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Characterization and speciation of mercury-bearing mine wastes using X-ray absorption spectroscopy

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Abstract

Mining of mercury deposits located in the California Coast Range has resulted in the release of mercury to the local environment and water supplies. The solubility, transport, and potential bioavailability of mercury are controlled by its chemical speciation, which can be directly determined for samples with total mercury concentrations greater than 100 mg kg^{-1} (ppm) using X-ray absorption spectroscopy (XAS). This technique has the additional benefits of being non-destructive to the sample, element-specific, relatively sensitive at low concentrations, and requiring minimal sample preparation. In this study, Hg L_{III}-edge extended X-ray absorption fine structure (EXAFS) spectra were collected for several mercury mine tailings (calcines) in the California Coast Range. Total mercury concentrations of samples analyzed ranged from 230 to 1060 ppm. Speciation data (mercury phases present and relative abundances) were obtained by comparing the spectra from heterogeneous, roasted (calcined) mine tailings samples with a spectral database of mercury minerals and sorbed mercury complexes. Speciation analyses were also conducted on known mixtures of pure mercury minerals in order to assess the quantitative accuracy of the technique. While some calcine samples were found to consist exclusively of mercuric sulfide, others contain additional, more soluble mercury phases, indicating a greater potential for the release of mercury into solution. Also, a correlation was observed between samples from hot-spring mercury deposits, in which chloride levels are elevated, and the presence of mercury-chloride species as detected by the speciation analysis. The speciation results demonstrate the ability of XAS to identify multiple mercury phases in a heterogeneous sample, with a quantitative accuracy of $\pm 25\%$ for the mercury-containing phases considered. Use of this technique, in conjunction with standard microanalytical techniques such as X-ray diffraction and electron probe microanalysis, is beneficial in the prioritization and remediation of mercury-contaminated mine sites. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Mercury; Mine; Calcine; Speciation; X-ray absorption spectroscopy; Extended X-ray absorption fine structure

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1. Introduction

Mercury deposits located throughout the California Coast Range are the source of the largest mercury mines in North America, some of which have actively mined mercury for over 100 years. Weathering of mine waste piles resulting from such long-term mining has resulted in the release of mercury to both surface water supplies and the surrounding environment (Wershaw, 1970). Because mercury deposition has taken place from 29 Ma to present (Rytuba, 1996) and within changing geological conditions and regions, a variety of mercury phases in addition to the main ore mineral, cinnabar, ($\text{HgS}_{\text{hexagonal}}$), is present in the ore bodies. Furthermore, the roasting process employed to extract mercury from the ores and subsequent weathering processes may have resulted in secondary mercury mineralization in the waste piles. Since different mercury phases have varying degrees of solubility, it is essential to determine the speciation of mercury in these materials in order to develop a better understanding of mercury release and transport from mine wastes. Mercury phase characterization is also critical for assessing the potential bioavailability of mercury and thus its potential impact on humans and other organisms.

The objective of this study is to demonstrate the use of X-ray absorption spectroscopy (XAS) to directly characterize the speciation of mercury in mine tailing (calcine) piles. Currently, there is no known technique available to determine directly the types and relative proportions of mercury phases in such samples. Other methods, such as sequential chemical extractions (Revis et al., 1989; Sakamoto et al., 1992) and thermal desorption (Azzaria and Aftabi, 1991; Biester and Scholz, 1997), have been used to indirectly determine the speciation of mercury by measuring extractable fractions of mercury and equating them to unique mercury species. However, these methods can be imprecise in their ability to isolate and extract individual mercury species. Also, these indirect techniques, particularly the sequential extraction procedures, may substantially alter the speciation of mercury from its initial state, thus misrepre-

senting the phases present and/or their relative concentrations in a sample (Barnett et al., 1995).

In this study, the speciation of mercury was characterized in heterogeneous mine tailings collected from several mines in the California Coast Range mercury mineral belt by comparison of the XAS spectra of the calcines with a spectral database of crystalline mercury minerals and sorption samples. To assess the accuracy of the technique, similar speciation analyses were applied to measured mixtures of mercury mineral standards. Speciation results of the calcines as characterized by XAS were compared with the standard microanalytical techniques of X-ray diffraction (XRD) and electron probe microanalysis (EPMA) to evaluate the inadequacy of the latter techniques in determining the mercury phases present in low-concentration mercury-bearing samples.

2. Background

2.1. Origin of mercury deposits in the California Coast Range

The mercury deposits of the California Coast Range mercury mineral belt are located primarily along the San Andreas fault (Fig. 1), a transform boundary which facilitated mercury ore formation in the region. The initial deposition of mercury resulted from the impingement of the Mendocino Triple Junction (MTJ) on Southern California at 29 Ma, converting the region south of the MTJ from a subduction to a transform zone (Atwater, 1970). This tectonic change resulted in a slab window environment, allowing hot asthenosphere to upwell into the area formerly occupied by the subducting slab and creating a thermal anomaly in the region (Dickinson and Snyder, 1979). As the MTJ migrated northward, the slab window also expanded northward. One effect of this migrating regional heat source was the alteration of serpentinite bodies, which had been previously emplaced along the fault zones, to silica-carbonate rock (Henderson, 1969). These brittle, fractured alteration zones served as favorable de-

positional environments for mercury. Extensive mercury deposits formed when hydrothermal fluids became trapped in anticlinal structures within the alteration zones, resulting in ‘silica-carbonate’ type mercury deposits such as those found in New Almaden, CA (Bailey and Everhart, 1964).

