

Geological and Anthropogenic Factors Influencing Mercury Speciation in Mine Wastes

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Introduction

Mercury (Hg) is a naturally occurring element that poses considerable health risks to humans, primarily through the consumption of fish which have accumulated harmful levels of mercury in their tissue. This bioaccumulation of mercury in fish is a result of elevated exposure from a number of sources including industrial emissions, atmospheric deposition, and mercury-bearing products such as thermometers, batteries, electrical switches, and fluorescent light bulbs. In California, however, a significant amount of mercury enters the environment through the dozens of mercury mines located throughout the California Coastal Range (Figure 2), where thousands of tons of mercury were recovered for use in gold recovery further east in the Sierra Nevada. The transport of mercury from these remote poorly-monitored mine sites has resulted in elevated mercury levels in more populated urban regions such as the San Francisco Bay Area. Understanding the movement and geochemistry of mercury from mines in California is therefore necessary in order to predict the potential impacts and hazards associated with this form of mercury contamination.



Figure 1. Dr. Christopher Kim collects a mine waste sample from the Oat Hill mercury mine in Northern California. The majority of mercury mine wastes at these sites are present as loose, unconsolidated piles, facilitating the transport of mercury-bearing material downstream into local watersheds.

The speciation of mercury is a critical determinant of its mobility, reactivity, and potential bioavailability in mercury- and gold-mine impacted regions. Mercury speciation in these complex natural systems is additionally influenced by a number of physical, geological, and anthropogenic variables. In order to investigate the degree to which several of these variables may affect mercury speciation, extended x-ray absorption fine structure (EXAFS) spectroscopy was conducted at SSRL Beam Lines 4-3 and 11-2 to determine the mercury species and relative proportions of these species present in mercury-bearing wastes from selected mine-impacted regions in California and Nevada. This work represents the first *in situ*, non-destructive method by which to identify mercury speciation in natural samples.

Mercury speciation protocol

The EXAFS-based speciation procedure for Hg is similar to that previously developed for and applied to other metal(loid)s such as arsenic^(1,2), lead⁽³⁻⁵⁾, and zinc^(6,7). It involves the comparison of an EXAFS spectrum collected from a Hg-bearing sample with a spectral library of model compounds previously generated from an assortment of Hg minerals and sorbed species (Figure 3). While each model compound spectrum serves as the spectral fingerprint of a single Hg species, the EXAFS spectrum of a heterogeneous natural sample represents a composite of the EXAFS contributions from all detectable Hg species present. Therefore, an EXAFS spectrum collected from a natural sample containing multiple Hg species can be decomposed using a linear least-squares fitting method into the sum of its individual components through direct comparison with the model compound spectra.

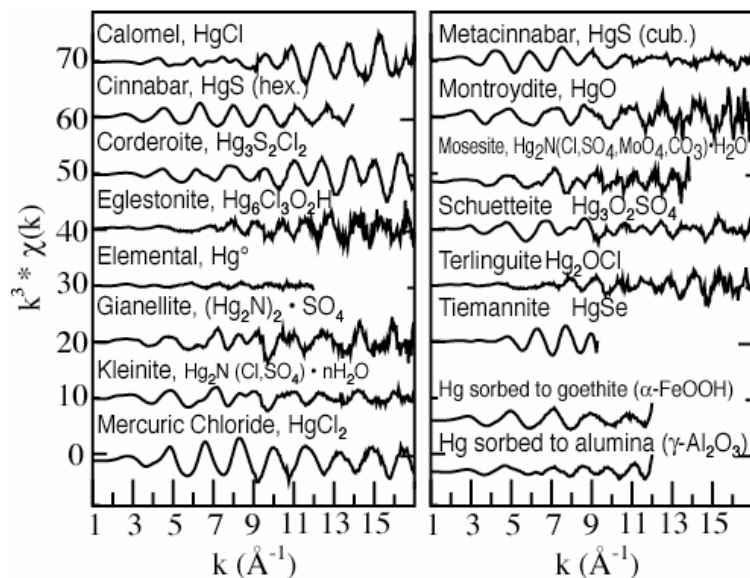


Figure 3. Mercury model compound database of a host of Hg minerals and sorbed species. Each Hg L_{III}-edge EXAFS spectrum is distinct from the others, reflecting the unique structural environment around Hg from phase to phase.

