

Mercury speciation of mine waste and contaminated road material and soils in McDermitt, Nevada

An X-ray absorption spectroscopic analysis

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Mercury speciation by extended X-ray absorption fine structure spectroscopy

Soil samples were dry sieved to below 64 μm , compacted into 4 by 14 mm well in aluminum alloy sample holders, and covered with Kapton tape. A sample holder was placed in a $-20\text{ }^{\circ}\text{C}$ freezer for at least 1 h, transferred to an $-80\text{ }^{\circ}\text{C}$ freezer, and stored for at least another hour. This procedure aimed to gradually cool any liquid elemental mercury [$\text{Hg}(0)_l$] below its freezing point to form crystalline $\alpha\text{-Hg}(0)$. At this point, the sample was cooled in two additional stages prior to extended X-ray absorption fine structure (EXAFS) spectroscopic analysis. After removing the sample from the $-80\text{ }^{\circ}\text{C}$ freezer, it was submerged in liquid nitrogen (77 Kelvin) and then transferred into a helium-flushed cryostat cooled with liquid helium (approximately 7 Kelvin). The samples were suspended in gaseous helium during EXAFS measurements.

Hg L_{III} -edge EXAFS was measured at approximately 7 Kelvin on end-station 11-2 at the Stanford Synchrotron Radiation Lightsource (SSRL). The energy of the incoming X-ray beam was controlled using a monochromator consisting of a pair of Si(220) ϕ 90° crystals and a 1 mm vertical opening inside the experimental hutch. One of the crystals was rotated slightly to avoid contamination of the incoming beam by harmonics; that is, the beam was detuned by 30%. The beam line monochromator was calibrated by determining the energy of the first inflection point of the absorption edge of HgCl_2 and assigning that monochromator position to 12,284 eV. Monochromator calibration was periodically checked by measuring the absorption edge of HgCl_2 and checking the energy of the same inflection, which was found to be stable during the remainder of the run.

X-ray fluorescence yield data were collected using a solid-state germanium detector. At the time of analysis, the detector had 17 functioning channels, allowing averaging of 17 simultaneously acquired spectra to improve signal to noise. For one scan, the incoming X-ray energy was scanned from 12,055 to 12,725 electron volts (eV). At each energy step, fluorescence was counted for 1 to 35 s, with counting time scaled as a function of energy to maintain a similar signal-to-noise throughout the scan. Eight to 12 consecutive scans were averaged to further improve signal to noise.

To provide reference spectra for speciation analysis, cinnabar ($\alpha\text{-HgS}$), metacinnabar ($\beta\text{-HgS}$), mercuric oxide (HgO) and frozen (see above) $\text{Hg}(0)$ were also analyzed.

To obtain EXAFS spectra from the raw data, the averaged X-ray absorption data were processed using the software package Athena, which runs IFEFFIT algorithms [1]. These measures included pre- and post-edge subtractions were performed in addition to cubic spline background removal [2].

Quantitative mercury speciation in the soils was determined by least-squares linear combination fitting of the soils EXAFS spectra with EXAFS spectra of the homogeneous Hg-bearing reference materials (Fig. 1). In the fitting procedure, the

component fractions were constrained to range from 0 to 1 and the sum of the components was unconstrained. All possible combinations of the four available reference materials measured under helium cryostat conditions were fit to the mine waste and soil spectra. The optimal fit was chosen on the basis of the reduced-chi-square parameter [3]:

$$\chi_v^2 = \frac{1}{N - P} \sum_{i=1}^N (\hat{\chi}_i - \chi_i)^2$$

where $\hat{\chi}$ is the measured EXAFS signal, χ is the fitted value, N is the number of data points, and P is the number of fitted components. χ_v^2 is useful for deciding which among alternate fits is statistically the best, but because the standard deviation associated with the uncertainty in the EXAFS signal is poorly defined, χ_v^2 is a poor description of how good an *individual* fit is. In the present case, if adding an additional component improved the χ_v^2 of the fit by 10% or more, the proposed fit was considered better.

