

Comparison of Synchrotron X-ray Fluorescence Mapping and Micro-XANES to Bulk X-ray Absorption Spectra in Metal-contaminated Sediments

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Introduction

Synchrotron x-ray absorption spectroscopy (XAS) is one of the few techniques that can supply molecular-scale information for a variety of elements at concentrations relevant to natural systems in nonvacuum conditions. Bulk XAS analysis supplies the dominant chemical bonding mode(s) for a specific element. In complex materials such as natural soils and sediments, however, the dominant mode may not necessarily be the most reactive, because changes in speciation at surfaces may result in changes in reactivity. Our previous work at Alameda Naval Air Station (NAS) in California focused on *in situ* metal chemistry in surface and deep sediments and the impact of metal mobility by sediment oxidation. Estuary sediments at the Alameda NAS have elevated metal concentrations that increase with increasing depth. The metal concentrations in these sediments are as follows: Cd (10-350 ppm), Cr (200-1000 ppm), Cu (100-230 ppm), Pb (200-1200 ppm) and Zn (250-600 ppm). We have extensively characterized these sediments by using bulk XAS and other nonsynchrotron supporting methods [1].

In this experiment, we collected fluorescence element maps by using a synchrotron x-ray microprobe of unreacted and seawater-oxidized sediment samples from Alameda NAS to determine the spatial distribution and correlation of lead, zinc, and iron. We then compared micro-XANES (x-ray absorption near-edge structure) spectra for lead and zinc collected with the x-ray microprobe to previously collected bulk XANES spectra. The results from our bulk XAS characterization of the sediments showed both oxide and sulfide components for the trace metals. However, from the bulk XAS data, neither the composition of the oxide component (i.e., carbonate or hydroxide) nor the absorbed species or solid solutions could be definitively identified. Our objective in using micro-XANES and fluorescence element maps was to attempt a more precise identification of metal speciation in or on individual particles.

Methods and Materials

Data were collected in February 2001 on the GeoSoilEnviro Consortium for Advanced Radiation Studies Collaborative Access Team (GSECARS-CAT) undulator beamline 13-ID-C with a Si(111) monochromator and K-B focusing mirrors. Fluorescence element maps and micro-XANES data were collected with

a beam spot size of $\sim 5 \mu\text{m}$. For micro-XANES, three to four scans were averaged for each spot. Sample particles were dispersed with alcohol onto glass slides. Samples mounted in epoxy were also tested, but particles were not dispersed adequately for mapping. Previous data collection and analyses of bulk XAS data are described in Refs. 1 and 2.

Results

Element mapping of lead, zinc, and iron showed a close spatial association among these elements in the sediment particles, with generally positive correlations between zinc and iron and between lead and iron. A significant problem with x-ray microprobe sample preparation is dispersion and separation of individual particles. We found that small particles tended to clump together, making it difficult to interpret spatial relationships among the mapped elements by using the beam spot size of $\sim 5 \mu\text{m}$. Figure 1 compares bulk XANES data collected at the Stanford Synchrotron Radiation Laboratory to micro-XANES data collected with a $5\text{-}\mu\text{m}$ beam spot. Good signal-to-noise ratio was obtained for micro-XANES measurements. For zinc and

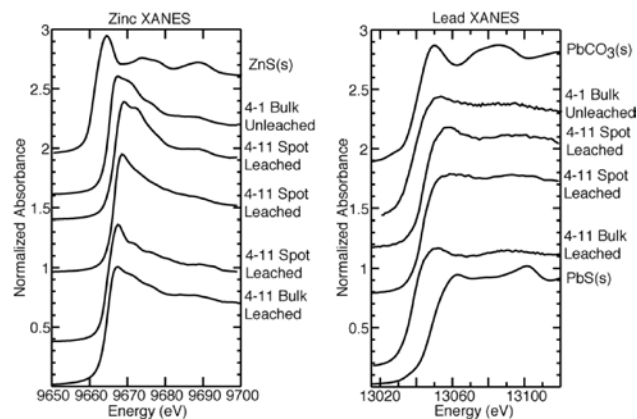


FIG. 1. Comparison of bulk and micro-XANES (spot) spectra for zinc and lead from NAS Alameda estuary sediments. Leached samples were reacted with seawater in the laboratory for 3 mo to simulate oxidation. Reference sulfide and carbonate compound spectra are shown for comparison.

lead spectra, bulk and micro-XANES were generally similar for the leached sample, although there were some differences among different spot measurements. Analyses of zinc and lead bulk EXAFS spectra showed that zinc was present in both sulfide and oxide phases but lead was present only in oxide phases [1]. Differences among the micro-XANES spectra shown in Fig. 1 reflect either heterogeneity among different particles or overlap of particles with different metal speciation.

Discussion

Micro-XAS has the potential to advance our understanding of trace metal biogeochemistry in contaminated sediments by spatially examining the molecular bonding of trace metals in the sediments. However, the current size of the beam spot (5 μm) may be too large to analyze individual grains for many natural environments, as was the case for our sediments that contained grains that, in general, were probably less than 2 μm in size. Our results indicate that beam spots sizes between 0.5 and 1 μm would provide the necessary spatial resolution for successful microprobe mapping and XANES data collection to unravel the complex geochemistry present in natural sediments. Although a smaller beam size might decrease fluorescence signal, we found high signal-to-noise ratio for these samples,

suggesting that smaller beam sizes are feasible. In the absence of a smaller beam spot size, success of microprobe mapping and XANES data collection could be achieved by dispersing fine particles on a substrate such that individual particles could be imaged and analyzed. However, the dispersal might involve the use solvents that might react with the sediments. Quantitative XANES analysis also requires a good reference compound library for accurate spectral pattern matching.

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