Rytuba, 2003). Nevertheless, environmentally relevant precipitation reactions of Hg$^{2+}$ at room temperature yield $\beta$-HgS, which then slowly transforms into the more stable $\alpha$-HgS (Clever et al., 1985). Thus, both $\alpha$-HgS and $\beta$-HgS can be observed in the environment, although $\beta$-HgS is more common as the sulfidation product of Hg. Due to the low solubility product constant of HgS ($k_{sp}(\alpha$-HgS) = $2 \times 10^{-53}$, $k_{sp}(\beta$-HgS) = $2 \times 10^{-52}$) (Clever et al., 1985), it is considered as the most insoluble Hg species and less toxic than HgCl$_2$ and methylmercury (Dong et al., 2016).

The precipitation of HgS can effectively remove Hg from further environmental cycling (Smith et al., 2015), resulting in HgS being one of the major Hg sinks in the environment (Barnett et al., 1997; Wolfenden et al., 2005). Besides Hg mine environments (derived from HgS in ore) (Bernaus et al., 2005), HgS is also widely detected in other environmental matrices, including coal (Rumayor et al., 2016), fly ash (Rumayor et al., 2016), gypsum (Rumayor et al., 2016), airborne particulate matter (Feng et al., 2004), soil (Barnett et al., 1997), sediment (Wolfenden et al., 2005), and organisms (Wang et al., 2012a; Wu and Wang, 2014b). For example, analysis of Hg-contaminated soil from flood plains in Oak Ridge, Tennessee, USA, revealed the presence of submicron, crystalline $\beta$-HgS particles (Barnett et al., 1997). The reaction model predicted that the soil redox and pH conditions during flooding favor the formation of HgS, with the fraction of HgS to total Hg reaching up to approximately 45% to 90% in the buried, most contaminated soils (Barnett et al., 2005).
et al., 1997). In both aerobic and seasonally anoxic sediments, most of the spiked Hg\(^{2+}\) was subsequently transformed into HgS, further suggesting that HgS is a general Hg sink in sediments (Wolfenden et al., 2005).

3. Analytical methods for the identification, characterization, and quantification of environmental cinnabar

As previously mentioned, the particle characteristics (e.g., heteroaggregation and inhomogeneity) of HgS result in difficulties in its extraction, identification, particle size characterization, and quantification. Unlike methylmercury, there is no standard approach to selectively extract HgS particles from solid environmental matrices (e.g., soil, sediment, and atmospheric particulates). In addition, there are great challenges posed in the identification (due to the need to simultaneously monitor Hg and S), size fractionation, and quantification of HgS particles of different sizes. Nevertheless, analytical methods have been developed to attempt to address these issues in real or simulated environments, including sequential chemical extraction, X-ray absorption spectroscopy, programmed thermal desorption, selective vapor generation, and other methods which will be described herein.

3.1. Sequential chemical extraction

Although there is currently no approach to selectively extract HgS particles from solid environmental matrices, by exploiting the “insoluble” nature of HgS, sequential chemical extraction by dissolving Hg species other than HgS, followed by total Hg analysis, is an effective method to indirectly identify and quantify HgS in solid phases. In sequential extraction procedures, a sequence of chemical solvents (from mild to harsher reagents) is applied to the same sample to dissolve and fractionate the total Hg into biogeochemically distinct categories (Reis et al., 2016). HgS does not dissolve in strong bases or mineral acids (e.g., 1 M KOH or 12 M HNO\(_3\)), but can be extracted with a saturated Na\(_2\)S solution (Revis et al., 1989) or aqua regia (Fernandez-Martinez and Rucandio, 2003). Therefore, following sequential extraction by KOH and HNO\(_3\) for all non-sulfide forms of Hg (Hall et al., 2005), a saturated Na\(_2\)S solution (Martian-Doimeadios et al., 2000; Han et al., 2006; Zverina et al., 2013) or aqua regia (Bloom et al., 2003; Kim et al., 2003) can be used to dissolve and subsequently quantify HgS. Nevertheless, the presence of chloride within the matrix induces the partial dissolution of \(\alpha\)-HgS and \(\beta\)-HgS in HNO\(_3\); therefore, removal of chloride by washing the sediment (e.g., with deionized water) significantly reduces the dissolution of HgS during concentrated HNO\(_3\) extraction (Mikac et al., 2003). Further, HNO\(_3\) does not totally dissolve Hg\(_2\)Cl\(_2\) (Han et al., 2003), and thus a sequential extraction by KOH and HNO\(_3\) is helpful to eliminate the potential interference from Hg\(_2\)Cl\(_2\) in subsequent HgS extraction (Bloom et al., 2003). A five-step sequential chemical extraction developed by Bloom et al. (Bloom et al., 2003; Kim et al., 2003) is the most common protocol, wherein the leaching media used are deionized water (fraction 1), 0.01 M HCl + 0.1 M CH\(_3\)COOH
(fraction 2), 1 M KOH (fraction 3), 12 M HNO₃ (fraction 4), and aqua regia (fraction 5) (Figure 2). Sequential chemical extraction profiles for individual Hg compounds using Bloom et al.’s (2003) protocol demonstrated that the extraction of fractions 1–4 can remove most Hg compounds (HgCl₂, HgO, HgSO₄, CH₃Hg⁺, Hg-humic complexation, Hg₂Cl₂, Hg⁰, and partial HgAu and Hg₃S₂O₄), with the residual α-HgS, β-HgS, and HgSe being then dissolved by aqua regia. However, the aqua regia extraction of fraction 5 also likely includes HgAu, Hg₃S₂O₄, and HgSe (Figure 2) due to their similarly insoluble properties. Generally, the proportion of Hg removed by aqua regia extraction in Hg-bearing samples correlates well with the proportion of insoluble HgS (α-HgS and β-HgS) and HgSe identified by X-ray absorption fine structure (XAFS) studies, further validating the protocol (Kim et al., 2003). It should be noted that sequential chemical extraction cannot distinguish α-HgS and β-HgS and also cannot give the information of HgS particle size.

