Utility of EXAFS in characterization and speciation of mercury-bearing mine wastes

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Extensive mining of large mercury deposits located in the California Coast Range has resulted in mercury contamination of both the local environment and water supplies. The solubility, dispersal, and ultimate fate of mercury are all affected by its chemical speciation, which can be most readily determined in a direct fashion using EXAFS spectroscopy. EXAFS spectra of mine wastes collected from several mercury mines in the California Coast Range with mercury concentrations ranging from 230 to 1060 mg/kg (ppm) have been analyzed using a spectral database of mercury minerals and sorbed mercury complexes. While some calcines have been found to consist almost exclusively of mercuric sulfide, HgS, others contain additional, more soluble mercury phases, indicating a greater potential for the release of mercury into solution. This experimental approach can provide a quantitative measurement of the mercury compounds present and may serve as an indicator of the bioavailability and toxicity levels of mercury mine wastes.

Keywords: EXAFS; mercury; mine; sorption; speciation

1. Introduction

Natural mercury ore bodies are located throughout the California Coast Range, occurring either as near-surface hot-spring deposits or coincident with silica-carbonate alteration rock (Rytuba, 1996). Weathering of mine waste piles generated from past mining of the mercury ore in these areas has resulted in the release of mercury to surface water supplies and the surrounding environment. The geological variety of mercury mines in the California Coast Range implies the presence of a range of solid mercury phases in addition to cinnabar (HgS), the primary ore mineral. As different mercury compounds possess varying degrees of solubility, the speciation of mercury in mine wastes is a critical factor in determining the degree to which mercury can be leached from calcine piles and mobilized into aqueous systems. This has direct implications for the bioavailability of mercury to living organisms and thus its toxicity in the environment.

The objective of this study is to demonstrate the feasibility of extended X-ray absorption fine structure (EXAFS) spectroscopy in characterizing the speciation of mercury in piles of roasted ore, or calcines. Currently, no direct technique exists to determine the types and proportions of mercury phases in such samples. Other methods such as chemical extraction, which attempt to determine extractable fractions of a metal and then equate them to individual species, are often imprecise in their ability to isolate and extract one metal species at a time. Furthermore, such methods may alter the speciation of mercury from its natural state and thus misrepresent both the phases present and their relative concentrations in a mercury-

contaminated sample. In this study, heterogeneous natural samples were analyzed *in situ* and compared with a collection of crystalline mercury minerals and with one sample featuring mercury sorbed to goethite (α-FeOOH), a common mineral found in mine environments.

2. Materials/Methods

Samples were collected from calcine piles at several major mercury-producing mines in the California Coast Range, primarily in the Clear Lake district in Lake County, CA. Splits of the samples were sent to ChemEx Labs, an independent analytical chemistry laboratory, to ascertain total mercury concentrations; those yielding concentrations greater than 100 mg/kg (ppm) were sufficiently concentrated to produce distinct absorption edges and visible EXAFS. These samples were analyzed using EXAFS spectroscopy as dry powders in fluorescence mode with a 13-element, high-throughput Ge detector. All data were collected on beamlines 4-2 and 4-3 at the Stanford Synchrotron Radiation Laboratory (SSRL).

In order to generate a database of model compounds against which to compare the EXAFS spectra of the natural calcines, EXAFS spectra of several mercury minerals were also obtained. Model compounds were powdered and diluted with boron nitride; spectra were collected in transmission mode. The linear combination fitting program DATFIT, part of the data analysis package EXAFSPAK (George and Pickering, 1995), was utilized to fit the spectra of natural samples with the minerals in the model compound database within a k-range of 1-9 Å^{-1}.

