This paper was presented at the National Academy of Sciences colloquium "Geology, Mineralogy, and Human Welfare," held November 8–9, 1998 at the Arnold and Mabel Beckman Center in Irvine, CA.

Mineral surfaces and bioavailability of heavy metals: A molecular-scale perspective

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ABSTRACT There is a continual influx of heavy metal contaminants and pollutants into the biosphere from both natural and anthropogenic sources. A complex variety of abiotic and biotic processes affects their speciation and distribution, including adsorption onto and desorption from mineral surfaces, incorporation in precipitates or coprecipitates, release through the dissolution of minerals, and interactions with plants and microbes. Some of these processes can effectively isolate heavy metals from the biosphere, whereas others cause their release or transformation to different species that may be more (or less) bioavailable and/or toxic to organisms. Here we focus on abiotic adsorption and precipitation or coprecipitation processes involving the common heavy metal contaminant lead and the metalloids arsenic and selenium in mine tailings and contaminated soils. We have used extremely intense x-rays from synchrotron sources and a structure-sensitive method known as x-ray absorption fine structure (XAFS) spectroscopy to determine the molecular-level speciation of these elements at concentrations of 50 to several thousand ppm in the contaminated environmental samples as well as in synthetic sorption samples. Our XAFS studies of As and Pb in the mine tailings show that up to 50% of these contaminants in the samples studied may be present as adsorbed species on mineral surfaces, which makes them potentially more bioavailable than when present in sparingly soluble solid phases. Our XAFS studies of Se(VI) sorption on Fe^{2+}-containing sulfates show that this element undergoes redox reactions that transform it into less bioavailable and less toxic species. This type of information on molecular-level speciation of heavy metal and metalloid contaminants in various environmental settings is needed to prioritize remediation efforts and to assess their potential hazard to humans and other organisms.

The earth's surface and near surface regions are dominated by interfaces among solids, liquids, and gases. Such interfaces, particularly those between natural solids and aqueous solutions, play an enormously important role in a number of geological and geochemical processes. For example, "water–rock" interactions over geologic time have been major contributors to both the rock cycle and the geochemical cycling of elements. In an environmental context, interfacial processes such as mineral dissolution, mineral precipitation, and the sorption and desorption of chemical species are responsible for the release and/or sequestration of heavy metals that may eventually become pollutants in soils and groundwater. The importance of interfacial processes is summed up well in the following quotation from Werner Stumm (1): "Almost all of the problems associated with understanding the processes that control the composition of our environment concern interfaces, above all the interfaces of water with naturally occurring solids."

Recognition of the importance of surface chemical reactions in geochemical and environmental contexts can be traced back to some of the pioneering work on soil–fluid interactions, particularly the papers by H. S. Thompson (2) and J. Thomas Way (3), who were early soil chemists. The paper by Way reported on the filtration of "liquid manure" through a loamy soil, which resulted in the manure being "deprived of color and smell." Almost 150 years later, we have a more fundamental understanding of the sorption and cation exchange phenomena that account for Way's observation. We are also beginning to develop a molecular-scale understanding of the complexity and interplay of the chemical and biological processes that control element cycling in soils and sediments, some of which are shown in Fig. 1. Such processes range from dissolution of mineral particles in soils, which can release natural contaminants into pore waters, to the binding or sorption of metals (M) and organic ligands (L) to mineral surfaces, which can effectively immobilize contaminants and reduce their bioavailability. Precipitation is another common means of sequestering a heavy metal if the precipitated phase is relatively insoluble. Some heavy metal contaminants such as lead normally exist in minerals in one dominant oxidation state, whereas others such as arsenic and selenium can exist in several oxidation states and can undergo oxidation or reduction when they interact with mineral surfaces or organic compounds, which act as oxidants or reductants. Microorganisms and plants can have a profound influence on chemical reactions involving contaminants. For example, microorganisms often play a major role in the degradation of organic contaminants and in the oxidation and reduction of heavy metals. In the case of plants, the root–soil interfacial region, referred to as the rhizosphere (circled area in soil profile in Fig. 1) is an area of particularly intense chemical and biological activity where organic acids, sugars, and other organic compounds are exuded by live plant roots. The pH can be as much as 2 units lower, and microbial counts can be 10- to 50-fold higher at the root surface than in the bulk soil a few millimeters away. Thus, mineral weathering rates and the solubility of mineral elements and anthropogenic contaminants are generally greater in surface soils, where plant and microbial activity are higher than in deeper parts of the soil and geologic column.