3.2. X-ray absorption fine structure (XAFS)

XAFS describes the oscillation of the X-ray absorption coefficient of a sample as a function of energy (Figure 3A), including the X-ray absorption near-edge structure (XANES) as well as the extended X-ray absorption fine structure (EXAFS). EXAFS refers to an absorption edge within the 30–1000 eV or even higher energy range of the oscillation structure, while XANES refers to the fine structure near the
30–50 eV absorption edge (Figure 3B). XANES can provide information on the oxidation state and geometry of Hg, while EXAFS can further probe the number, type, and proximity of atoms neighboring Hg. Due to the advantages of it being a non-destructive analytical technique, requiring no extraction, and with a high elemental specificity, XAFS has been increasingly applied to characterize the Hg species as well as their structure and bonding in environmental samples, although a high concentration of Hg is generally required, usually >100 mg kg⁻¹ (Lowry et al., 2004; Bernaus et al., 2005). This technique has been used to identify and quantify the percentage of α-HgS and β-HgS in environmental samples, including ore (Bernaus et al., 2005), mine waste (Kim et al., 2004; Lowry et al., 2004; Bernaus et al., 2005), and soil (Bernaus et al., 2005; Bernaus et al., 2006; Terzano et al., 2010), as well as the formation and dissolution of HgS in simulated environmental samples or solutions (Lennie et al., 2003; Wolfenden et al., 2005; Slowey and Brown, 2007; Skyllberg and Drott, 2010) (Figure 3C). In Hg-polluted soils surrounding a chlor-alkali plant in the Netherlands, direct determination of Hg species by XANES showed that α-HgS is one of the main Hg species (26%–37%) in all the sampled soils (Bernaus et al., 2006). A further study on the Hg species in polluted soils collected near an industrial area (Val Basento, Basilicata Region, Southern Italy) demonstrated that the main Hg species were α-HgS (14%–28%) and β-HgS (14%–25%), and the amount of β-HgS increased in the fraction of particles less than 2 μm in size (Terzano et al., 2010). In a study of Hg sulfidation, the observation of first-shell Hg-S distances by \( k^3 \)-weighted Hg L₃-edge EXAFS spectra of Hg
adsorbed on mackinawite (FeS) and sediment suggest a cinnabar-like environment, indicating sulfidation of spiked Hg$^{2+}$ on mackinawite and sediment (Wolfenden et al., 2005).

The recent technological advances in high-energy resolution fluorescence-detected X-ray absorption spectroscopy (HERFD-XAS) further enhance the capability of XAS in speciation of Hg (Proux et al., 2017). HERFD-XAS has many advantages over conventional XAS. The lower detection limit provided by HERFD-XAS facilitates the analysis of diluted elements in environmental and biological samples. More importantly, the sharper and well-marked features of HERFD-XANES spectra also unambiguously improve the precision of XANES quantitative analysis (Proux et al., 2017). Recently, HERFD-XANES has been applied in identification and quantification of HgS in soil (Manceau et al., 2015; Poulin et al., 2016), organic matter solution (Manceau et al., 2015), human hair (Manceau et al., 2016), and sewage sludge ash based P-fertilizers (Vogel et al., 2016). By using HERFD-XANES, the chemical state and bonding environment of Hg can be revealed at concentrations even as low as 1 mg Hg kg$^{-1}$ (Manceau et al., 2016; Vogel et al., 2016).

3.3. Programmed thermal desorption

It is well known that all the Hg species can be transformed into volatile Hg$^{0}$ by heating; thus, isothermal desorption coupled with atomic spectrometry has been widely used as a simple method for the determination of total Hg in solid samples without pre-digestion. In 1994, Bombach et al. (1994) observed that the various Hg species have different Hg$^{0}$ release curves as a function of temperature during temperature programming. The authors then proposed programmed thermal desorption coupled with atomic spectroscopy as a method for the speciation of Hg in a solid matrix. In environmental sample analysis, the homogenized sample (e.g., sieving to <2 mm; Reis et al., 2015) is continuously heated at a specified rate to release Hg$^{0}$ from the different Hg species, which is then transported by a carrier gas (N$_2$ or Ar) for in situ (in most cases) detection by atomic absorption spectrometry (as the most commonly used detector) (Rumayor et al., 2015c; Rumayor et al., 2016; Rumayor et al., 2017), atomic fluorescence spectroscopy (Lopez-Anton et al., 2010; Rallo et al., 2010), inductively coupled plasma optical emission spectrometry (Hojdova et al., 2008), or inductively coupled plasma mass spectrometry (Feng et al., 2004; Figure 4A). The HgS content in samples can be identified by a comparison of the peak temperature with the characteristic temperatures of HgS reference samples (Figure 4B). In addition, distinct Hg release temperatures for $\alpha$-HgS (330–370 °C) and $\beta$-HgS (200–300 °C) also make it possible to distinguish these two different HgS in crystallinity (Liu et al., 2013). Due to the partial overlap of HgS with other Hg species (e.g., HgO and HgSO$_4$) in the thermal desorption curves, peak differentiation by deconvolution is necessary for the extraction of the HgS signal from the thermogram and its quantification (Rumayor et al., 2015b).
Programmed thermal desorption has been widely applied for Hg speciation and HgS identification and quantification in various solid samples, including mine-waste (Gray et al., 2006; Hojdova et al., 2008; Coufalik et al., 2012; Rumayor et al., 2017), coal (Rumayor et al., 2015c, 2016), fly ash (Feng et al., 2004; Lopez-Anton et al., 2010; Rallo et al., 2010; Rumayor et al., 2015a, 2016), gypsum (Rallo et al., 2010; Liu et al., 2013; Rumayor et al., 2015b, 2016), soil (Biester and Nehrke, 1997; Palmieri et al., 2006; Reis et al., 2012; Rumayor et al., 2013, 2015a, 2016, 2017; Coufalik et al., 2014), sediment (Bombach et al., 1994; Biester and Nehrke, 1997; Reis et al., 2012; Rumayor et al., 2017), and airborne particulate matter (Feng et al., 2004). For example, using this technique, the content of HgS in coal samples was observed to be from undetected to 69.6% (Rumayor et al., 2015c), and in flue gas desulfurization gypsum, β-HgS was detected as one of the primary Hg compounds, with α-HgS also being occasionally detected (Liu et al., 2013). Similarly, HgS has been identified as among the main Hg species in fly ash samples (Rumayor et al., 2015a). Finally, the mean concentration of HgS in airborne particulate matter samples collected in Toronto was observed to be 2.3 pg m⁻³ with this technique, accounting for approximately 10% of the total Hg in airborne particulate matter (Feng et al., 2004).

### 3.4. Selective vapor generation

In acidic reduction conditions (10% SnCl₂ in 10% HNO₃), cysteine-Hg²⁺, protein and non-protein thiol chelates, and nucleoside chelates of Hg²⁺ can be fully transformed into Hg⁰ and detected by atomic spectrometry (Kelly et al., 2006a). Conversely, organic Hg (methylmercury and ethylmercury) cannot be transformed into Hg⁰ under either acid or alkaline reduction conditions (6.0 mL of 10% SnCl₂ in 10% HNO₃ and 3.5 mL of 45% aqueous KOH), while β-HgS can only be reduced into Hg⁰ under alkaline but not acid SnCl₂ reduction conditions (Kelly et al., 2006a). Therefore, exploiting these characteristics,
the concentration of $\beta$-HgS in biological samples can be selectively measured under alkaline reduction conditions. This selective vapor generation method has been successfully used in the characterization of $\beta$-HgS in inorganic Hg exposed algae (Kelly et al., 2006a, 2007; Lefebvre et al., 2007; Wu and Wang, 2014b) and microfungi (Kelly et al., 2006b).