To study mercury adsorption to mineral surfaces, laboratory experiments were conducted in which very high surface area
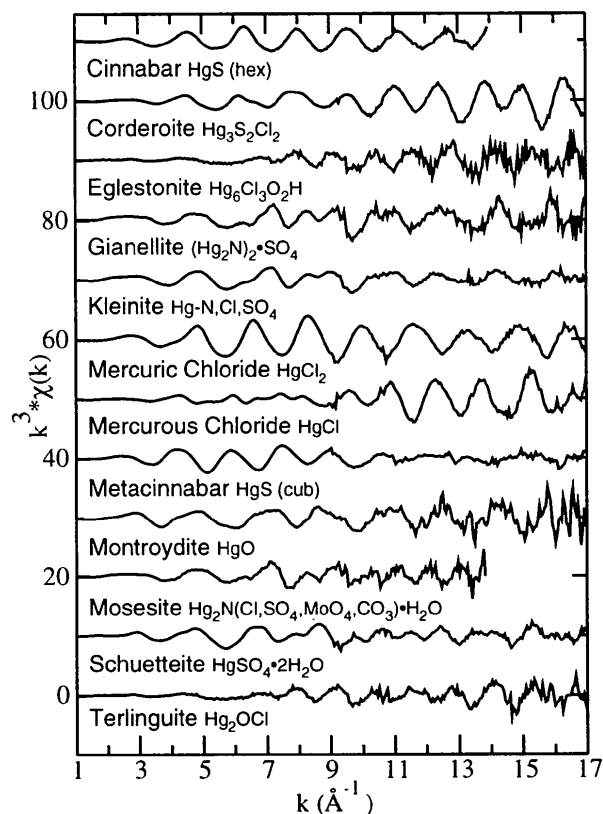
Figure 1
EXAFS spectra of mercury minerals in the model compound database used for linear combination fitting of the contaminated calcines.
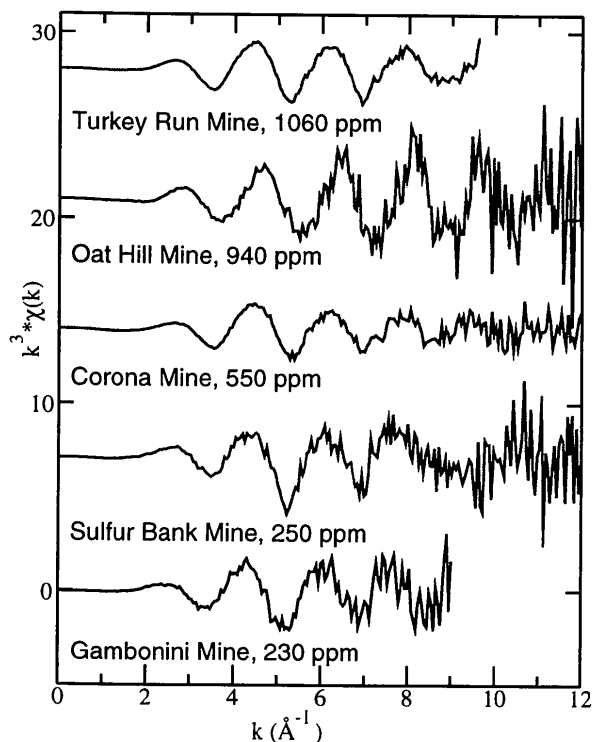
Figure 2

EXAFS spectra of natural mercury-bearing calcines from mercury mines in the California Coast Range.

($>90m^2/g$) samples of goethite synthesized according to Atkinson et al. (1968) were exposed to mercury in aqueous solution. Sorption samples were prepared by first suspending 0.5 g of the substrate in 40 mL of 0.1 M $NaNO_3$ with N_2 gas bubbling through the solution. 0.1 M HNO_3 was used to bring the pH level down to 4 to maximize sorption to goethite (Barrow and Cox, 1992) before adding aqueous mercury in the form of mercuric nitrate, $Hg(NO_3)_2$. Initial mercury concentrations of 10^{-3}, 5×10^{-3}, and 10^{-4} M were achieved with each suspension before the pH was brought back up to 6 using NaOH. Sorption was allowed to proceed for a minimum of 24 hours before the samples were centrifuged, blotted on filter paper to remove excess moisture, and subjected to EXAFS analysis as moist pastes. Spectra were collected in fluorescence mode using the Ge detector and analyzed with the curve-fitting program OPT within EXAFSPAK. Theoretical phase and amplitude functions for use in OPT were generated using the *ab' initio* single- and multiple-scattering code FEFF, version 7.00 (Rehr et al., 1991).

3. Results

L_{III}-edge EXAFS spectra of the mercury model compounds and natural calcines are shown in Figures 1 and 2, respectively. It is evident from the natural samples that the quality of the spectra tends to decrease as the total concentration of mercury in the samples decreases; thus the minimum required concentration is 100 ppm for EXAFS analysis. Linear fitting results of the calcine spectra to the model compound database are displayed in Figure 3, with the raw data and fits shown. The composition of each calcine sample has been scaled so that the sum of the mercury components equals 100%. Also included is the residual of each fit, which indicates the amount of the spectra unfitted by any model compounds. Often the residual is

affected by noisy data, which can be distinguished through a visual comparison of the data to the fit.

Figure 4 shows the fit to the EXAFS spectrum and the Fourier transform of the sorption sample with the highest initial concentration of mercury, which yielded the highest quality data. This spectrum is unique relative to the other mercury minerals in the model compound database, including the spectrum of aqueous $Hg(NO_3)_2$. The Fourier transform shows distinct evidence for two shells of neighboring atoms, which were fit using a mercury-oxygen pair and a mercury-iron pair, respectively. Attempts to fit the second shell feature with a mercury-mercury pair, which would be more indicative of mercury precipitation, resulted in a poorer fit to the data (not shown). The final fit results (Table 1) show oxygen atoms at distances of 2.02 and 2.94 Å and iron atoms at distances of 3.15 and 3.32 Å. This is permissive evidence for mercury sorption onto goethite as observed macroscopically by Barrow and Cox (1992). The sorption spectrum was included in the linear fitting procedures but was not found to make a significant contribution to the speciation of the calcine samples with respect to the mercury mineral phases.