As the thermal flux diminished, low-temperature hot-spring systems developed in the near-surface environment. These geothermal systems represent a complex mixture of meteoric groundwater, connate fluids, and possibly magmatic waters (Henderson, 1969). The result is a continu-

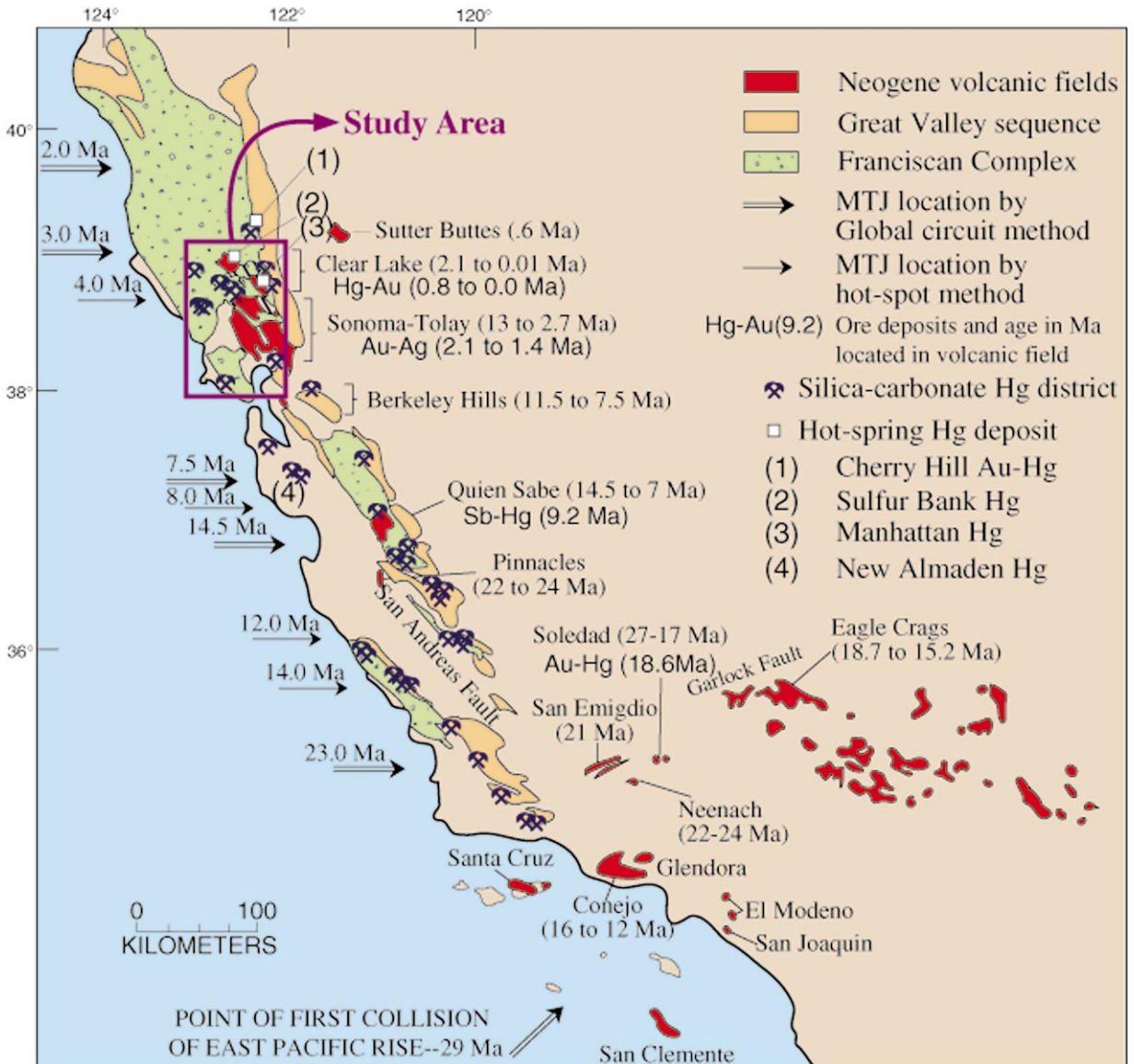


Fig. 1. Geologic map of volcanic centers and mercury deposits developed above the slab window as the Mendocino Triple Junction migrated northward along the California Coast Range. Silica-carbonate type mercury deposits formed during the early phase of the regional increase in heat flow above the slab window, while hot-spring type mercury deposits formed later as the thermal flux diminished (Rytuba, 1996). The study area from which all calcine samples were collected is indicated.

ous, active source of near-surface mercury deposition such as at the Sulfur Bank mine in Clear Lake, CA (White and Roberson, 1962). Advanced argillic alteration accompanied by elevated levels of aqueous chloride and sulfate are secondary features of these 'hot-spring' type mercury deposits (White and Roberson, 1962; Dickson and Tunell, 1968). Although cinnabar is the primary ore mineral in the mercury deposits of the California Coast Range, several minor and rare mercury oxide, oxychloride, and sulfate minerals as well as elemental mercury have been observed.