3.5. Electron microscopy

Although electron microscopy (scanning electron microscopy (SEM) and transmission electron microscopy (TEM)) cannot provide quantitative information on HgS, morphologic (SEM; Prol-Ledesma et al., 2002; Kocman et al., 2011 and TEM; Barnett et al., 1997; Higueras et al., 2003) and crystallographic (TEM; Satake et al., 1990) characterization of HgS particles is possible. Combined with energy dispersive X-ray spectroscopy (EDS, for elemental identification; Satake et al., 1990; Barnett et al., 1997; Kocman et al., 2011) and selected area electron diffraction (SAED, for crystallographic characteristics; Satake et al., 1990; Barnett et al., 1997; Higueras et al., 2003), TEM or SEM is helpful in the morphologic and particle size characterization of HgS particles in an environmental matrix, which is critical to understand the formation and evolution of HgS particles in the environment. By using SEM/TEM, combined with EDS and SAED, nano- or micron-sized HgS particles have been identified in soil (Barnett et al., 1997; Higueras et al., 2003), suspended matter in precipitation (Kocman et al., 2011), and aquatic bryophytes (Satake et al., 1990). Subsamples within the <2 $\mu$m fraction in Hg-contaminated soil were analyzed by TEM with SAED, confirming the presence of multiple nanosized (<50 nm) crystalline HgS grains, usually closely associated with clay particles (Barnett et al., 1997). Further, by using high-resolution TEM, combined with SAED and EDS, the distribution of single crystalline (5–15 nm) and polycrystalline HgS particles (10–200 nm) in the cell wall of aquatic bryophytes J. vulcanicola and S. undulata was elucidated (Satake et al., 1990).

3.6. X-ray powder diffraction

X-ray powder diffraction (XRD) is a rapid analytical technique useful in phase identification of a crystalline material. Due to its low sensitivity (detection limit is ~2% HgS (w/w) in sample), the application of XRD to probe the HgS species in real environmental matrices remains difficult; however, the technique is useful in the identification and differentiation of $\alpha$-HgS and $\beta$-HgS in the simulated chemical and biological transformation process of Hg (e.g., Hg sulfidation in the presence sulfide (Pham et al., 2014), thiol (Manceau et al., 2015), FeS (Svensson et al., 2006; Liu et al., 2008; Skyllberg and Drott, 2010), and bacteria (Baldi et al., 1993; Glendinning et al., 2005)). It should also be noted that XRD is sensitive to the presence of crystalline phases, but not to non-crystalline phases, and thus the results could underestimate the presence of non-crystalline phases in Hg sulfidation.
3.7. **Dynamic light scattering**

Dynamic light scattering (DLS), or time-resolved DLS, is a technique used to determine the size distribution profile of small particles in suspension. However, due to the possible interference from ubiquitous environmental colloids (e.g., clay, biodebris), this technique is only useful to probe the hydrodynamic diameter of HgS and its evolution in a simple matrix (e.g., precipitation of HgS nanoparticles in a dissolved organic matter (DOM) solution) (Deonarine and Hsu-Kim, 2009; Slowey, 2010; Pham et al., 2014). Indeed, an HgS concentration as high as 1 mg L\(^{-1}\) (as Hg) is often needed for DLS characterization. Therefore, DLS is limited for simple and controlled laboratory systems.

4. **Environmental formation of cinnabar**

HgS can be formed in the environment through various chemical or biological pathways, with Hg\(^{2+}\) or methylmercury as the Hg precursor. In some cases, the absolute distinction between chemical and biological pathways is particularly challenging. For example, most of the reducing sulfur (i.e., S\(^2-\)) is believed to be produced by microorganisms. For convenience, we refer herein to a chemical pathway when the system does not directly involve organisms, while systems directly involving organisms were classified as biological pathways.

4.1. **Chemical formation of cinnabar**

4.1.1. **Hg\(^{2+}\)-dissolved organic matter (DOM) binary system**

In an environmental scenario (low Hg/DOM ratio), Hg\(^{2+}\) preferentially binds to DOM at reduced organic S sites (Hesterberg et al., 2001; Haitzer et al., 2002). Recently, the formation of \(\beta\)-HgS directly from Hg\(^{2+}\)-thiolate complexes in DOM and in cysteine solutions was demonstrated under aerated conditions (Manceau et al., 2015). Molecular-orbital computation studies revealed that four-coordinate metacinnabar can be obtained through the sequential cleavage of the S-C bond in a thiolate group and transfer of the resulting alkyl group to another thiolate to form thioether (Reactions 1 and 2, Figure 5A; Enescu et al., 2016). Indeed, such a dealkylation mechanistic pathway of HgS formation is thermodynamically favorable (Enescu et al., 2016).

\[
\begin{align*}
\text{RS} - \text{Hg} - \text{SR} + \text{RS} - \text{Hg} - \text{SR} & \rightarrow \text{RS} - \text{Hg} - \text{S} - \text{Hg} - \text{SR} + \text{R} - \text{S} - \text{R} \quad (1) \\
\text{RS} - (\text{Hg} - \text{S})_n \text{R} + \text{RS} - \text{Hg} - \text{SR} & \rightarrow \text{RS} - (\text{Hg} - \text{S})_{n+1} \text{R} + \text{R} - \text{S} - \text{R} \quad (2)
\end{align*}
\]

This theoretical calculation agrees well with the evolution of Hg in a DOM (Elliott soil humic acid fraction) or L-cysteine ethyl ester model solution (Manceau et al., 2015). High energy resolution XANES revealed that, after a 6-month reaction in an aqueous DOM system in the dark, approximately 74% of Hg\(^{2+}\) was
transformed into $\beta$-HgS, with the formation of $\beta$-HgS nanoparticles of 3–5 nm in size being further confirmed by high-resolution TEM (Manceau et al., 2015). It should be emphasized that this formation of $\beta$-HgS from Hg$^{2+}$–thiolate complexes in natural organic matter can occur in oxic zones in the absence of biogenic sulfide (Manceau et al., 2015), which has great environmental implication in topsoil and surface water.

Light can significantly accelerate the formation of $\beta$-HgS nanoparticles in a DOM solution. Upon UV irradiation (300–400 nm), DOM model solution of thioglycolic acid transformed approximately 89% of Hg$^{2+}$ into Hg$^0$ (Si and Ariya, 2015). However, TEM-SAED-EDS characterization also demonstrated the simultaneous formation of sphere- and rod-like HgS nanoparticles in this photolysis process (Si and Ariya, 2015). In DOM solutions and environmental water samples, besides the formation of Hg$^0$, UV or sunlight irradiation results in a loss of Sn$^{2+}$-reducible (i.e., reactive) Hg (from 60% to nearly 100%) and decrease (up to 80%) in methylmercury production by methylating bacteria (Luo et al., 2017). Indeed, loss of reactive Hg proceeded at a faster rate, with a decrease in the Hg to DOM ratio, attributed to the possible formation of HgS. Nevertheless, due to the difficulty in characterizing HgS at trace concentration levels, the sulfidation of Hg$^{2+}$ and formation of HgS was confirmed by SEM-EDS at higher Hg$^{2+}$ concentrations (0.1 mmol L$^{-1}$) (Luo et al., 2017). These results suggest that HgS and Hg$^0$ formation cooccur simultaneously in photo-irradiated Hg$^{2+}$-DOM solution, which could decrease the bioavailability and methylation of Hg.
4.1.2. $\text{Hg}^{2+}$–DOM–$\text{S}^{2-}$ ternary system