Results and discussion

EXAFS spectra are commonly plotted using photoelectron momentum k as the x -axis; it is equivalent to energy and has units of inverse angstroms, or \AA^{-1} . A threshold absorption energy (E_0) of 12,284 eV was used to convert all spectra from energy to momentum space. In doing so, the energy 12,284 eV is equivalent to $k = 0 \text{ \AA}^{-1}$ for all reference, mine waste, and soil spectra during linear combination fits. Having calibrated the monochromator and verified its stability (see above), the positions of all spectra are therefore referenced to a common point where $k = 0$.

The results of the linear combination fits of EXAFS are shown in Table 1 and Fig. 2 (appended). In all cases, cinnabar dominated the mercury speciation of the samples (30 to 50%), followed by metacinnabar (10 to 40%). Playground Lot 1-13 contained appreciable HgO (10%). EXAFS fits also suggest that North Road material and Lots 1-10 and 1-13 soils may contain liquid elemental mercury [Hg(0)]. In previous studies, fitted fractions below about 10% would be considered dubious. However, the mercury EXAFS collected at 7 Kelvin have much more spectroscopic information than EXAFS collected at room temperature. This additional spectroscopic information is revealed because noise from thermal atomic vibrations is dramatically reduced at temperatures approaching absolute zero. Although no systematic study has been performed, the linear combination fitting of EXAFS collected with a helium cryostat is likely more accurate than fitting spectra collected at room temperature. In conclusion, the presence of Hg(0) should be considered provisional and may be worth verifying through independent analysis.

It is clear from Table 1 that species other than cinnabar, metacinnabar, HgO, and Hg(0) are present in the waste and soil materials. The sums of the fitted components are all less than 1, and the residuals of the fits have discernible

structure in the region of the spectrum of $k = 2$ to 8 \AA^{-1} . A likely candidate for a missing species is the mineral corderoite ($\text{Hg}_3\text{S}_2\text{Cl}_2$), which is known to occur in the McDermitt mining district.

Table 1. Fractions of mercury species fitted to the EXAFS spectra of McDermitt mine waste and contaminated materials. The numbers in parentheses represent the standard deviations in the last digit arising from the fit uncertainties alone. Numbers shown in grey indicate fractions statistically indistinguishable from zero.

Sample	Cinnabar	Metacinnabar	HgO ^a	Hg(0) ^b	<i>R</i> factor ^c
CorMine04	0.34(3)	0.38(2)	0.01(4)	0.01(2)	0.28
North Road	0.51(3)	0.12(2)	0.01(4)	0.03(2)	0.28
South Road	0.38(5)	0.25(4)	0.04(7)	0.01(3)	0.59
Lot 1-10	0.55	0.18	0	0.02	0.41
Lot 1-13	0.36(3)	0.27(3)	0.10(4)	0.04(2)	0.38

(a) also known as the mineral Montroydite

(b) Frozen elemental mercury

(c) Goodness of fit parameter: $\sum(\hat{\chi} - \chi)^2 / \sum \hat{\chi}^2$, where $\hat{\chi}$ is the measured EXAFS signal and χ is the fitted value.

The ‘fingerprinting,’ or linear combination fitting, of EXAFS spectra to identify (and quantify) different metal species in a complex sample has been applied to a variety of materials contaminated with mercury and other metals (see bibliography and works cited therein). The robustness of this approach derives from the physical nature of the measurements. EXAFS is a manifestation of the physical interaction between X-rays of known wavelength and the electrons of the atoms that make up a material. It explicitly reflects the (mole-weighted average) number of atoms surrounding mercury and how far away these neighboring atoms are. If these characteristics differ among species, they can be identified in a complex mixture [2, 4].

EXAFS has its limitations. Where there is no repeatable molecular structure (within roughly 6 \AA), there can be no EXAFS signal. Thus, while EXAFS is useful for identifying and characterizing structured materials, including minerals like cinnabar [2, 4] and nanocrystalline mercuric sulfide [5], it may be unable to detect small fractions of disordered materials, such as sorption complexes. This is especially true where such species coexist with more structured materials [4, 6]. Mercury EXAFS fingerprinting is well suited for mine waste and mine waste-contaminated soils and is complimentary to other speciation techniques capable of quantifying much lower concentrations of the more soluble forms of mercury.