The varying geological conditions surrounding the formation of individual mercury deposits help determine the variety of mercury species present in a particular deposit, which in turn will determine the relative solubility, transport, and potential availability of mercury in the larger regional environment. These properties are further enhanced after mining and ore processing techniques have greatly increased the surface area of mercury-containing mine wastes, thus facilitating the interaction of mercury phases with surface and rain water. This study reports our findings on the speciation of mercury in mine wastes from both silica-carbonate and hot-spring type mercury deposits and discusses potential differences in speciation that might be expected on the basis of their different geologic origins.

2.2. Mining procedure / environmental hazards

The mining, roasting, and waste disposal processes at mercury mine sites have all contributed to local and regional mercury contamination, which continues to the present day despite the cessation of most mining by the mid-1900s. Mercury ores were mined by both underground and open pit methods, then crushed and roasted in retorts or large furnaces at temperatures approaching 600°C. This process volatilized most of the mercury into elemental form, which was subsequently passed through condenser columns and collected as liquid mercury in flasks. Waste gases, including SO₂ and residual gaseous Hg⁰, were vented through a stack and dispersed into the atmosphere. The roasted mine wastes, or calcines, were typically transported a short distance from

the furnace and dumped in loose, unconsolidated piles. Most calcine piles have been partially eroded due to their placement in or adjacent to stream channels.

Abandoned calcines remain one of the primary concerns for persistent mercury release into the aquatic ecosystem. As surface and/or rain water passes through the highly permeable piles, it can leach and mobilize mercury in both the dissolved and particulate phase. This process is particularly enhanced at mines where acid mine drainage increases the degree of leaching. Although sorption/precipitation reactions can be effective in removing mercury from the aquatic system and sequestering it in the sediments, a significant fraction of the mercury continues downstream or is remobilized from the sediment bedload by intermittent flooding events. This results in the introduction of mercury into larger bodies of water, exposing organisms to elevated levels of mercury. In these established ecosystems, mercury has the capacity to bioaccumulate in the food chain, posing potential health threats to organisms higher in the food web.

2.3. X-ray absorption spectroscopy

Synchrotron radiation-based XAS has been shown to provide direct, in situ information on heavy metal speciation, and has been used successfully for such elements as arsenic, lead, and zinc (Cotter-Howells et al., 1994; Manceau et al., 1996; Hesterberg et al., 1997; Foster et al., 1998; Morin et al., 1999; Ostergren et al., 1999). The technique possesses the additional benefits of being non-destructive, element-specific, relatively sensitive at low concentrations, and requiring minimal sample preparation, thus allowing the analysis of samples in conditions similar to those observed in their natural state. XAS involves bombarding a sample with high energy X-rays, generating photoelectrons from a specific element in the sample when the incident beam possesses sufficient energy to excite or eject core electrons from that element. The generation of photoelectrons induces specific electronic scattering interactions between the central absorbing atom and neighboring atoms (Brown and Parks, 1989). The

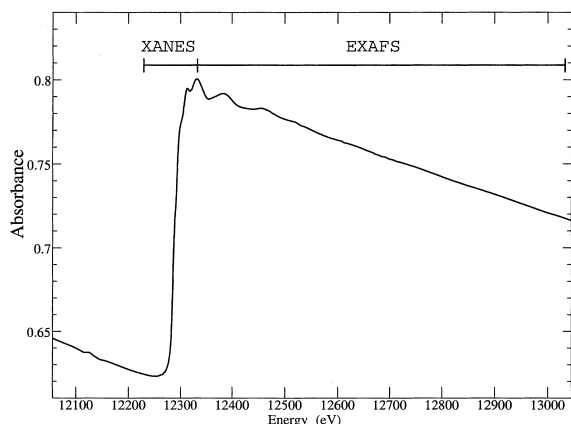


Fig. 2. X-ray absorption spectrum of cinnabar ($\text{HgS}_{\text{hexagonal}}$) indicating the X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) regions. The EXAFS spectrum is used in this study to determine mercury speciation.

incident X-ray energy at that point corresponds to the absorption edge of the element for a given electron shell (K, L_{III} , etc.), while the electron scattering interactions give rise to the X-ray absorption near-edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS) regions (Fig. 2).

The EXAFS and XANES regions can be analyzed to derive detailed molecular-scale information such as interatomic distances, oxidation states, coordination number, identity of nearest neighbors around a contaminant ion, and degree of structural disorder in the sample. These parameters define the chemical speciation of the element at the molecular level and can be used to distinguish one chemical species from another, assuming there are sufficient differences in the spectra. Since the EXAFS region contains information about the structure and bonding of mercury atoms with their first- and second-shell neighbors, the EXAFS spectrum of most homogeneous mercury phases should be distinct from those of other pure phases. This uniqueness of EXAFS spectra from one compound to the next permits them to be used as species ‘fingerprints’ for the identification of unknowns. In this study, the fingerprinting capability of EXAFS spectroscopy is employed by comparing heterogeneous

natural samples with a collection of different mercury-containing phases, including crystalline compounds and phases in which mercury(II) is sorbed to a mineral substrate.