It is well known that $\text{Hg}^{2+}$ can rapidly react with sulfide ($\text{S}^{2-}$ or $\text{HS}^-$) to produce insoluble $\beta$-$\text{HgS}$ (Chai et al., 2010). In real aquatic environments, the introduction of fresh $\text{Hg}^{2+}$ within a DOM system first leads to complex formation, followed by the diffusion of $\text{Hg}^{2+}$–DOM complexes to the hypoxic environment (e.g., sediment layer), which further facilitates its reaction with abundant sulfide and induces the formation of $\beta$-$\text{HgS}$ nanoparticles (Slowey, 2010) (Figure 5B). Therefore, a preequilibration of $\text{Hg}^{2+}$ with DOM prior to the addition of sulfide is essential to better simulate the sulfidation of $\text{Hg}$ in real environments (Miller et al., 2007; Deonarine and Hsu-Kim, 2009). Over the course of aging, the newly formed $\text{HgS}$ nanoparticles agglomerate to form mass-fractal aggregates, with the crystallinity of $\text{HgS}$ particles increasing with aging (Pham et al., 2014). DOM plays a dual role in the formation of $\text{HgS}$ nanoparticles: (i) The complexation of $\text{Hg}^{2+}$ with thiol in DOM partially inhibits the reaction between $\text{Hg}^{2+}$ and sulfide and thus the formation of $\text{HgS}$ (Slowey, 2010; Graham et al., 2012) and (ii) DOM, as the capping agent for the newly formed $\text{HgS}$ nanoparticles, inhibits their growth, aggregation, and precipitation (Ravichandran et al., 1999; Slowey, 2010). Therefore, the characteristics of the DOM solution and the concentration ratio of $\text{Hg}$:DOM have a crucial impact on the formation of $\text{HgS}$ nanoparticles and their evolution. Indeed, a DOM solution rich in aromatic moieties was shown to preferential bind on the $\text{HgS}$ surface and inhibited the size growth of $\text{HgS}$ particle more effectively (Ravichandran et al., 1999). Additionally, hydrophobic humic and fulvic acids inhibited $\text{HgS}$ aggregation more effectively than hydrophilic organic acids (Ravichandran et al., 1999). Similar to humic and fulvic acids, thiol-containing organic ligands (e.g., cysteine, thioglycolate) were also shown to decrease the growth of $\text{HgS}$ particles (Deonarine and Hsu-Kim, 2009; Gondikas et al., 2010). The increasing DOM concentration (lower $\text{Hg}$:DOM ratio) significantly decreased the size of $\text{HgS}$ nanoparticles (Deonarine and Hsu-Kim, 2009), while an increase in the $\text{Hg}$:DOM ratio and sulfide resulted in progressively increasing particle size or crystalline order of $\text{HgS}$ particles (Slowey, 2010; Gerbig et al., 2011). Finally, a calcium concentration and ionic strength above $10^{-4}$ M were able to enhance $\text{HgS}$ aggregation, even in the presence of DOM (Ravichandran et al., 1999).

4.1.3. Reaction between $\text{CH}_3\text{Hg}^+$ and inorganic/organic reduced sulfur

$\text{H}_2\text{S}$ is ubiquitous in sediments of aquatic environments. In the 1970s, it was observed that $\text{H}_2\text{S}$ could enhance the volatilization of $\text{CH}_3\text{Hg}^+$ through the formation of volatile ($\text{CH}_3)_2\text{Hg}$ and black $\beta$-$\text{HgS}$ precipitation, as indicated in Reactions 3 and 4 (Rowland et al., 1977; Craig and Bartlett, 1978).

$$2\text{CH}_3\text{Hg}^+ + \text{H}_2\text{S} \rightarrow (\text{CH}_3\text{Hg})_2\text{S} + 2\text{H}^+ \quad (3)$$

$$\text{(CH}_3\text{Hg})_2\text{S} \rightarrow (\text{CH}_3)_2\text{Hg} + \text{HgS} \quad (4)$$

The binding of $\text{CH}_3\text{Hg}^+$ to reduced sulfur groups from the dissolved $\text{S}^{2-}$, mineral ($\text{FeS}_m$), or organic surfaces (e.g., 1, 2-ethanedithiol) facilitates the formation of
(CH₃)₂Hg and HgS by degradation of the adsorbed CH₃Hg⁺ (Figure 6; Banerjee et al., 2015; Jonsson et al., 2016). Comparably, the formation of (CH₃)₂Hg and HgS was greater on mineral (FeSm) surfaces than that in the presence of S²⁻ and organic sulfur surfaces.

4.1.4. Hg²⁺–FeS system
As one of the major constituents of acid volatile sulfide, mackinawite is widely present in anoxic sediments (Burton et al., 2009). XRD analysis revealed that, after a fast adsorption of Hg²⁺ onto the surface of FeS, it gradually transforms into α-HgS and β-HgS, in which 77% of Hg²⁺ presents as HgS and the remaining 23% exists as adsorbed Hg²⁺ (Liu et al., 2008). Another study (Jeong et al., 2010), using a combination of XRD, high-angle annular dark-field scanning TEM, and TEM-SAED, further demonstrated that β-HgS is the transformation product of Hg²⁺ immobilized by FeS (Figure 5C). Examination of the solid phase using Hg LIII-edge EXAFS revealed the formation of β-HgS-like clusters associated with the FeS surface or as a mixture of β-HgS and surface-associated species (Bone et al., 2014). Concurrently with HgS precipitation, the dissolved Fe content increased accordingly, indicating the replacement of Hg²⁺ with Fe²⁺ in FeS (Reaction 5) (Jeong et al., 2007).

\[
\text{Hg}^{2+} + \text{FeS} \rightarrow \text{HgS} + \text{Fe}^{2+}
\]  

(5)

In the presence of Cl⁻ and conditions of high molar ratios (>1) of [Hg²⁺]₀/[FeS]₀, the precipitation of HgS is inhibited by formation of chloride salts (Hg₂Cl₂ at acidic pH and HgCl₂·3HgO at basic pH) as alternatives (Jeong et al., 2007). Similarly, due to the competition between FeS and DOM-associated thiols for Hg²⁺, the precipitation of HgS is partially inhibited by the formation of Hg²⁺–DOM complexes (Skyllberg and Drott, 2010).