Because of this complexity, experimental and theoretical studies that probe the nature of these processes at a fundamental level are difficult to perform on natural samples, and the results are sometimes difficult to interpret because of the large number of interacting abiotic and biotic processes. In fact, it is often difficult to distinguish between abiotic and biotic transformation mechanisms involving heavy metals and metalloids, as both can affect the pathways of reactions in a synergistic fashion (see, e.g., ref. 4). One approach to this problem involves analytical and experimental studies of simplified model systems in which variables can be controlled to simulate processes in more complex natural systems.

Abbreviations: XAFS, x-ray absorption fine structure; EXAFS, extended x-ray absorption fine structure; XANES, x-ray absorption near edge structure.
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FIG. 1. Schematic illustration of a variety of molecular environmental science processes affecting contaminant elements in soils and groundwater.

It is also essential to carry out parallel studies of the natural systems to place constraints on the variables and types of processes that control contaminant speciation and distribution and to develop testable hypotheses that can be addressed by appropriately chosen model systems. We have adopted this combined model system/natural system approach to help interpret analytical results on natural systems containing heavy metal and metalloid contaminants.

Ultimately, the impact of heavy metals and other environmental contaminants on humans and other organisms depends on their concentration levels, toxicity, and bioavailability, i.e., the extent to which they are absorbed by the blood or stored in internal organs. The toxicity and bioavailability of a heavy metal, in turn, depend in part on reactivity and solubility, which are determined by the speciation or chemical form of the element. The term "speciation," as used here, refers to (*i*) the identity of the element, (*ii*) its oxidation state, (*iii*) its physical state [i.e., phase association; presence in a liquid, gaseous, or solid phase (amorphous or crystalline), colloidal particle, animal or plant cell, or biofilm; presence as a surface coating or thin film on a solid, as a sorption complex (monomeric or polymeric) on a solid, colloidal particle, or an organic substance; etc.], (*iv*) its empirical

formula, and (*v*) its detailed molecular structure. For example, chromium in the Cr(VI) form occurs as a tetrahedral oxoanion in aqueous solution, is quite soluble and mobile in groundwater and surface waters, and is toxic to organisms (5, 6). In contrast, when in the Cr(III) form, chromium is typically bonded to six oxygens in an octahedral complex, is relatively insoluble and immobile, and poses little risk to organisms (5). As shown by this example, a fundamental understanding of the potential impact of a particular environmental contaminant on humans must include a molecular-level description of its speciation, as well as a number of other interrelated factors (7). This point is illustrated by the blood lead levels measured in humans in several sites, where lead levels in surface soils range from hundreds to thousands of ppm (Fig. 2). These data (8) show that significantly different levels of blood lead are found in human populations at the different sites and do not correlate directly with bulk Pb soil concentrations. One possible explanation for these differences is the presence of different species of lead at these sites, with lead at some sites being in a more bioavailable form. When present in crystalline solids such as galena or pyromorphite, lead should be less soluble, less mobile, and less bioavailable than when present as sorbed species on mineral surfaces, where it may be relatively easily removed into solution by a reduction in pH from neutral to acidic, such as might occur when a lead-contaminated soil sample is ingested by an organism (see, e.g., ref. 9). These differences are well illustrated by the results of *in vivo* swine studies using soil and mine waste material from Leadville, CO, which have shown that Pb bioavailability ranges from <5% for selected tailings materials, which are dominated by galena (PbS), to 45% for surface soils where the majority of Pb occurs as "Fe-Mn-Pb oxide" phase(s) (10).

Although the correlation between speciation of environmental contaminants and their bioavailability has been shown in recent studies (11–17), there is relatively limited use of information on molecular-level speciation in setting maximum contaminant levels (see, e.g., ref. 18). For example, the current EPA limit for arsenic in drinking water is 50 ppb total arsenic without designation of the species of As present, which can occur as inorganic oxoanions [As(III)O_3^{3-} and As(V)O_4^{3-}], as organic arsenicals, or in other forms; the trivalent form of As, either in inorganic or organic compounds, is generally more toxic than pentavalent compounds of As (19). In the past, cleanup efforts for contaminated soils or mine tailings were often driven by total contaminant element concentration without sufficient attention to speciation or the relative toxicities or bioavailabilities of individual

FIG. 2. Blood lead levels in humans in several major lead mining districts (modified after ref. 12).

species of a contaminant element (18). This practice is due in large part to the difficulty in deriving molecular speciation information for low concentration levels of a given contaminant and in applying this information to field-scale situations. Potential consequences of this approach are remediation efforts and major expenditures that may not be warranted because of the presence of a heavy metal or metalloid in chemical forms that are not readily bioavailable.