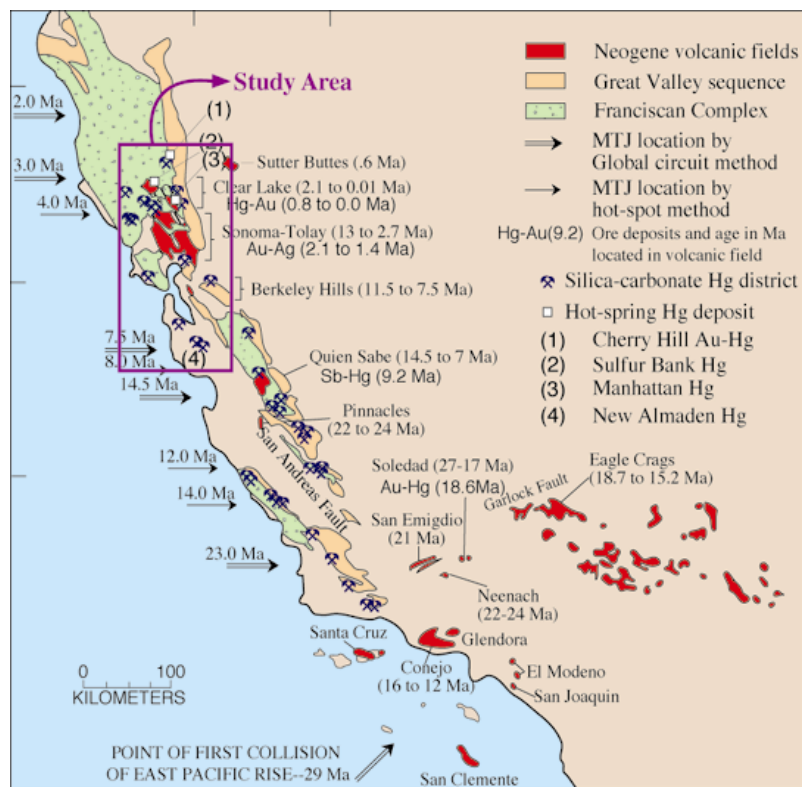


Figure 2. Geologic map of mercury mining areas in the California Coast Range, distinguishing between silica-carbonate deposits and hot-spring Hg deposits. Samples were primarily collected from a variety of mine waste media at multiple sites in the outlined region. From Rytuba⁽¹²⁾.

fitting method into the sum of its individual components through direct comparison with the model compound spectra. Furthermore, determining the relative proportion of each model compound's contribution to the least squares linear combination fit directly yields the molar percentage of the respective Hg species identified in the sample.

Figure 4 presents an example of such a linear fit, showing the fitted Hg L_{III}-EXAFS spectrum of a Hg-bearing sample from the Bessels Mill in Nevada and the related fit components. In this case, cinnabar (HgS, hex.), metacinnabar (HgS, cub.), and

schuetteite ($\text{Hg}_3\text{O}_2\text{SO}_4$) have been identified as the significant components contributing to the final fit; when scaled to 100%, they contribute in proportions of 42% and 39%, and 19%, respectively. This identification of the relevant Hg species present and the proportions at which they are present in the sample represents the formal, EXAFS-determined Hg speciation of the sample. Application of the EXAFS technique to determine Hg speciation in calibrated mixtures of model Hg compounds⁽⁸⁾ and a separate comparison of results from EXAFS spectroscopy and sequential chemical extractions on a selected suite of Hg-bearing samples⁽⁹⁾ further validated the use of EXAFS spectroscopy for determining Hg speciation in complex samples and better defined its limitations, where fit components should be considered accurate to $\pm 25\%$ of their stated value and fit components comprising less than 10% of a fit should be viewed with caution.

Sampling

Samples were collected from a number of inactive Hg mine sites located along the California Coast Range Hg mineral belt. Hg-contaminated samples from former gold mine workings were also collected from the Carson River basin in western Nevada. The sampled media included calcines (roasted ore), condenser soot, waste rock (unroasted low-grade Hg-bearing material), distributed sediments, Hg-bearing gold mine tailings, and an amorphous Fe-oxyhydroxide precipitate forming downstream from an acid mine drainage seep at a Hg mine. Most samples contained Hg concentrations of 100 mg/kg (ppm) or greater, although a few samples with Hg concentrations below 100 ppm were also successfully analyzed using EXAFS spectroscopy.