References

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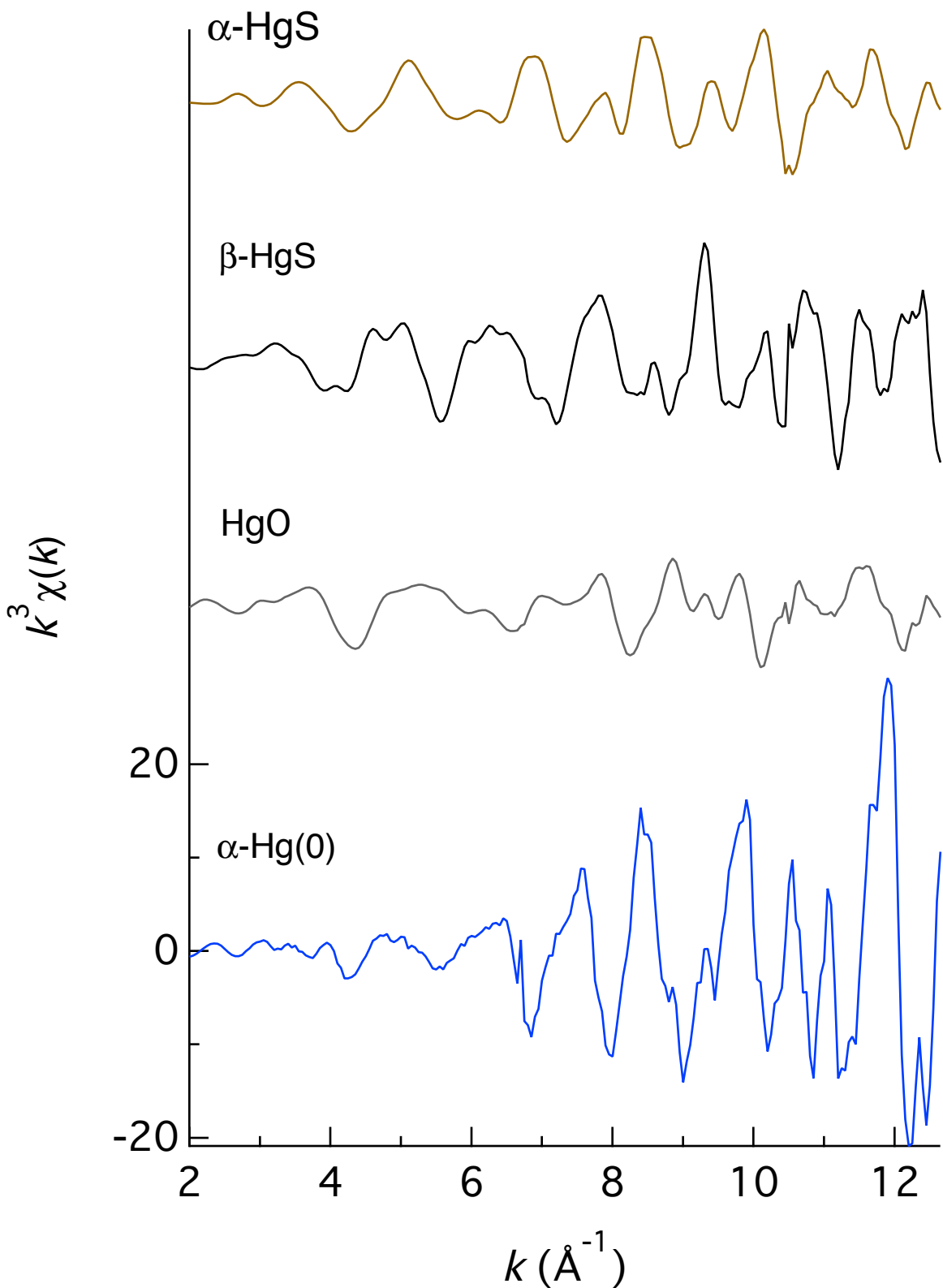


Figure 1. Mercury EXAFS ($\chi(k)$, where k is the photoelectron momentum) of homogeneous mercury-bearing materials used as reference spectra for linear combination fits of the McDermitt materials. The spectra were measured at approximately 7 Kelvin.