In this paper, we summarize recent spectroscopic work on the molecular-scale speciation of arsenic, selenium, and lead in contaminated soils and mining wastes with the objective of relating speciation to potential bioavailability. We also briefly discuss some of the natural sources of these elements as well as general concepts needed to understand variations in their uptake or sorption on mineral surfaces in contact with bulk aqueous solutions. These heavy metals (Pb) and metalloids (As, Se) are among the most important environmental contaminants, affecting millions of people. For example, arsenic pollution in drinking water in Bangladesh is currently causing a health risk to over 70 million people (20). Arsenic also poses a potential risk in the Mother Lode District of California, where tailings from gold mining activities of the 1800s contain arsenic levels as high as 5,000 ppm (21, 22). Similarly, selenium contamination in the Central Valley of California threatens wildfowl populations as well as agricultural production in this region where Se concentrations in topsoils and efflorescences are as high as 50 ppm (23). Lead is arguably the most widespread elemental contaminant worldwide and has had a major impact on human welfare (24, 25). Lead has many diverse physiological and biochemical effects in animals and humans, particularly children, where it has been shown to affect intelligence quotients in children exposed to lead-containing paints and soils (26, 27).

In the contaminated soil and mine tailings samples considered in this paper, As, Se, and Pb concentrations ranged from as low as 50 ppm to as high as several weight percent. In the model laboratory sorption samples considered here, the amount of heavy metal present on particle surfaces, measured in percentage of an ideal monolayer (ML), ranged from less than 10% ML to greater than 100% ML, or, in terms of concentration/unit area, from as low as 0.1 μmol/m^2 to >20 μmol/m^2. At these very low concentrations, sensitive element-specific probes capable of providing molecular-scale structure–composition information on heavy metal speciation are essential. Synchrotron-based x-ray absorption fine structure (XAFS) spectroscopy methods are well suited for this type of work because of the extremely high intensity of synchrotron x-rays and their energy tunability, which provide element sensitivity and element specificity, respectively. XAFS spectroscopy is capable of providing quantitative information on the geometry, composition, and mode of attachment (inner- vs. outer-sphere surface complexes vs. three-dimensional precipitates; monodentate vs. bidentate surface attachment, etc.) on specific elements at surface coverages as low as ≈0.05 ML by using existing synchrotron radiation sources and x-ray detectors (28–30).

The information derived from this work includes a molecular-scale description of the dominant type(s) of surface complexes or precipitates that form when these metals or metalloids partition from aqueous solution onto the mineral surface, a process generally referred to as sorption when the details of the adsorption mechanism are not fully known. We also present similar spectroscopic studies on the speciation of these heavy metals/metalloids in several natural multiphase systems, including Se-contaminated soils and sediments and As- and Pb-contaminated mining wastes. We show that significant fractions (up to 50 atom%) of As and Pb in our samples of mine tailings from the Mother Lode District of Central California and Leadville, CO, respectively, occur as sorbed species that are potentially bioavailable. We also discuss spectroscopic results on Se in contaminated soils that indicate redox transformations from more toxic to less toxic species.

Natural Sources of Heavy Metal Contaminants and Pollutants. One common public misconception is that inorganic contaminants or pollutants (contaminants at sufficiently high concentrations to pose a hazard to exposed organisms) are introduced into soils and natural waters only through anthropogenic emissions. Because of their presence in minerals and the fact that minerals undergo dissolution caused by chemical weathering, heavy metals and metalloids are continually released into the environment at various rates and concentrations from natural materials. When concentrated in certain types of mineral deposits exposed at the earth's surface, they can be released at sufficient concentrations to be considered pollutants (e.g., arsenic released from the weathering of arsenical pyrite and arsenopyrite). When such deposits are mined, the release is typically enhanced because of the crushing of ore and gangue (waste) materials and the resulting increase in surface area of material exposed to weathering processes. In these cases, pollution can become a serious problem, especially if the oxidation of sulfide minerals, which are often present in heavy metal ore deposits, causes acid mine drainage, which can enhance the mobility of heavy metal cations (see ref. 31 for a case study). For example, the oxidation of pyrite (FeS$_2$) produces ferric hydroxide solids, sulfate, and hydrogen ions by means of a reaction of the following type:

$$FeS_2(s) + 15/4\ O_2(g) + 7/2\ H_2O(l) \rightarrow Fe(OH)_3(s)$$
$$+\ 2\ SO_4(aq) + 4\ H^+(aq) \qquad [1]$$
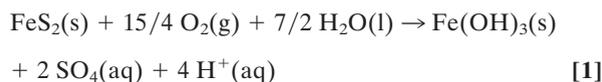
which results in decreased pH, enhanced dissolution of minerals, and enhanced release of cations that are adsorbed on mineral surfaces in the vicinity of the dissolving pyrite. Desorption of surface-bound Pb(II) and other cations from mineral surfaces under acidic solution conditions results in an increase in the concentration level of potentially bioavailable forms of heavy metal cations in surface waters and groundwater.

The following four sections are intended to provide a brief overview of some of the minerals that contain arsenic, selenium, and lead as major, minor, or trace components. Some of the phases listed are potential candidates for secondary minerals in various types of base-metal deposits or tailings (e.g., Pb-Zn-Cu sulfide deposits); others are primary minerals. A relatively comprehensive list of primary and secondary minerals containing these elements can be found on the Internet at the address: http://un2sg4.unige.ch/athena/mineral/minppcl.html. Although some of the minerals listed below are rare and may seem unimportant, they could be present at relatively high concentrations in certain contaminated or polluted environments containing one or more of these heavy metals or metalloids.

Natural Forms of Arsenic in the Environment. Arsenic is the 51st most abundant element in crustal rocks (average concentration = 1.8 ppm) and can occur in the 5+, 3+, 0, 1−, and 2− oxidation states in different geological environments (32). In general, reduced inorganic As found in sulfide minerals is relatively low in toxicity, but oxidized inorganic As(III) and As(V) compounds are significantly more toxic than many organoarsenicals. Moreover, As(III) compounds are two to three times more toxic than As(V) compounds (20). Both As(III) and As(V) form anionic species when in aqueous solution, adsorbed to mineral surfaces, or incorporated into precipitates. As(V) adsorbs more strongly to mineral surfaces than does As(III), thus is generally less mobile and potentially less bioavailable (33, 34).

Arsenic occurs naturally as a major component in *arsenates* [containing As(V)O$_4$ units] (e.g., adelite [CaMgAsO$_4$(OH)], chalcophyllite [Cu$_{18}$Al$_2$(AsO$_4$)$_3$(SO$_4$)$_3$(OH)$_{27}$·3^{3}H$_2$O], clinoclase [Cu$_3$(AsO$_4$)(OH)$_3$], duftite [CuPb(AsO$_4$)(OH)], hoernesite [Mg$_3$(AsO$_4$)$_2$·8H$_2$O], scorodite [FeAsO$_4$·2H$_2$O]); *arsenites* [containing As(III)O$_3$ units] (e.g., armangite [Mn$_{26}$(As$_{18}$O$_{50}$)(OH)$_4$CO$_3$], ecdemite [Pb$_6$As$_2$O$_7$Cl$_4$], finnemanite [Pb$_5$(AsO$_3$)$_3$Cl], paulmooreite [Pb$_2$As$_2$O$_5$], trigonite [Pb$_3$Mn

$(AsO_3)_2(AsO_2(OH)]$, trippkeite $[CuAs_2O_4]$); *elemental arsenic* [As(0)], *sulfides and arsenides* (e.g., arsenopyrite [FeAsS], lautite [CuAsS], skutterudite [(Cu, Ni)As$_3$], smaltite [(Co, Ni)As$_{3-x}$]); *sulfosalts* (e.g., orpiment [As$_2$S$_3$], realgar [AsS], tennantite [(Cu, Fe)$_{12}$As$_4$S$_{13}$]); or as a minor or trace component in minerals (e.g., in arsenical pyrite, where As can occur in arsenopyrite inclusions or as part of a solid solution, in jarosite [KFe$_3$(SO$_4$)$_2$(OH)$_6$], where As(V) substitutes for S(VI), or in hydrotalcite-like anionic structures, which have the general formula $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}(A^{n-}{}_{x/n})\cdot mH_2O$, where M(II) and M(III) are divalent and trivalent cations, respectively, and A^{n-} represents anions such as CO_3^{2-}, SO_4^{2-}, CrO_4^{2-}, AsO_3^{3-}, and AsO_4^{3-}, which could occupy inner-layer positions to neutralize the positive layer charge (35).