Effect of Geological Background on Hg Speciation

Since Hg ore deposits are known to form in a variety of geological settings, a comparison of Hg speciation in mine wastes between different ore depositional environments was expected to reveal fundamental differences in the types of Hg species present. Speciation results determined by EXAFS spectroscopy of Hg-contaminated mine wastes from California and Nevada are shown in Figure 5. Briefly, there are two primary types of Hg deposits in the California Coast Range: (1) silica-carbonate Hg deposits, in which Hg is deposited in the highly fractured zones of hydrothermally altered serpentinite bodies emplaced along fault zones such as the San Andreas Fault, and (2) hot-spring Hg deposits, where Hg is deposited in low-temperature, near-surface active hydrothermal systems enriched in chloride and sulfate⁽¹⁰⁾.

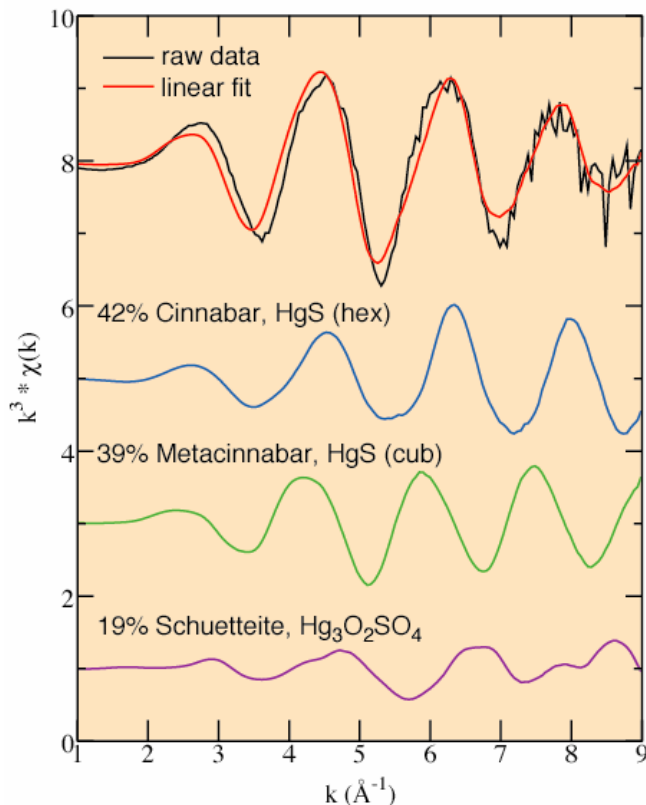


Figure 4. Linear fitting results for a sample from the Besseles Mill, Carson River, NV, showing the raw data (top, in black) best linear combination fit (top, in gray) and the components (below) of the linear fit, scaled to the proportions to which they contribute to the fit.