4.2. Biological formation of cinnabar

4.2.1. Microorganism-mediated formation of cinnabar from Hg²⁺
In 1985, Aiking et al. (1985) observed that Klebsiella aerogenes NCTC 418, which reduces sulfate to S²⁻, could also precipitate Hg²⁺ as HgS (Figure 7A). These HgS particles were located near the cell perimeter due to the relatively high local
concentrations of sulfide. Similarly, the formation $\beta$-HgS by *Klebsiella pneumoniae* M426 was identified by TEM-EDS and XRD (Lopez-Anton et al., 2010). The Hg-resistant strain *Bacillus cereus* MRS-1, isolated from electroplating industrial effluent, can covert HgCl$_2$ into extracellular $\alpha$-HgS nanoparticles 10–100 nm in size, as evidenced by TEM-EDS and XRD (Sathyavathi et al., 2013). The exogenous cysteine-induced sulfide biosynthesis by aerobically respiring *Escherichia coli* can promote the formation of particulate $\beta$-HgS associated with both the cell envelope and cytoplasm (Thomas and Gaillard, 2017).

In a column study to mimic reactive transfer in an anoxic aquifer, when sulfate-reducing bacteria were dominant, the produced sulfide induced the direct precipitation of HgS or indirect formation of HgS by adsorption on iron sulfides (e.g., mackinawite) (Hellal et al., 2015), which is consistent with the formation of HgS induced by the sulfate-reducing bacterium *Desulfovibrio desulfuricans* under anoxic conditions (Truong et al., 2013). A further study employed transmission X-ray microscopy and Hg L3 XANES to observe the hollow HgS particles, clustered mainly at the surface, formed on the root surface of Hg-exposed *Spartinapoliosa* (Patty et al., 2009). These HgS-assembled hollow particles were also observed following the formation of HgS at the surface of microbes such as sulfate-reducing bacteria (Patty et al., 2009).

Hg resistant thermophilic *Bacillus sp.* and *Ureibacillus sp.* have been observed to precipitate Hg$^{2+}$ as $\beta$-HgS, as identified by XRD; however, no H$_2$S was produced by the bacteria in the absence or presence of Hg$^{2+}$, suggesting that a new mechanism of HgS formation, other than sulfidation with sulfide, was involved based on the production of non-volatile thiol species (Glendinning et al., 2005). Further, it

*Figure 7. The biological formation pathways of HgS in microorganisms (A) and microalgae (B).*
was also proposed that HgS precipitation surrounding *Yarrowia spp.* was derived from interaction of Hg\(^{2+}\) with thiol moieties of protein molecules of extracellular polymeric substances (Oyetibo et al., 2016).

### 4.2.2. Microorganism-mediated formation of cinnabar from CH\(_3\)Hg\(^+\)

H\(_2\)S is widely produced by various bacteria in anaerobic conditions; therefore, it has also been proposed that H\(_2\)S-producing bacteria (e.g., sulfate-reducing *Desulfovibrio* species) could induce the degradation of CH\(_3\)Hg\(^+\) via \(S^2^-\)-catalyzed disproportionation to volatile (CH\(_3\))\(_2\)Hg and insoluble HgS (Reactions 3 and 4) (Wood and Wang, 1983). In addition, at an acidic pH, CH\(_3\)HgS\(^-\) from (CH\(_3\)Hg)\(_2\)S formed methane and HgS (Reactions 6 and 7), representing an alternative mechanism to the production of (CH\(_3\))\(_2\)Hg and HgS (Wollast et al., 1975).

\[
(CH_3Hg)_2S + S^2^- \rightarrow 2CH_3HgS^- \quad (6)
\]

\[
CH_3HgS^- + H^+ \rightarrow CH_4 + HgS \quad (7)
\]

Further, it was demonstrated that the methylmercury resistance of *D. desulfuricans* can degrade methylmercury from cultures by transformation to (CH\(_3\))\(_2\)Hg, \(\beta\)-HgS, methane, and trace ionic Hg (Baldi et al., 1993; Baldi et al., 1995). During a 15-day experiment, insoluble (CH\(_3\)Hg)\(_2\)S (identified by gas chromatography-mass spectrometry) formed instantly in the reaction of methylmercury with Hg\(_2\)S, slowly decomposing under anaerobic conditions to \(\beta\)-HgS (identified by XRD), (CH\(_3\))\(_2\)Hg, and methane (Baldi et al., 1993). As very high concentration of methylmercury (∼80 mg L\(^{-1}\)) was used in this microorganism-mediated sulfidation, this pathway and mechanism should be further tested under environmentally relevant conditions. Nevertheless, considering the methylation and demethylation processes could cooccur for some sulfate-reducing bacteria (e.g., *Desulfovibrio desulfuricans* ND132) (Gilmour et al., 2011), the simultaneous determination of the methylation and demethylation capacities of various bacteria is important to evaluate their potential environmental effect in Hg cycling.

### 4.2.3. Other organisms mediated formation of cinnabar

The in situ formation of \(\beta\)-HgS has been observed in yeast (*Candida xylop-soci*) (Amin and Latif, 2013), microalgae (Kelly et al., 2006a, 2007; Lefebvre et al., 2007; Wu and Wang, 2014b), *Brassica juncea* (Wang et al., 2012a), and horehound (*Marrubium vulgare*; Carrasco-Gil et al., 2013). In addition, \(\beta\)-HgS was identified in the cell wall of the aquatic bryophytes (*Jungermannia vulcanicola* and *Scapania undulata*) in an acidic stream, Kashiranashigawa, Japan (Satake et al., 1990), although the source of \(\beta\)-HgS (from uptake or in situ formation) is still not known. For the in situ formation of \(\beta\)-HgS in cyanobacteria (*Limnothrix* and *Synechococcus*), after a 1-hr exposure, 58% and 35% of the applied HgCl\(_2\) (120 \(\mu\)g L\(^{-1}\)) were transformed into \(\beta\)-HgS, respectively,
demonstrating that \( \beta \)-HgS constitutes a major biotransformed Hg pool (Lefebvre et al., 2007). Additionally, increasing the temperature enhanced the amount of \( \beta \)-HgS produced, with a concomitant decrease in \( \text{Hg}^0 \) volatilization. Blocking intra- and extracellular thiols using dimethylfumarate and iodoacetamide further revealed that an intracellular thiol pool was required for the conversion of \( \text{Hg}^{2+} \) into \( \beta \)-HgS (Kelly et al., 2007; Lefebvre et al., 2007). These results also suggested that, similar to the formation of HgS from \( \text{Hg}^{2+} \)-thiolate complexes in DOM (Manceau et al., 2015), the intracellular formation of HgS may involve \( \text{Hg}^{2+} \)-induced dealkylation of phytochelatin (Figure 7B; Wu and Wang, 2014a, 2014b). The high \( \beta \)-HgS transformation and phytochelatin induction ability of \textit{T. weissflogii} (Wu and Wang, 2014b) also suggested that the phytochelatin–Hg complex is the likely precursor for HgS formation. Another possible formation mechanism was proposed for thiosulfate-treated plants, in which \( \beta \)-HgS (66%–94%) was observed in roots and shoots of two cultivars of \textit{Brassica juncea} under Hg-contaminated field with thiosulfate treatment (Wang et al., 2012a). In this procedure, Hg may be absorbed and transported in plants as the Hg–thiosulfate complex (Wang et al., 2014, 2017), which further decomposes to \( \text{Hg}^{2+} \) and \( \text{SO}_4^{2-} \) ions in the presence of free protons inside the plasma membrane (Reaction 8). Sulfide ions would be produced by the assimilation of sulfate (Koprivova and Kopriva, 2016) (Reaction 9), and the concomitant \( \text{Hg}^{2+} \) and \( \text{S}^{2-} \) would precipitate as \( \beta \)-HgS (Reaction 10).