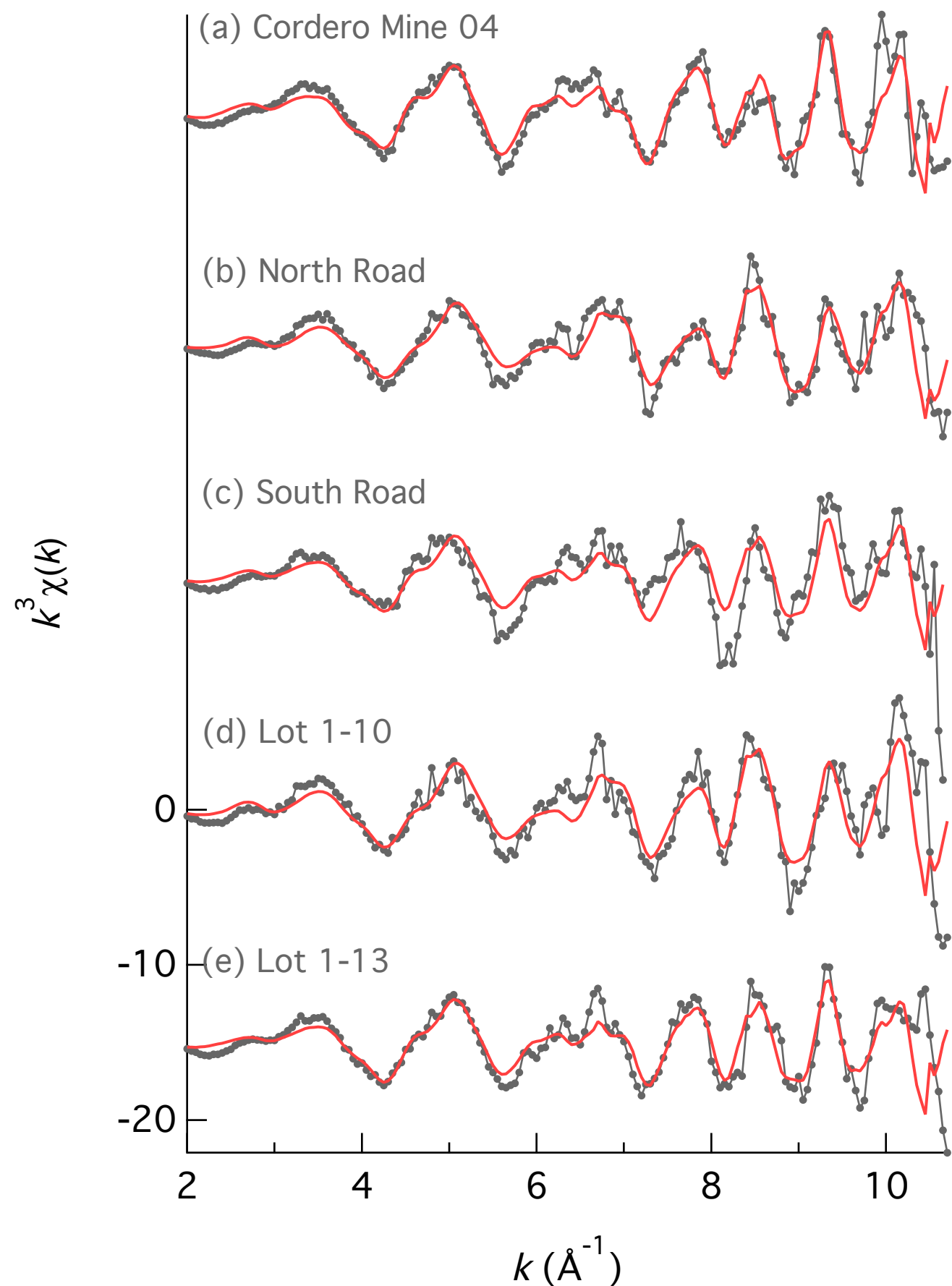


Figure 2. Mercury EXAFS ($\chi(k)$, where k is the photoelectron momentum) of the McDermitt mine waste and nearby contaminated materials. The dots are the measured data and the red lines are linear combination fits using the reference spectra shown in Fig. 1. The spectra were measured at approximately 7 Kelvin.