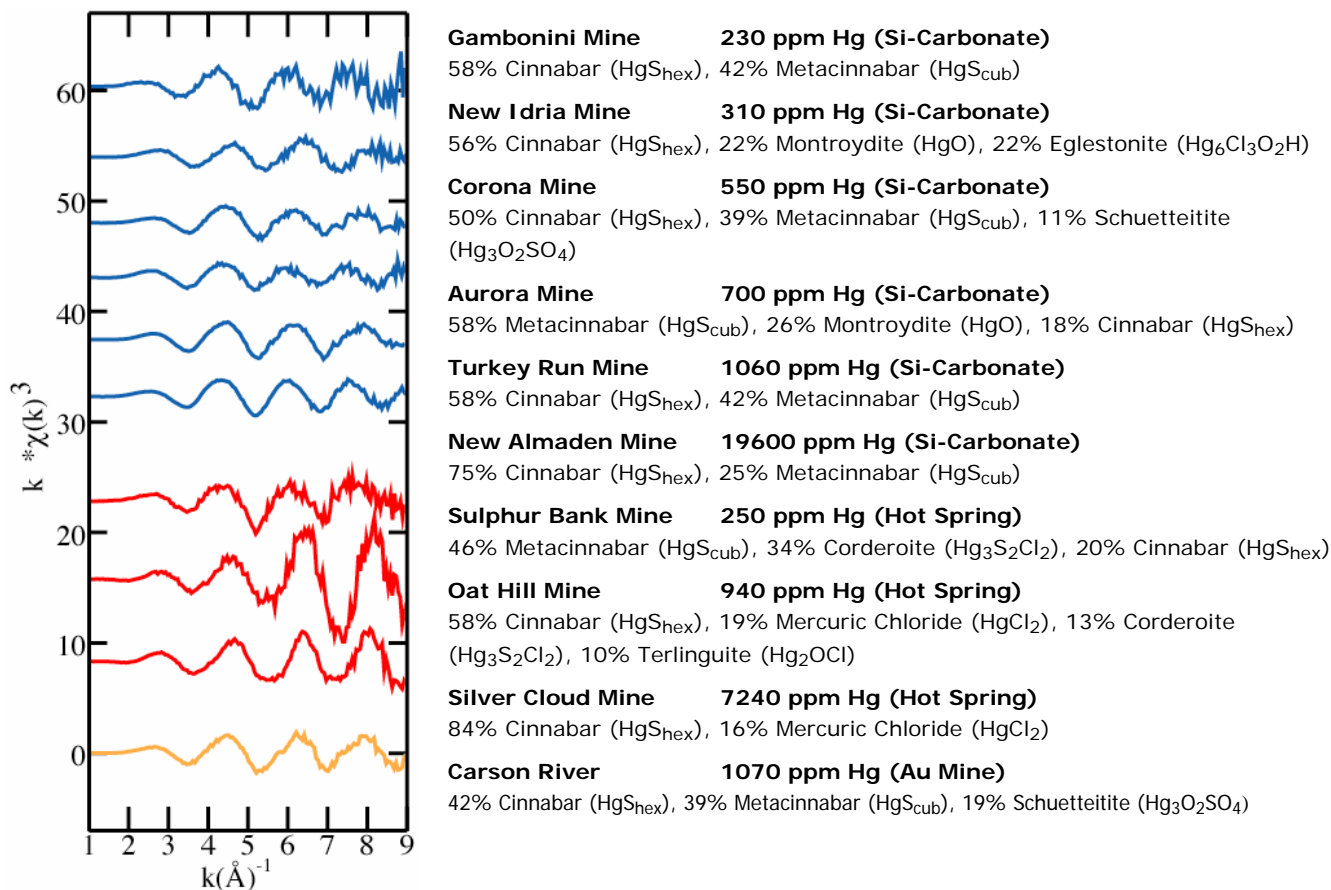


Figure 5. Summarized linear fitting results for a variety of Hg-bearing mine wastes, with original EXAFS spectra shown.

The majority of Hg in all samples was found by EXAFS analysis to be present as Hg-sulfides, either as cinnabar or metacinnabar; this finding is common to nearly all global Hg deposits. Corderoite ($\text{Hg}_3\text{S}_2\text{Cl}_2$), a Hg-sulfide-chloride, was also observed in two samples from hot-spring Hg deposits. In addition, minor proportions of non-Hg-sulfide species, including as mercuric chloride (HgCl_2), eglestonite ($\text{Hg}_6\text{Cl}_3\text{O}_2\text{H}$), montroydite (HgO), schuetteite ($\text{Hg}_3\text{O}_2\text{SO}_4$), and terlinguite (Hg_2OCl), were identified in several samples. The high solubility of many of these species compared to the extremely insoluble Hg-sulfides suggests that, although comprising a smaller percentage of the total Hg in the sample, these species may be disproportionately larger contributors of ionic Hg to the surrounding environment.

The influence of the Hg depositional environment on Hg speciation in mine wastes is demonstrated by the consistent presence of Hg-chloride species in samples collected at hot-spring Hg deposits, and their relative absence in samples collected at silica-carbonate Hg deposits. Some exceptions exist, such as the presence of eglestonite in the New Idria sample, although this could be due to overprinting of a silica-carbonate Hg deposit with later hot-spring hydrothermal systems. Nevertheless, based on the range of samples analyzed, a general distinction in Hg speciation can be observed, with the presence of Hg-chloride species as the primary difference between the two deposit types. This implicates hot-spring Hg deposits as sites of higher priority for remediation and introduces a new level of sophistication for such prioritization, as speciation can now be considered alongside total Hg concentration.