Natural Forms of Selenium in the Environment. Selenium is the 66th most abundant crustal element (average concentration = 0.05 ppm) and occurs in the 6+, 4+, 0, and 2− oxidation states in different geologic settings depending on the Eh and pH values (32). In reduced forms, selenium is relatively insoluble and immobile, thus poses little danger to organisms. However, in oxidized forms, particularly Se(VI), selenium is mobile in aqueous solutions and poses a significant risk to organisms. Selenium is present as a major component in *selenates* [containing Se(VI)O$_4$ units] (e.g., olsacherite [Pb$_2$(SeO$_4$)(SO$_4$)], schmiederite [Pb$_2$Cu(II)$_2$(Se(IV)O$_3$)Se(VI)O$_4$(OH)$_4$]); *selenites* [containing Se(IV)O$_3$ units] (e.g., chalcomenite [CuSeO$_3\cdot$2H$_2$O], hannebachite [Ca$_2$(SeO$_3$)$_2\cdot$H$_2$O], molybdomenite [PbSeO$_3$], sofiite [Zn$_2$SeO$_3$Cl$_2$]); *elemental selenium* [Se(0)]; *selenides* (e.g., berzelianite [Cu$_2$Se], umangite [Cu$_3$Se$_2$]); or as a minor to trace component in others (e.g., substituting for S in sulfides such as pyrite and in sulfates such as barite and jarosite).

Natural Forms of Lead in the Environment. Lead is the 36th most abundant element in the earth's crust (average concentration = 13 ppm) and is generally present in the 2+ oxidation state in inorganic compounds and rarely present as elemental lead (32); it is not sensitive to oxidation or reduction over the normal range of Eh and pH values encountered in various geologic settings at or near the earth's surface. Lead can occur as a major element in a wide variety of minerals (e.g., anglesite [PbSO$_4$], cerrusite [PbCO$_3$], galena [PbS], pyromorphite [Pb$_5$(PO$_4$)$_3$(Cl, OH, F)]), and as a trace or minor element, especially by substitution for Ca^{2+} and K$^+$ (e.g., Pb-bearing apatites and jarosites).

Heavy Metal Uptake on Mineral Surfaces. Sorption on mineral surfaces is an important process that can bind and sequester heavy metals and other aqueous contaminant ions. Sorption can dramatically reduce the mobility of contaminants in groundwater and, in the case of redox-sensitive elements, result in their transformation into a less (or more) toxic species through reduction or oxidation reactions. The effectiveness of sorption reactions in binding an ion is determined by a number of variables, including (*i*) pH, (*ii*) the charge on the mineral surface as a function of pH, (*iii*) the type of sorption complex formed, (*iv*) competition between different ions for the same types of reactive surface sites, (*v*) the presence of organic and/or inorganic ligands that can inhibit or enhance sorption of a metal ion, and (*vi*) the presence of surface coatings such as biofilms that may block reactive sites and/or create new sorption sites. A discussion of each of these variables is beyond the scope of this paper. In this section we review the general modes of sorption of aqueous cations and anions on mineral surfaces and discuss the specific types of surface complexes formed by As, Se, and Pb, as revealed by x-ray absorption spectroscopy.

Mineral surfaces in contact with aqueous solutions have a point of zero charge (pH$_{pzc}$), which is the pH value (or small range of pH values) at which the surface is electrically neutral. Points of zero charge of silicate and oxide surfaces have been critically evaluated in several studies [e.g., (36, 37)] and range from 2–3 (SiO$_2$) to ≈12 (MgO). Below the pH$_{pzc}$ value, the charge of a mineral surface is positive, indicating an excess of protons bonded to the surface. Above the pH$_{pzc}$, the surface is negatively charged

indicating an excess of OH$^-$ groups. At very high pH values, oxo ions (O^{2-}) may occur on the surface of an oxide or silicate in contact with an aqueous solution. The pH of uptake or release of a heavy metal depends to a significant extent on whether the heavy metal occurs as a cation or anion in solution. For example, Pb(II) in aqueous solutions exists as a cation over a wide pH range, thus its affinity for a given mineral surface generally increases with increasing pH. In contrast, As(III), As(V), Se(IV), and Se(VI) behave as anions in aqueous solutions, thus are not strongly sorbed at high pH values where the mineral surface is negatively charged.