3. Sample collection and analysis

Although mercury is broadly distributed throughout the mercury mine environment, sampling and speciation analysis were primarily confined to the calcine piles, where total mercury concentrations are typically elevated to several hundred mg kg^{-1} (ppm). Calcines were sampled from multiple piles at representative mercury mines (Turkey Run, Oat Hill, Sulfur Bank, and Gambonini) in the northern part of the California Coast Range mercury mineral belt (Fig. 1). One sample of fine-grained calcine residue was taken directly from within a Scott-type roasting furnace at the Corona mine. After removing the top several cm of a pile to avoid sampling outer surficial material, 2 kg of calcines were collected. Splits of each sample were sent to ChemEx Laboratories to determine total mercury concentration using aqua regia chemical extractions and cold vapor atomic fluorescence spectroscopy (CVAFS).

All samples were ground to a powder and inspected using XRD to identify the bulk mineralogy and primary matrix components of the calcines. An XRD-131 Rigaku Geigerflex diffractometer equipped with a Cu X-ray tube and graphite monochromator before the solid state detector was used; samples were scanned from 5 to $65^\circ 2\theta$ at angular increments of 0.05° . A JEOL Superprobe 733 electron microprobe was used on those samples with highest measured total mercury concentrations (Turkey Run, Oat Hill, Corona) to search for isolated areas of mercury concentration and determine the elemental composition of both those areas and other matrix phases.

Samples with > 100 ppm total mercury were found to be sufficiently concentrated for detailed speciation analysis using EXAFS spectroscopy. All data were collected on wiggler-magnet beamlines 4–2 and 4–3 at the Stanford Synchrotron Radiation Laboratory (SSRL) using Si(220) and

Si(111) monochromator crystals. Mercury L_{III} -edge EXAFS spectra were collected on calcine samples as dry powders at room temperature in the fluorescence-yield mode, a collection method more sensitive to dilute samples (Waychunas and Brown, 1994), with a 13-element, high-throughput germanium detector. Arsenic (3T) filters were used to attenuate elastic scattering at the mercury L_{III} edge (12284 eV), and aluminum filters were used to attenuate fluorescence from iron and other elements in the sample matrices. These steps helped to enhance the signal-to-noise ratio during data collection, allowing mercury EXAFS spectra to be obtained despite relatively low concentrations in dense natural matrices.

In order to generate a database of pure model compound spectra against which to compare the EXAFS spectra of the natural calcines, mercury L_{III} -edge EXAFS spectra of a number of mercury minerals were obtained using the same SSRL beamlines as indicated above. These model compounds were powdered and diluted with boron nitride, a compound transparent to the incident X-ray beam, before their EXAFS spectra were collected in transmission mode, a method more appropriate for concentrated samples. Model sorption samples in which aqueous mercury was sorbed to synthetic goethite (α -FeOOH) and γ -alumina (Al_2O_3) were also included in the model compound database; EXAFS spectra of the sorbed phases were collected in the same manner as those of the natural calcines.

The linear least-squares fitting program DATFIT, which is part of the data analysis package EXAFSPAK (George and Pickering, 1995), was utilized to fit the spectra from the natural samples with the spectra in the model compound database within a k -range of $1-9 \text{ \AA}^{-1}$. Single-component fits of the spectra from the calcines to each individual spectrum in the database were first attempted to identify significant contributors ($> 10\%$ of the overall spectrum) to the fit. Using the revised subset of model compounds, two-component fits were then attempted in a methodical manner. This iterative process was continued until no significant contributors remained.

To assess the accuracy of the EXAFS speciation analyses, several model compound mixtures

were created using known proportions of various minerals from the model compound database. These mixtures were prepared and examined in an identical fashion to the pure model compounds. Two- and three-component mixtures were prepared in order to simulate the compositions of natural multi-component calcines. The EXAFS spectra of these mixtures were fit using the linear least-squares fitting procedure described above.

4. Results

4.1. XRD / microprobe studies

The mineralogies of the identifiable crystalline components in the various calcines as determined by XRD analysis are summarized in Table 1. In all cases, quartz (SiO_2) is present, being an abundant mineral in mercury deposits. In addition, hematite (Fe_2O_3) was identified in the Corona Mine sample, likely formed from Fe-oxyhydroxides or by oxidation of Fe-sulfides. Various clay mineral weathering products were also detected. Notably, no mercury minerals were identified using XRD, presumably because they exist in proportions too small to be detected in the presence of dominant matrix minerals. Microprobe analysis was generally unable to locate mercury grains within the samples despite extensive searching, but it was successful in identifying one small grain of HgS within a weathered matrix of quartz, K-feldspar, and mica grains in the Oat Hill calcine sample (Fig. 3). EPMA cannot, however, distinguish between the polymorphs cinnabar

Table 1
Mineralogy of the identifiable crystalline components in the calcine samples as determined by X-ray diffraction^a

Location	Mineralogy
Turkey Run Mine	Quartz
Oat Hill Mine	Quartz, kaolinite, muscovite
Corona Mine	Quartz, hematite
Sulfur Bank Mine	Quartz
Gambonini	Quartz, montmorillonite

^aNo mercury minerals could be detected with this technique due to the dominance of other matrix minerals.