Effect of Ore Roasting on Hg Speciation

As seen, Hg-sulfides in the form of cinnabar and metacinnabar constitute the highest proportion of Hg-containing species in Hg mine wastes, consistent with the fact that cinnabar is the primary ore mineral in Hg deposits. However, the proportions of metacinnabar detected in several roasted samples (Figure 5), sometimes as high as 58%, are much greater than anticipated based on field studies of Hg ore deposits, which only rarely report minor amounts of metacinnabar. The transformation of cinnabar to metacinnabar during the roasting process is a likely explanation for the elevated metacinnabar levels detected in these calcines. Figure 6 shows Hg speciation results for Hg-bearing mine wastes from the Sulphur Bank and Ora Stimba mines in California. At both mines, a calcine pile and (unroasted) waste rock pile were sampled to assess potential effects of ore roasting on Hg speciation. The results show that cinnabar is the dominant Hg species in the unroasted waste rock samples (present in proportions from 81-100%), while metacinnabar is more prevalent in the calcines (46-81%). This suggests that ore roasting converts cinnabar to metacinnabar by heating it above the cinnabar-metacinnabar inversion temperature of 345°C ⁽¹⁷⁾. During the mining process, Hg ore was crushed and then roasted in excess of 600°C to release Hg as volatile elemental Hg⁰ gas⁽¹²⁾, thereby providing temperatures sufficient to cause the conversion of non-released cinnabar to metacinnabar. Such a process may also have introduced impurities such as Fe, Se, and Zn that impeded the conversion back to cinnabar upon cooling and are more common to the metacinnabar structure^(13,14). The higher solubility of metacinnabar compared with cinnabar indicates that calcines are of greater concern for cleanup than waste rock.

Effect of Particle Size on Hg Speciation

Particle size can exhibit a governing influence on factors such as the concentration, speciation, solubility, and mobility of heavy metals in contaminated wastes. The dependence of total Hg concentration and speciation on particle size in Hg mine wastes was explored by collecting samples from different Hg mines and separating them by dry sieving into a number of discrete size fractions. Hg speciation of selected size fractions was then determined using EXAFS spectroscopy⁽¹⁵⁾.

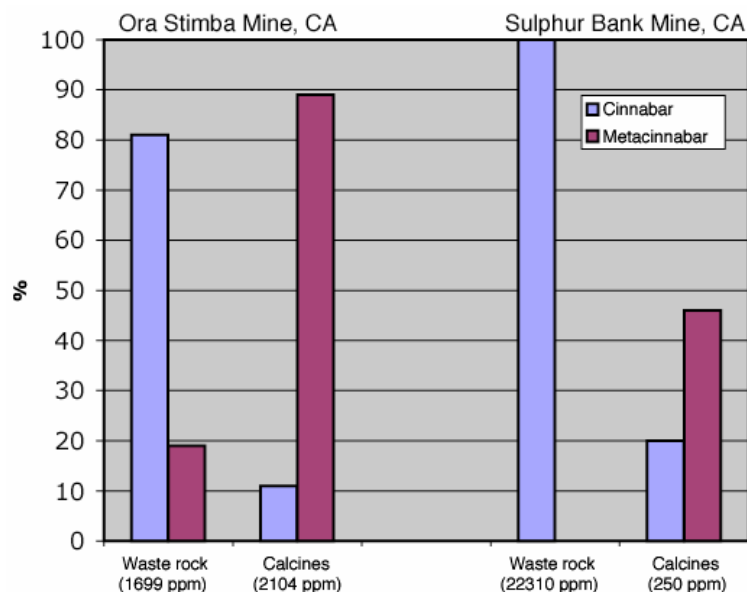


Figure 6. Hg speciation of calcine and waste rock samples from two separate mines, showing a distinct shift between the proportions of cinnabar (HgS, hex) and metacinnabar (HgS, cub) as a result of roasting.