The type of surface complex formed has an important effect on the mobility of a metal ion. Some metal ions bond directly to the mineral surface, losing waters of hydration and forming an inner-sphere complex (see Fig. 1). Such ions are relatively difficult to desorb except for large pH changes, thus are relatively immobile. However, if the metal ion forms a weakly bound outer-sphere complex in which the ion is surrounded by waters of hydration and no direct chemical bonds to the surface are formed, the metal can be easily desorbed when pH changes. An indication of the strength of binding of an aqueous cation or anion to a mineral surface can be obtained from the macroscopic uptake behavior as a function of ionic strength. For example, when an increase in the ionic strength of the background electrolyte (e.g., NaNO$_3$) reduces the degree of uptake of an ion, the ion is less strongly bound to a mineral surface than when adsorbate uptake shows no ionic strength dependence. In the former case, the ion may form a weakly bound outer-sphere complex, whereas in the latter case, a strongly bound inner-sphere complex may be indicated. However, direct spectroscopic verification of the mode of sorption is required to verify conclusions drawn from macroscopic measurements alone.

Among the ions examined here, Pb(II) forms strongly bound inner-sphere complexes on many mineral and metal oxide surfaces (38–40), as do the oxoanions AsO$_4^{3-}$ (41–45), AsO$_3^{3-}$ (46), and SeO$_3^{2-}$ (47). In contrast, the oxoanion SeO$_4^{2-}$ (47) forms more weakly bound complexes that are thought to be predominantly of the outer-sphere type, although there is still some controversy about the dominance of inner-sphere vs. outer-sphere complexes in the case of selenate sorption on iron (oxy)hydroxides (48). The mode of sorption of these species was determined by using XAFS spectroscopy.

The strength of binding and stability of an inner-sphere complex will depend in part on how many bonds it forms with surface functional groups. For example, bidentate or tridentate surface complexes, attached by two and three bonds, respectively, will typically be more difficult to desorb than monodentate complexes (attached by a single bond), all other factors being equal. Another important factor in the effectiveness of sorption reactions in removing contaminant metal ions from solution is the possibility of multinuclear complex formation (49). In this case, more than one metal ion is involved in the surface complex. The progression from mononuclear to multinuclear surface complexes generally occurs with increasing sorbate metal concentration (29, 50), with precipitation occurring at a point where the solution becomes supersaturated with respect to the hydroxide of the metal-ion sorbate (50). When other ions are present, such as the anions carbonate, sulfate, or phosphate, additional complications can arise, including competition for surface sites, formation of solution complexes, or precipitation of solids made up of the sorbate ion and the anion.

In addition to the types of adsorption described above, another potentially important sorption mechanism involves incorporation of certain types of metal ions into a solid coprecipitate made up of the sorbate ion and metal ions derived from dissolution of the mineral surface. Studies by several groups over the past few years have shown that this type of sorption product can form in aqueous systems containing sorbate ions like Co(II) (refs. 51–53) and Ni(II) (54, 55) and sorbents like α-Al$_2$O$_3$, kaolinite [Al$_2$Si$_2$O$_5$(OH)$_4$], and pyrophyllite [Al$_2$Si$_4$O$_{10}$(OH)$_2$]. The result-

Ruth Mine (Trona, CA)   Argonaut Mine (Jackson, CA)