($\text{HgS}_{\text{hexagonal}}$) and metacinnabar ($\text{HgS}_{\text{cubic}}$). Thus both XRD and EPMA analysis were generally unable to characterize the mercury phases present and their relative abundances in the mercury-bearing calcine samples.

4.2. EXAFS studies — natural samples

The L_{III} -edge EXAFS spectra of the mercury model compounds comprising the current database are shown in Fig. 4. The EXAFS spectra of the calcine samples are shown in Fig. 5. Whereas the spectrum of a model compound represents specific pair correlations between the mercury atom and its neighboring atoms in a relatively homogeneous phase, the spectrum of a calcine sample represents a composite of EXAFS contributions from all individual mercury-containing phases, weighted according to the atom percent of mercury they contain and the degree of structural order in the local environment around mercury. As such, this composite spectrum can be deconvoluted, using a linear least-squares fitting

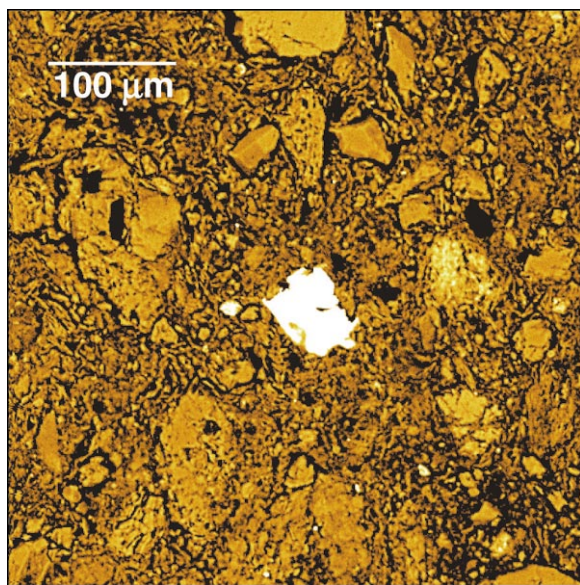


Fig. 3. Microprobe image of a mercury-rich grain (shown in white) located within a weathered matrix of quartz, K-feldspar, and mica grains in a calcine sample from the Oat Hill Mine. EPMA identified the grain as HgS but cannot distinguish between cinnabar ($\text{HgS}_{\text{hexagonal}}$) and metacinnabar ($\text{HgS}_{\text{cubic}}$).

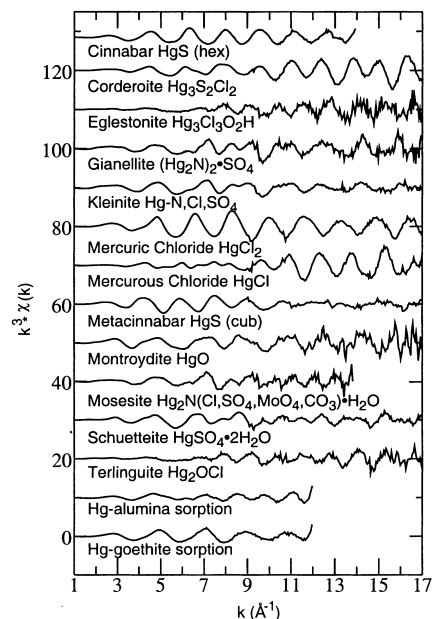


Fig. 4. EXAFS spectra of mercury minerals and mercury sorption complexes in the model compound database used for linear least-squares fitting of the heterogeneous mercury-bearing calcines. The horizontal axis represents the conversion of energy to momentum space following the normalization of the EXAFS data to a fixed point in energy space; the vertical axis is a k -cubed weighted expression of the EXAFS function, which is modeled as the sum of scattering contributions from each neighboring shell of atoms.

routine, into the sum of its separate components by comparison with the spectra in the model compound database. Determining the relative proportion of each model spectrum's contribution to the spectrum of a calcine sample allows quantification of the various phases present within the sample. An example of this deconvolution is shown in Fig. 6, where the Turkey Run calcine's mercury EXAFS spectrum is found to consist of two primary components, cinnabar and metacinnabar. These two components contribute to the overall fit in proportions of 58% and 42%, respectively, when scaled to a total of 100%.

Fitting results for all natural calcines are tabulated in Fig. 7, which shows the raw data and fits, quantitative compositions, and residual values. The residual can be interpreted as the amount of the spectrum that remains unfitted by the procedure described above. In some cases, a significant