\[
\text{Hg(S}_2\text{O}_3)_2 + 3\text{O}_2 \rightarrow \text{Hg}^{2+} + 2\text{SO}_4^{2-} + 2\text{SO}_2 \tag{8}
\]

\[
\text{SO}_4^{2-} + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{S}^{2-} + 4\text{H}_2\text{O} \tag{9}
\]

\[
\text{Hg}^{2+} + \text{S}^{2-} \rightarrow \text{HgS} \tag{10}
\]

5. Environmental dissolution of cinnabar

Cinnabar may partially dissolve under environmental conditions, enhancing its chemical and biological activity, e.g., methylation (Jonsson et al., 2012). Thus, dissolution of HgS can again incorporate Hg into environmental cycling, and could be mediated by chemical or biological processes. Similar to the formation of HgS, it is sometimes difficult to completely distinguish between chemical and biological pathways in HgS dissolution. For instance, in some cases, ligands involved in HgS dissolution were produced by biological processes (e.g., thiosulfate, cysteine, and cyanide). Thus, for convenience, we classified HgS dissolution as involving either chemical or biological processes. It should be noted here that, although the dissolution of cinnabar is environmentally important, this dissolution process is quite slow and the dissolution rate is generally lower than 0.1% (Waples et al., 2005; Barnett et al., 2011; Vazquez-Rodriguez et al., 2015; Jiang et al., 2016).
5.1. Chemical dissolution and transformation of cinnabar

The chemical dissolution of HgS commonly involves three possible pathways (Figure 8). First, enhanced HgS dissolution by a Hg$^{2+}$-complexing ligand (e.g., DOM (Wallschlager et al., 1996; Ravichandran et al., 1998; Waples et al., 2005; Slowey, 2010), polysulfide (Paquette and Helz, 1995; Slowey and Brown, 2007), thiosulfate (Han et al., 2017), cysteine (Ravichandran et al., 1998), mercaptoacetic acid (Ravichandran et al., 1998), cyanide (Shaw et al., 2006), and ethylenediaminetetraacetic acid (EDTA; Han et al., 2008)). Second, transformation of S$^{2-}$ in HgS into soluble or volatile S species and thus release of Hg$^{2+}$ (e.g., oxidation to SO$_4^{2-}$ (Hsieh et al., 1991; Barnett et al., 2001; Holley et al., 2007) or methylation to (CH$_3$)$_2$S (Thayer et al., 1984; Minganti et al., 2007)). Finally, displacement of Hg$^{2+}$ in HgS by thiophile metals (e.g., Cu$^+$, Fe$^{2+}$) (Han et al., 2017).

Besides enhancing the formation of HgS (as discussed in Section 4.1.1), DOM as complexing agent for Hg$^{2+}$, can also facilitate the dissolution of HgS. The enhanced dissolution of HgS by DOM was considerable even at pH 1, highlighting the critical role of extremely strong complexation (e.g., by sulfur-containing ligands in DOM) in HgS dissolution (Wallschlager et al., 1996). In addition, the enhanced dissolution of HgS by DOM is usually more significant than that by various inorganic (chloride, sulfate, or sulfide) or organic ligands (salicylic acid, acetic acid, EDTA, or cysteine) (Ravichandran et al., 1998). It should be noted that this enhanced dissolution of HgS by DOM may include both the truly dissolved Hg$^{2+}$ (as Hg$^{2+}$-DOM complex) and DOM-dispersed HgS nanoparticles (which could penetrate the 0.1 µm pore-sized filter). There is still a need for methods to distinguish the truly dissolved Hg$^{2+}$ and the HgS nanoparticles. Nevertheless, the “dissolution” rate of HgS correlates positively with three DOM characteristics, namely, the specific ultraviolet absorbance, aromaticity, and molecular weight (Waples et al., 2005), possibly due to the DOM characteristics dependence on dispersion and formation of small “filter-penetrable” HgS nanoparticles (Louie et al., 2013).

![Figure 8. Chemical dissolution of HgS in the environment.](image-url)
The presence of cuprous (Cu\(^{+}\)) may facilitate the dissolution of HgS by thiosulfate, possibly due to the displacement of Hg\(^{2+}\) in HgS by Cu\(^{+}\) (Reaction 11) (Han et al., 2017).

\[
\text{HgS} + 2\text{Cu}(\text{S}_2\text{O}_3)^{2-} \rightarrow \text{Cu}_2\text{S} + \text{Hg}(\text{S}_2\text{O}_3)^6^{-} \tag{11}
\]

This displacement of Hg\(^{2+}\)-induced HgS dissolution is potentially important in mine environment considering its high metal (e.g., Cu, Fe) abundance.

The presence of dissolved oxygen enhances the dissolution of \(\alpha\)-HgS (Holley et al., 2007; Jiang et al., 2016) and \(\beta\)-HgS (Hsieh et al., 1991; Barnett et al., 2001) due to the oxidation of S\(^{2-}\) to sulfate on the HgS particle surface or in the bulk phase (Reaction 12) (Barnett et al., 2001; Holley et al., 2007). For example, the released Hg from purging \(\alpha\)-HgS with oxygen was observed to reach a concentration of several hundred \(\mu\text{g} \text{ L}^{-1}\), while no significant cinnabar dissolution was detected under anaerobic conditions (Jiang et al., 2016).

\[
\text{HgS} + 2\text{O}_2 \rightarrow \text{Hg}^{2+} + \text{SO}_4^{2-} \tag{12}
\]

In this oxidative dissolution, besides SO\(_4^{2-}\), monodentate-bound thiosulfate (S\(_2\)O\(_3^{2-}\)) was also identified as an oxidation intermediate on the HgS surface, which may further facilitate the dissolution of adsorbed Hg\(^{2+}\) (Holley et al., 2007). Due to the readsorption of Hg\(^{2+}\) on the HgS surface (Barnett et al., 2001; Holley et al., 2007; Jiang et al., 2016), the dissolution of HgS in this procedure may be underestimated. Following the correction of Hg\(^{2+}\) readsorption by using isotope tracing, it was found that the cinnabar dissolution rate, when considering Hg readsorption, was approximately twice the value calculated without considering readsorption process (Jiang et al., 2016). Iodomethane, a natural metabolite of marine organisms (e.g., algae, bacteria, and fungi) and a fumigant, is able to methylate S\(^{2-}\) in HgS to volatile (CH\(_3\))\(_2\)S, thereby releasing Hg\(^{2+}\) from HgS (Reaction 13) (Thayer et al., 1984; Minganti et al., 2007). Comparably, iodomethane-mediated release of Hg\(^{2+}\) was greater from \(\alpha\)-HgS than from \(\beta\)-HgS (12 times at 10 mM iodomethane) (Minganti et al., 2007).