Hg total concentration and selected speciation results of these size fractions are shown in Figure 7. As particle size decreases within each bulk sample the total Hg concentration increases (Figure 7a), in some cases by nearly an order of magnitude (*e.g.*, a calcine from the Sulphur Bank mine shows an increase in Hg concentration from 97 ppm in the 500-2000 μm size fraction to 810 ppm in the <45 μm size fraction). This trend agrees with other studies^(16,17) which showed elevated concentrations of Hg-sulfides in very fine sand and silt fractions among Hg-mine wastes in northern California and Alaska. In addition to total Hg concentration, EXAFS analysis reveals that the relative proportions of Hg-sulfides (cinnabar, metacinnabar, and corderoite) in the sieved fractions of calcines also increase with decreasing particle size (Figure 7b), although this trend is less pronounced than that of total Hg concentration, increasing between 8-18% among the samples studied.

These trends may be linked to the low solubility and hardness of cinnabar and metacinnabar. As Hg-sulfides feature K_{sp} values in the range of 10^{-36} ⁽¹⁸⁾ and hardness levels of 2.5-3⁽¹⁹⁾, physical weathering (*i.e.* abrasion, fracturing, and disaggregation) may exceed chemical weathering, (*i.e.* dissolution) under certain conditions; furthermore, Hg-sulfides should weather at more rapid rates than the quartz, silicates, and metal oxides that comprise the bulk of most sample matrices. Mechanical weathering therefore likely yields the observed enrichment in total Hg as particle size decreases. Additionally, with decreasing particle size the increased available surface area of soluble Hg minerals such as Hg-chlorides, oxides, and sulfates would facilitate the dissolution of these species, resulting in the greater proportions of relatively insoluble Hg-sulfides observed in the finest-grained fractions. A study of Hg speciation in stream sediments of the Almadén cinnabar mining region in Spain described a similar relationship between the proportion of Hg present as Hg-sulfides and total Hg concentration⁽²⁰⁾. The combined results of these studies indicate that these trends are common in cinnabar mine environments.

The interested reader is referred to a comprehensive review of Hg speciation in mining environments recently published by C. Kim⁽²⁷⁾ for more information and details about the EXAFS speciation technique.

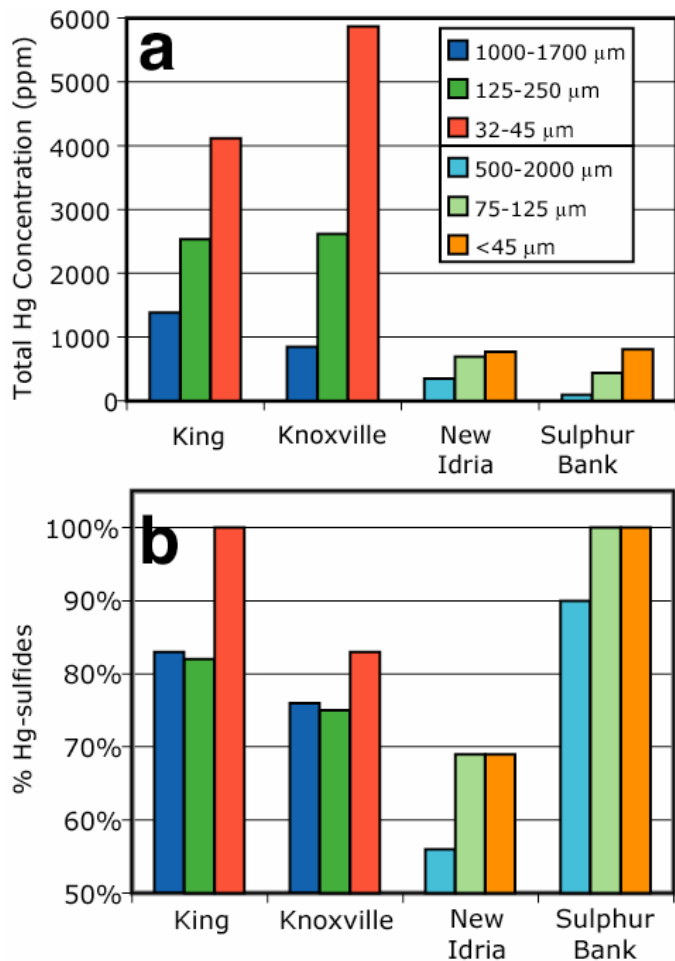


Figure 7. (a) Total Hg concentration of various sieved size fractions from different Hg mine calcines as determined by cold vapor atomic fluorescence spectroscopy (CVAFS). (b) Percent Hg-sulfides as determined by EXAFS spectroscopy of various sieved size fractions from different Hg mine calcines.

Primary Citation

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