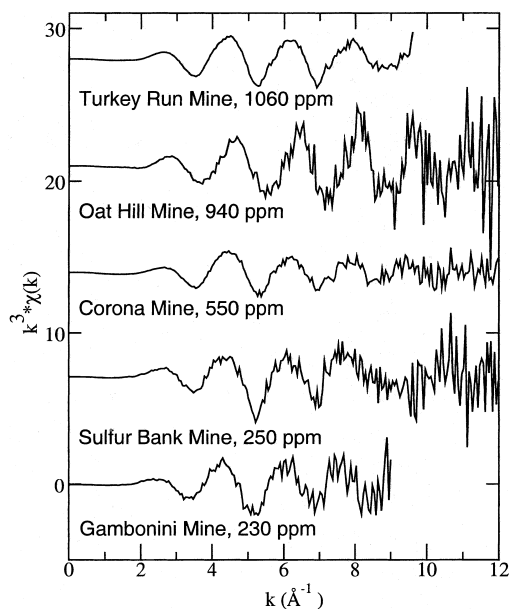


Fig. 5. EXAFS spectra of natural mercury-bearing calcines from mercury mines in the California Coast Range. Total mercury concentrations are indicated in mg kg^{-1} (ppm).

residual value may result from noisy data or other experimental error, low total mercury concentrations, or the presence of an additional unknown component that is not represented in the model compound database. To measure the degree of experimental noise within each spectrum, a sec-

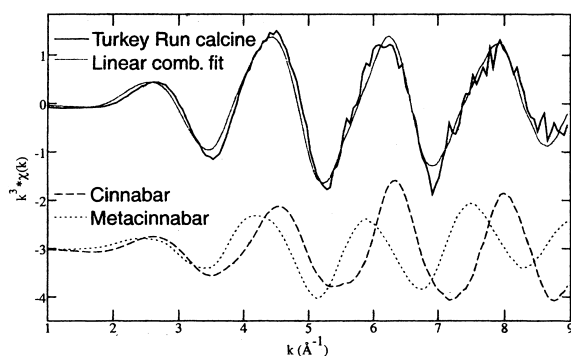


Fig. 6. Linear fitting results for the Turkey Run calcine, showing the natural EXAFS spectrum (black line), the linear combination fit (gray line), and the components which contribute to the linear fit (dashed lines). In this case, the calcine is found to consist of cinnabar and metacinnabar in proportions of 58% and 42%, respectively, when scaled to a total of 100%.

ond residual was generated by fitting smoothed data to the raw data. This value represents the residual inherent in experimental EXAFS data using the aforementioned data collection procedure and helps explain the apparently large residuals resulting from certain fits. Because of considerable noise in many of the calcine spectra, model compound spectra that contributed less than 10% of an overall fit were ignored.

4.3. EXAFS studies — mixed models

Linear least-squares fitting results of the calculated model mixtures are summarized in Table 2, with the initial measured proportions, proportions determined by linear fitting, deviations, and residuals shown. In all cases, the fitting technique correctly identified the contributing phases in the mixtures, even when present in proportions as low as 10% of the total mercury in the sample (Table 2G). The quantitative accuracy of the fitting technique varied among the mixtures, with the deviations between the measured proportions and the fitting-derived proportions averaging 7.9% among all model mixtures studied. For two-component mixtures, deviations averaged 5.6%, while three-component mixtures were less accurate, with deviations averaging 10.5%; in one case, the calculated proportion underestimated the actual proportion by 23.6% (Table 2F). The low residual values in these fits can be attributed to high total concentrations of mercury in the model mixtures, resulting in less noisy data.

5. Discussion and conclusions

XRD and microprobe methods are useful in identifying the dominant phases present in a mercury-bearing sample. This information helps constrain the mineralogical and geochemical environment in which the mercury species formed. However, for identifying and characterizing mercury phases at levels on the order of 100–1000 ppm total mercury, neither technique is sufficient. XRD analysis was able to identify only the primary crystalline phases in the sample, while microprobe analysis required extensive searching of

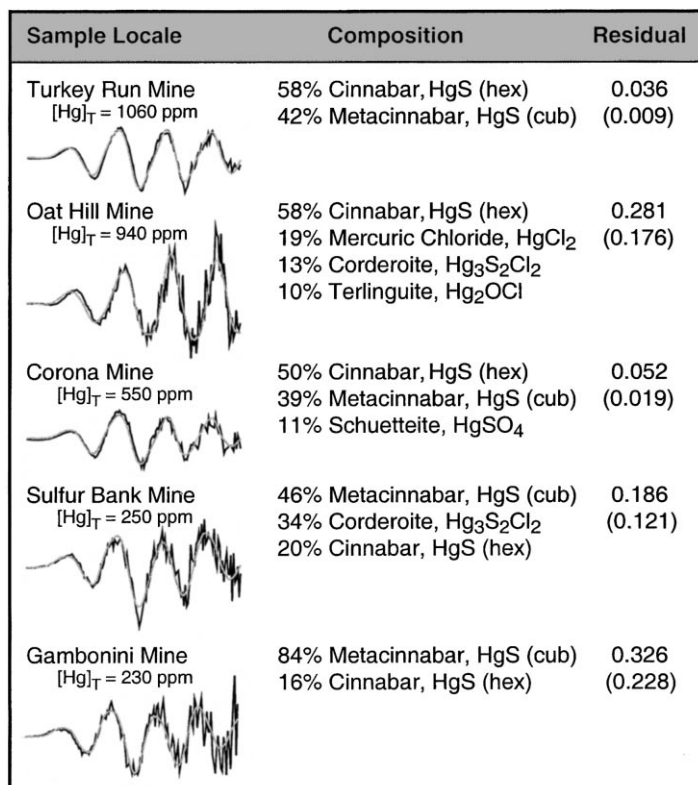


Fig. 7. Linear fits of the calcines (black line = raw data, gray line = fit), quantitative compositional results, and residual values corresponding to the quality of the fit. The value in parentheses represents the residual generated by fitting smoothed data to the raw data and indicates the degree of experimental noise inherent in data collection.

a sample and then could only analyze individual spots at a time, creating problems of both efficiency and sample representation.