\[
\text{HgS} + 2\text{CH}_3\text{I} \rightarrow \text{HgI}_2 + (\text{CH}_3)_2\text{S} \tag{13}
\]

Sunlight irradiation is able to induce the chemical transformation of \(\alpha\)-HgS (McCormack, 2000; Radepent et al., 2011; Radepent et al., 2015) and \(\beta\)-HgS (Hsieh et al., 1991) in the solid phase or in a HgS(s)–water interface; this transformation can be further enhanced in the presence of Cl\(^-\) (McCormack, 2000; Radepent et al., 2011; Radepent et al., 2015), with calomel (Hg\(_2\)Cl\(_2\)), cordierite (\(\alpha\)-Hg\(_3\)S\(_2\)Cl\(_2\)), kenhsuite (\(\gamma\)-Hg\(_3\)S\(_2\)Cl\(_2\)), or dissolved Hg\(^{2+}\) as products (Hsieh et al., 1991; Radepent et al., 2011). In addition, upon irradiation with visible light, the
vaporization of Hg$^0$ from $\alpha$-HgS (Anaf et al., 2013) or $\beta$-HgS (Hsieh et al., 1991) was observed, suggesting there is a photochemical reduction of HgS.

### 5.2. Microbial-mediated dissolution and transformation of cinnabar

Bacterial leaching, or bio-oxidation, of metal sulfides to soluble metal ions and thiosulfate or polysulfides has long been known to occur for diverse groups of bacteria, including aerobic Fe$^{2+}$-oxidizing bacteria and sulfur-oxidizing bacteria (Schippers and Sand, 1999; Vera et al., 2013). Hg-resistant strains of *Thiobacillus ferrooxidans* were seen to transform HgS into Hg$^0$, and the concurrence of pyrite (FeS$_2$) increased the production of Hg$^0$ (Baldi and Olson, 1987), possibly due to the catalytic oxidation of Fe$^{3+/2+}$ (Schippers and Sand, 1999; Vera et al., 2013). The presence of Fe and O$_2$ also increased the dissolution of HgS by *Acidithiobacillus ferrooxidans*, following Reactions 14 and 15 (Wang et al., 2013a, 2013b).

\[
2\text{HgS} + 4\text{Fe}^{3+} + 3\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Hg}^{2+} + 4\text{Fe}^{2+} + 2\text{H}_2\text{SO}_4 \tag{14}
\]

\[
4\text{Fe}^{2+} + 4\text{H}^+ + 3\text{O}_2 \overset{A. \text{ferrooxidans}}{\rightarrow} 4\text{Fe}^{3+} + 2\text{H}_2\text{O} \tag{15}
\]

Sulfur-oxidizing bacteria of the genus *Thiobacillus thioparus* led to the release of $\beta$-HgS-hosted Hg$^{2+}$, reduction to Hg$^0$ and subsequent volatilization (Vazquez-Rodriguez et al., 2015). This dissolution and volatilization was greatly enhanced (over 10-fold) in the presence of thiosulfate, which plays dual roles by enhancing HgS dissolution through Hg complexation and providing an additional growth substrate for *T. thioparus* (Vazquez-Rodriguez et al., 2015). Microbial community inocula from an acid mine drainage, dominated by Fe-oxidizing and S-oxidizing bacteria, were capable of releasing significantly more Hg into solution compared to inactivated or abiotic controls from $\alpha$-HgS, $\beta$-HgS, and mine tailings, possibly due to the direct oxidation of S$^{2-}$ or catalytic oxidation of S$^{2-}$ by Fe$^{3+}$ (Jew et al., 2014). In the microcosm with $\beta$-HgS, the presence of the acid mine drainage microbial community significantly increased dissolved Hg concentrations up to 500 $\mu$g L$^{-1}$ (vs. <100 ng L$^{-1}$ in abiotic control) during the first 30 days. This finding is important for risk assessment and future management of Hg mines and acid mine drainage. Recently, it was also observed that under anaerobic conditions iron-reducing bacteria *Shewanellaoneidensis* MR-1 could leach HgS as Hg$^{2+}$, with the process being enhanced by Na$_2$S and humic acid and favorable at an initial of pH 6.0, although the mechanisms for this enhanced biodissolution remains unknown (Chen et al., 2013, 2014). These studies suggested that, in either anoxic or oxic environments, various bacteria are capable of enhancing the dissolution of HgS.
6. Formation and dissolution of cinnabar on environmental geochemical cycle, bioaccumulation, and toxicity of Hg

The chemical/biological formation and dissolution of HgS have critical impacts on the mobility, reduction, methylation, bioavailability, and toxicity of Hg. Although the mobilization of HgS can be enhanced with DOM and organic acids in eluent (Slowey et al., 2005; Gai et al., 2016), especially in the high molecular weight DOM fraction (Poulin et al., 2016), compared with other Hg species (dissolved inorganic Hg\(^{2+}\) species, Hg\(^{2+}\)-DOM complex, and Hg\(^0\)), HgS nanoparticles had the poorest mobility in sand- and soil-packed columns with partial water saturation under simulated rainfall and landfill leachate influent conditions (Gai et al., 2016). Therefore, the sulfidation of Hg\(^{2+}\) potentially decreased its transport in terrestrial and aquatic environments (Liem-Nguyen et al., 2017). Due to its low solubility product constant, HgS is considered more chemically “inert” than other Hg species (Han et al., 2006), and thus the formation of HgS decreases the transformation of Hg. Photoinduced formation of HgS from Hg–DOM complexes could decrease the photo-production of dissolved gaseous Hg\(^0\) (Luo et al., 2017) and the biotransformation of Hg\(^{2+}\) to HgS by cyanobacteria occurs with a concomitant decrease in Hg\(^0\) formation and volatilization (Lefebvre et al., 2007). As the methylation rate of HgS by bacteria is considerably lower compared to that of Hg\(^{2+}\) and Hg\(^{2+}\)-DOM complexes (Fagerstrom and Jernelov, 1971; Jonsson et al., 2012), the formation of HgS in the solid phase could partially inhibit Hg methylation by methylating bacteria (Benoit et al., 2001; Liu et al., 2009; Gilmour et al., 2011; Yu et al., 2013). It should also be noted that the methylation rate of HgS nanoparticles is higher than that of HgS aggregates or microparticles (Graham et al., 2012; Zhang et al., 2014), possibly due to their higher bio-uptake or dissolution. Considering the size-dependent bioavailability of HgS particles and their wide occurrence, the size fractionation and quantification of HgS particle is important to understand the environmental fate and toxicity of Hg. Due to the low bioavailability (Schoof and Nielsen, 1997; Hsu-Kim et al., 2013) and toxicity (Beers and Mousavi, 2013; Liu et al., 2016) of HgS, extra- and intracellular formation of HgS could also be an important detoxification pathway of Hg\(^{2+}\) and methylmercury for Hg-resistant bacteria and other organisms (Aiking et al., 1985; Baldi et al., 1993; Glendinning et al., 2005; Wu and Wang, 2014b). Indeed, the exposure of marine phytoplankton to Hg\(^{2+}\) revealed a negative relationship between growth inhibition and the percentage of intracellularly formed \(\beta\)-HgS, implying a role of \(\beta\)-HgS in Hg detoxification (Wu and Wang, 2014b).