4. Discussion and Conclusions

Although the mercury ore removed during the active period of mining in California predominantly consisted of cinnabar, speciation of the mercury remaining in calcine piles using EXAFS spectroscopy shows more variable compositions than previously recognized. The calcines are still composed primarily of mercuric sulfide in the form of cinnabar (HgS, hexagonal) and/or metacinnabar (HgS, cubic); of the two, metacinnabar comprises a substantial amount of the total mercury in several samples. This could be due to the calcining process itself, which would have roasted the ores above the cinnabar-metacinnabar inversion temperature of 345°C (Kullerud, 1965). Such a process may have introduced impurities, which
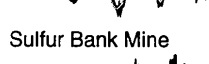
Sample Locale	Composition	Residual
Turkey Run Mine	58% Cinnabar 42% Metacinnabar	0.036
Oat Hill Mine	58% Cinnabar 19% Mercuric Chloride 13% Corderoite 10% Terlinguite	0.281
Corona Mine	50% Cinnabar 39% Metacinnabar 11% Schuetteite	0.052
Sulfur Bank Mine	43% Metacinnabar 30% Corderoite 20% Cinnabar 7% Mercurous Chloride	0.185
Gambonini Mine	84% Metacinnabar 16% Cinnabar	0.326

Figure 3

Visual linear combination fits of the contaminated calcines, compositional results, and residual values corresponding to the quality of the fit.
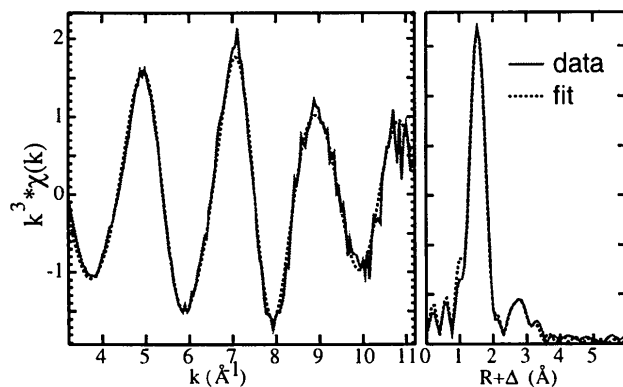
Figure 4

EXAFS spectrum and Fourier transform of mercury sorbed to goethite. The fit indicates that the second shell consists of iron atoms, consistent with mercury sorption.

Table 1

Fitting parameters of mercury sorbed to goethite based on FEFF 7.0 phase and amplitude functions.

Path	CN	R (Å)	σ^2 (Å^2)	E_0 (eV)
Hg-O	2.56	2.02	0.005	-11.09
Hg-O	1.20	2.94	0.01*	-11.09*
Hg-Fe	1.35	3.15	0.01*	-11.09*
Hg-Fe	1.12	3.32	0.01*	-11.09*

*Value fixed.

impede the conversion back to cinnabar and are more common in the metacinnabar structure (Dickson and Tunell, 1959). These results are notable considering the rare natural occurrence of metacinnabar.

According to the linear fit results, other mercury phases are present as well and are likely to be disproportionately larger contributors of mercury to the surrounding environment, as they are more soluble than the relatively insoluble mercuric sulfides in typical surface oxidizing conditions. Furthermore, speciation of calcines from the two mines located in hot-spring environments (the Oat Hill and Sulfur Bank mines) identified the presence of mercury as a chloride, consistent with elevated levels of chloride in the local hydrothermal systems (Rytuba, 1986).

Although the linear combination fits presented yield the lowest possible residual values, they should not necessarily be considered unique; noise in the data results in residuals large enough to introduce significant errors among individual components' contributions. A similar study which compared known mixtures of lead phases to DATFIT results indicated that contributions should be considered accurate to +/- 25% of their stated value, and that contributions <10% should be viewed with caution (Ostergren et al., 1998). Nevertheless, the total proportions of mercury chloride phases in the Oat Hill and Sulfur Bank samples, 42% and 37% respectively, are substantial enough to confirm that mercury is forming relatively soluble chloride species in the samples collected in hot-spring environments. Similarly, the high amounts of metacinnabar (up to 84% of total mercury) detected in some natural samples indicate that the phase is indeed present in proportions higher than previously reported, even when accounting for statistical uncertainties.

Mercury was found to sorb to goethite, producing unique EXAFS spectra which will be useful in detecting sorbed mercury in the natural environment. No sorbed complexes were identified in the natural samples using the linear fitting technique; therefore the mercury in mine calcines can be considered to be present primarily in the mineral phase, although small but significant amounts of sorbed mercury could be present in these samples but are currently not detectable. Sediments and precipitates located downstream from mine areas are more likely to feature mercury sorbed to mineral surfaces and may thus provide a real-life analog to the model sorption processes investigated in this study.

Despite the degree of error inherent in the linear fits, EXAFS spectroscopy appears to be sufficiently sensitive in distinguishing the presence and relative proportions of major mercury phases in mine waste samples. The variety of mercury phases identified in this study indicates that total mercury concentration should not be the sole consideration in assessing the contamination level of a particular site. Species characterization of mercury-bearing waste samples should provide additional information regarding the solubility and toxicity of the mercury; this information can then assist in the prioritization of contaminated sites which have been targeted for remediation.

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