EXAFS spectroscopy, by comparison, can focus exclusively on phases that contain mercury and thereby determine its speciation in a direct and non-invasive manner. The success of this method in this context requires sufficient mercury in the sample to generate an EXAFS spectrum that can be analyzed. It also requires that the EXAFS spectra of the various species present can be distinguished from one another using the model compound database. From the EXAFS results, it is apparent that mercuric sulfide is the dominant mercury phase present in the calcines, consistent with the fact that cinnabar is the primary ore mineral in mercury deposits. However, the high proportions of metacinnabar in many samples

were not expected; metacinnabar has been reported in some mercury ores, but usually in minor amounts. It is possible that the high levels of metacinnabar are due to the roasting process, where the ore was heated at temperatures in excess of the cinnabar-metacinnabar inversion temperature of 345°C (Kullerud, 1965). Such a process may also have introduced impurities that impede the conversion back to cinnabar and are more common in the metacinnabar structure (Dickson and Tunell, 1959).

In addition to high proportions of mercuric sulfide, several of the samples contained minor proportions of HgSO₄ or Hg-Cl species according to linear fitting analysis. Although comprising a smaller percentage of the total mercury in a sample, these species are likely to be disproportionately larger contributors of mercury to the sur-

Table 2

Linear fitting results of two- and three-component measured model mixtures. The measured proportions, proportions determined by linear fitting, deviations, and residual values are displayed^a

	Cinnabar	Metacinnabar	Mercuric chloride	Corderoite	Schuetteite	Residual
<i>Two-component mixtures</i>						
A						
Measured %	50.00	50.00				
Linear fit %	46.92	53.08				0.004
Total % change	-3.08	3.08				
B						
Measured %	24.50	75.50				
Linear fit %	25.28	74.72				0.007
Total % change	0.78	-0.78				
C						
Measured %	50.00		50.00			
Linear fit %	43.95		56.05			0.010
Total % change	-6.05		6.05			
D						
Measured %	72.30		27.70			
Linear fit %	65.66		34.34			0.005
Total % change	-6.64		6.64			
E						
Measured %	69.80			30.20		
Linear fit %	58.27			41.73		0.012
Total % change	-11.53			11.53		
<i>Three-component mixtures</i>						
F						
Measured %	50.00	25.00		25.00		
Linear fit %	26.44	26.33		47.22		0.040
Total % change	-23.56	1.33		22.22		
G						
Measured %	49.70	40.40			9.90	
Linear fit %	39.33	42.48			18.19	0.003
Total % change	-10.37	2.08			8.29	
H						
Measured %	55.00		27.00		18.00	
Linear fit %	59.96		14.15		25.89	0.006
Total % change	4.96		-12.85		7.89	

^aDeviations for two- and three-component mixtures averaged 5.6% and 10.4%, respectively.

rounding environment because they are more soluble than the mercuric sulfides under typical surface oxidizing conditions. In fact, the amounts of the minor phases determined in this study likely under-represent the initial amounts present, as weathering may already have removed a certain soluble fraction of mercury from the calcines. Furthermore, Hg-Cl species were identified only in calcines located at hot-spring mercury

deposits (i.e. the Oat Hill and Sulfur Bank mines), consistent with elevated levels of chloride in the local hydrothermal systems (Dickson and Tunell, 1968). The other samples were collected from silica-carbonate mercury deposits, where mercury is primarily or exclusively present as mercuric sulfide as verified by linear fitting of the EXAFS spectra of these samples. These results show both a dependence of mercury speciation on the geo-

logical origin of the initial mercury ore and the sensitivity of the EXAFS technique in distinguishing between samples from the different ore types.

Although the speciation results discussed above represent the best possible linear fits obtained using the database of available mercury model compounds, they should not necessarily be considered unique, since experimental noise in the data often yields substantial residual values which in turn may introduce significant errors in the estimated amounts of different mercury-bearing phases. Ostergren et al. (1999) determined from fitting the EXAFS spectra of mixtures of lead-containing phases that fit components should be considered accurate to $\pm 25\%$ of their stated value, and that fit components comprising less than 10% of a fit should be viewed with caution. This is consistent with the mixed model results presented here for Hg-containing phases and should apply similarly to the calcine speciation analyses. It is anticipated that with the development of improved detectors and beamlines with higher X-ray fluxes, it will be possible to characterize mercury speciation with greater quantitative accuracy and at lower total mercury concentrations. In addition, EXAFS spectromicroscopy using high brightness beamlines at third generation synchrotron sources will allow EXAFS spectra to be collected from individual grains in complex matrices that are 1–5 μm in diameter, offering the possibility of mapping mercury speciation at this spatial resolution.