The chemical/biological formation and dissolution of HgS could explain Hg aging and activation in periodical flooding of natural and constructed wetlands (e.g., paddy soils; Rothenberg and Feng, 2012) (Figure 9; St Louis et al., 2004). In flooding conditions, the anaerobic environment is favorable for methylation of newly deposited Hg by methylating bacteria. Meanwhile, the anaerobic environment also results in sulfate reduction and sulfide accumulation, and thus in the
formation of HgS, decreasing the bioavailability and methylation of Hg$^{2+}$ (i.e., aging of Hg$^{2+}$). Although the subsequent conversion to the aerobic condition by drainage decreases the activity of anaerobic methylating bacteria, it facilitates the oxidative dissolution of HgS (Barnett et al., 2001; Wang et al., 2013b), and then provides bioavailable Hg$^{2+}$ for methylating bacteria in a subsequent anaerobic environment. Therefore, the anaerobic–aerobic cycle induced by periodical flooding overall enhances the methylation of Hg.

7. Conclusion and perspectives

The above studies demonstrated that HgS is one of the major environmental sinks of Hg, which is widely available in various environmental compartments. In the past decades, analytical methods have been developed for the identification, characterization, and quantification of HgS and its environmental behavior. Various chemical and biological pathways could result in the environmental formation and dissolution of HgS, which play a crucial role in the transport, reduction, methylation, and toxicity of Hg. The above studies also call for further critical research efforts toward gaining a better understanding of the environmental formation/dissolution of HgS and its role in the geochemical cycle of Hg. The following examples show possible future research directions:

7.1. Additional analytical requirements for cinnabar

Although the analytical methods above could be used for the identification and quantification of HgS, the identification (in composition) and characterization (in size and concentration) of HgS particles in environmental and biological matrices.

Figure 9. Critical role of formation and dissolution of HgS in an anaerobic–aerobic cycle.
remain a challenge. The in situ identification of HgS particles without extraction (e.g., TEM/SEM, X-ray micro fluorescence imaging combined with micro-XAFS) is highly desirable for environmental and biological samples. In addition, the low concentration of HgS particles and the wide particle size distribution call for highly sensitive methods for HgS particle identification and quantification. Single particle inductively coupled plasma-mass spectrometry (sp-ICP-MS) is an emerging method for the detection, characterization, and quantification of engineered nanoparticles that can provide information on particle number, diameter, and concentration, with detection limits down to several nanograms per liter (Laborda et al., 2014). sp-ICP-MS also has great potential in the analysis of natural nanoparticles, e.g., HgS nanoparticles, due to its high sensitivity. Further, the multi-element detection capability of time of flight-MS would also have considerable advantages in identifying HgS nanoparticles and characterizing their purity in complex substrates. However, it should be noted that the size detection limit of sp-ICP-MS is usually over 10 nm, and thus the technique is unsuitable for newly formed HgS nanoparticles under 10 nm in size. The on-line coupling of particle size-separation techniques (e.g., size exclusion chromatography (Zhou et al., 2014, 2017), capillary electrophoresis (Liu et al., 2014), field-flow fractionation (Tan et al., 2015)) with highly sensitive detectors (e.g., ICP-MS) enable the simultaneous separation and detection of nanoparticles with a wide particle size range (from approximately 1 nm to $\mu$m) at a detection limit within the sub-microgram per liter level; this could represent a complementary technique to sp-ICP-MS for particle size characterization. Further, isotope tracing techniques are useful in tracking the transport and transformation of HgS nanoparticles (Jonsson et al., 2012, 2014; Jiang et al., 2016), e.g., distinguishing the differential methylation potentials of geochemically relevant Hg$^{2+}$ species (DOM$-^{198}$Hg$^{2+}$ complex, $^{198}$Hg(NO$_3$)$_2$, $\alpha$-$^{199}$HgS, $\beta$-$^{201}$HgS, and $^{202}$Hg$^{2+}$ reacted with mackinawite) (Jonsson et al., 2012). Hg isotope fractionation has been observed in the formation (Smith et al., 2015) and decomposition (Wiederhold et al., 2013) of HgS particles, and may be used as a possible tracer of HgS cycling in the environment.

7.2. Probing the sulfdation of Hg in environment-related media and scenarios

To date, HgS has been identified in various environmental and biological compartments; however, there remain several media to be explored. Considering the similarly thiophil properties of Hg and Ag and the sulfdation of Ag in waste water and organisms (Kaegi et al., 2011; Miclaus et al., 2016), highly similar sulfdation processes of Hg are also possible in waste water treatment plants and higher organisms (e.g., mammalian). In addition, the importance of HgS in atmospheric particulate matter and its role in global Hg cycling remain to be determined. Therefore, probing for the presence of HgS in these media (atmospheric particulate matter, waste water treatment plants, and higher organisms) is helpful to understand its environmental/biological cycle and toxicity/detoxification. In previous studies on the
aqueous formation and dissolution of HgS, due to limitations in the sensitivity of analytical methods, the Hg concentration used is often up to the milligram per liter level, which is much too high compared to environmental scenarios. Further studies should focus on the detection of low Hg concentrations (ng L$^{-1}$ to μg L$^{-1}$ for surface water and interstitial water, respectively) to accurately reflect such scenarios.

### 7.3. Environmental remediation of Hg pollution through sulfdation

Due to the environmental and health risks arising from Hg pollution, the development of remediation methods for an Hg contaminated atmosphere, water, soil, and sediment is of major importance (Wang et al., 2004, 2012b). The chemical and biological formation of low toxicity, “inert” HgS could prove an effective protocol for the environmental remediation of Hg contamination in various compartments. Further, engineered FeS nanoparticles could be delivered to contaminated soil or sediment to facilitate the in situ immobilization of Hg$^{2+}$ as HgS (Gong et al., 2014). Hg- or methylmercury-resistant bacteria could transform Hg$^{2+}$ or methylmercury into HgS (Baldi et al., 1993; Essa et al., 2005), and microalgae could extract Hg$^{2+}$ from surrounding water to form intracellular HgS, possibly using Hg$^{2+}$-phytochelatin complexes as intermediates (Kelly et al., 2007). Finally, the genetic modification of bacteria, algae, and plants to enhance H$_2$S and phytochelatin synthesis could further facilitate the formation of extracellular/intracellular HgS. It should also be noted that for environmental remediation of Hg through sulfdation, the possible redissolution and methylation of HgS in postremediation should be carefully evaluated. In addition, besides acute toxicity, the knowledge gap in long-term toxicity of HgS should also be explored and filled before the field application of Hg sulfdation in environmental remediation.

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