The variety of mercury phases identified in the calcines indicates that total mercury concentration should not be the sole consideration in assessing the level of mercury contamination at a particular mine site. The relative proportions of soluble mercury phases present must also be known in order to better determine the potential mobility of mercury from the piles into the environment. A more detailed characterization of mercury speciation in mine wastes using XAS, coupled with standard microanalytical techniques and other speciation techniques currently in use, will provide useful information on the relative solubility, transport, and reactivity of mercury in natural, heterogeneous mercury-bearing samples. This information can be used to help prioritize

the thousands of mercury-contaminated sites in the California Coast Range and to identify those in most immediate need of remediation.

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References

- Atwater T. Implications of plate tectonics for the Cenozoic tectonic evolution of western North America. *Geol Soc Am Bull* 1970;81:3513–3536.
- Azzaria LM, Aftabi A. Stepwise thermal-analysis technique for estimating mercury phases in soils and sediments. *Water Air Soil Pollut* 1991;56:203–217.
- Bailey EH, Everhart DL. Geology and quicksilver deposits of the New Almaden District, Santa Clara County, California. USGS Professional Paper 360. US Dept. of the Interior, 1964:209.
- Barnett MO, Harris LA, Turner RR, Henson TJ, Melton RE, Stevenson RJ. Characterization of mercury species in contaminated floodplain soils. *Water Air Soil Pollut* 1995;80: 1105–1108.
- Biester H, Scholz C. Determination of mercury binding forms in contaminated soils: mercury pyrolysis versus sequential extractions. *Environ Sci Technol* 1997;31(1):233–239.
- Brown Jr GE, Parks GA. Synchrotron-based X-ray absorption studies of cation environments in earth materials. *Rev Geophys* 1989;27(4):519–533.
- Cotter-Howells JD, Champness PE, Charnock JM, Patrick RAD. Identification of pyromorphite in mine-waste contaminated soils by ATEM and EXAFS. *Eur J Soil Sci* 1994;45(4):393–402.
- Dickinson WR, Snyder WS. Geometry of subducted slabs related to the San Andreas transform. *J Geol* 1979;87: 609–627.

- Dickson FW, Tunell G. The stability relations of cinnabar and metacinnabar. *Am Mineralogist* 1959;44(5/6):471–487.
- Dickson FW, Tunell G. Mercury and antimony deposits associated with active hot springs in the western United States. In: Ridge JD, editor. *Ore deposits of the United States, 1933–1967, 2*. New York: The American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc, 1968: 1673–1701.
- Foster AL, Brown Jr GE, Tingle T, Parks GA. Quantitative arsenic speciation in mine tailings using X-ray absorption spectroscopy. *Am Mineralogist* 1998;83(5/6):553–568.
- George GN, Pickering IJ. EXAFSPAK, a suite of computer programs for the analysis of X-ray absorption spectra. Stanford, CA: Stanford Synchrotron Radiation Laboratory, 1995:63 pp.
- Henderson FB. Hydrothermal alteration and ore deposition in serpentinite-type mercury deposits. *Econ Geol* 1969;64(5): 489–499.
- Hesterberg D, Savers DE, Zhou W, Plummer GM, Robarg WP. X-ray absorption spectroscopy of lead and zinc speciation in a contaminated groundwater aquifer. *Environ Sci Technol* 1997;31:2840–2846.
- Kullerud G. The mercury-sulfur system. *Carnegie Institution Yearbook* 1965;64:194–195.
- Manceau A, Boisset MC, Sarret G et al. Direct determination of lead speciation in contaminated soils by EXAFS spectroscopy. *Environ Sci Technol* 1996;30(5):1540–1552.
- Morin G, Ostergren JD, Juillot F, Ildefonse P, Calas G, Brown Jr GE. XAFS determination of the chemical form of lead in smelter-contaminated soils and mine tailings: importance of adsorption processes. *Am Mineralogist* 1999; 84:420–434.
- Ostergren JD, Brown Jr GE, Parks GA, Tingle TN. Quantitative speciation of lead in selected mine tailings from Leadville, CO. *Environ Sci Technol* 1999;33(10):1627–1636.
- Revis NW, Osborne TR, Holdsworth G, Hadden C. Distribution of mercury species in soil from a mercury-contaminated site. *Water Air Soil Pollut* 1989;45:105–113.
- Rytuba JJ. Cenozoic metallogeny of California. *Geology and Ore Deposits of the American Cordillera Symposium Proceedings*, Reno, NV, 1996:803–822.
- Sakamoto HT, Tomiyasu T, Yonehara N. Differential determination of organic mercury, mercury(II) oxide and mercury(II) sulfide in sediments by cold vapor atomic adsorption spectrometry. *Anal Sci* 1992;8:35–39.
- Waychunas GA, Brown Jr GE. Fluorescence yield XANES and EXAFS experiments: application to highly dilute and surface samples. *Adv X-ray Anal* 1994;37:607–617.
- Wershaw RL. Sources and behavior of mercury in surface waters, USGS Professional Paper 713, 1970:29–34.
- White DE, Roberson CE. Sulphur Bank, California: a major hot-spring quicksilver deposit. In: Engel AEJ, James HL, Leonard BF, editors. *Petrologic studies: a volume in honor of A.F. Buddington*. The Geological Society of America, 1962:397–428.