• no sulfides
• Total As = 2000 ppm
• As(V) only

• ≈ 2% sulfides
• Total As = 200 ppm
• As(V) and reduced As

As-Al 3.16 Å   As-Fe = 3.25 Å

4 As-O 1.68 Å
4 As-Fe 3.34 Å
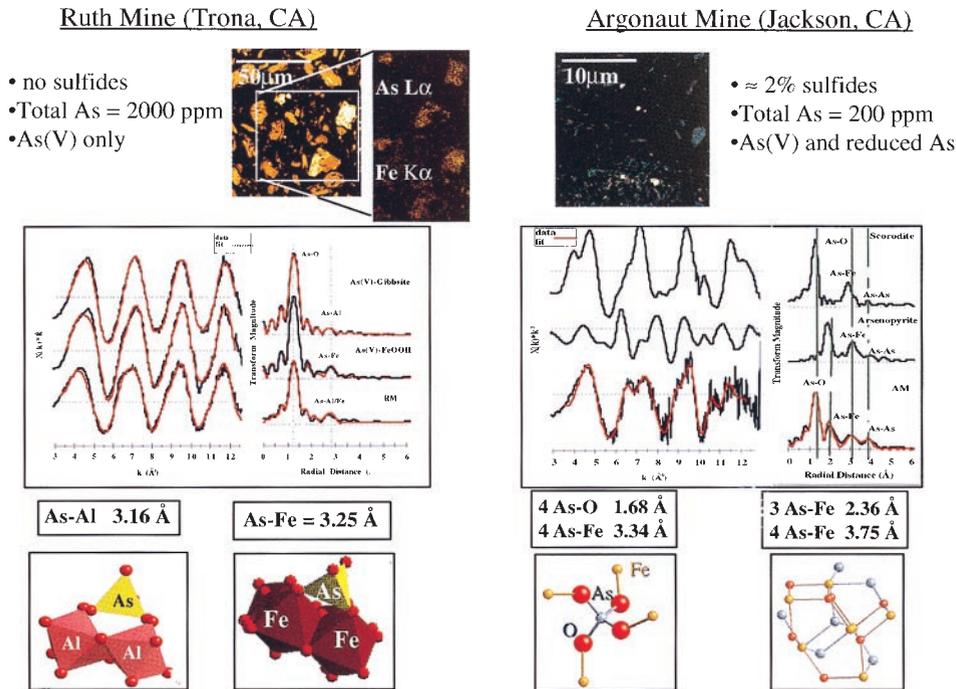
3 As-Fe 2.36 Å
4 As-Fe 3.75 Å

FIG. 3. As K-edge EXAFS data and fluorescent x-ray images for As-contaminated mine tailings from the Mother Lode District of California (derived from data reported in ref. 59). Fits to the EXAFS data are shown in red and molecular models of the As(V) environments in the model compounds used in the fits are also shown.

ing solid phase can have a hydrotalcite-type structure (35) and may be relatively insoluble, and therefore decreases the metal ion bioavailability. A different mechanism of heavy metal sequestration by means of a coprecipitation mechanism is produced by amending Pb-contaminated soils with phosphate, resulting in the growth of the Pb-phosphate pyromorphite (56).

EXPERIMENTAL APPROACH

Details of the procedures we used in preparing model heavy metal sorption samples for XAFS spectroscopy studies can be found in Bargar *et al.* (38, 39). All sorbents were synthetic high-surface area powders (≈50 ≥ 100 m²/g) and are available commercially or can be synthesized. The identity and phase purity of the powdered sorbents were determined by powder x-ray diffraction, and in selected cases by transmission electron microscopy coupled with energy dispersive x-ray analysis. Surface area

was determined for powdered sorbents by N_2-Brunauer–Emmet–Teller (BET) measurements. Powdered sorbents were placed in 0.01M $NaNO_3$ solutions and pH was allowed to equilibrate. In separate experiments, the heavy metal was added to each solution in contact with the sorbent at initial aqueous concentrations ranging from ≈0.1 to 0.01 M. pH was adjusted by addition of NaOH to achieve a desired percentage uptake of the heavy metal onto each sorbent, which was verified by graphite furnace atomic absorption (GFAA) spectrophotometry analysis of the supernatant. The resulting sorption densities ranged from ≈0.1 to >20 μmol/m². Each sample was allowed to "equilibrate" at the final pH for 24–36 hr, then before GFAA analysis the sample was centrifuged and about 95% of the supernatant was removed. Except at the highest metal concentrations, the solutions were undersaturated with respect to the stable precipitate; thus, for example, no $Pb(OH)_2$ or PbO precipitate phase was expected to

Apache Tailings:
• Sulfide-rich
• acidic pH
• total Pb = 8330ppm

Pb L_{III}-EXAFS model spectra:

vanadinite, $Pb_5(VO_4)_3Cl$

plumbojarosite, $Pb[Fe_3(SO_4)_2(OH)_6]_2$

plumboferrite, $Pb_2Fe_{12}O_{19}$

pyromorphite, $Pb_5(PO_4)_3Cl$

hydrocerussite, $Pb_3(CO_3)_2(OH)_2$

adsorbed Pb (on goethite, α-FeOOH)

Hamms Tailings:
• Carbonate-buffered
• near-neutral pH
• total Pb = 8520ppm

Pb-O = 2.26Å
Pb-Fe = 3.33Å
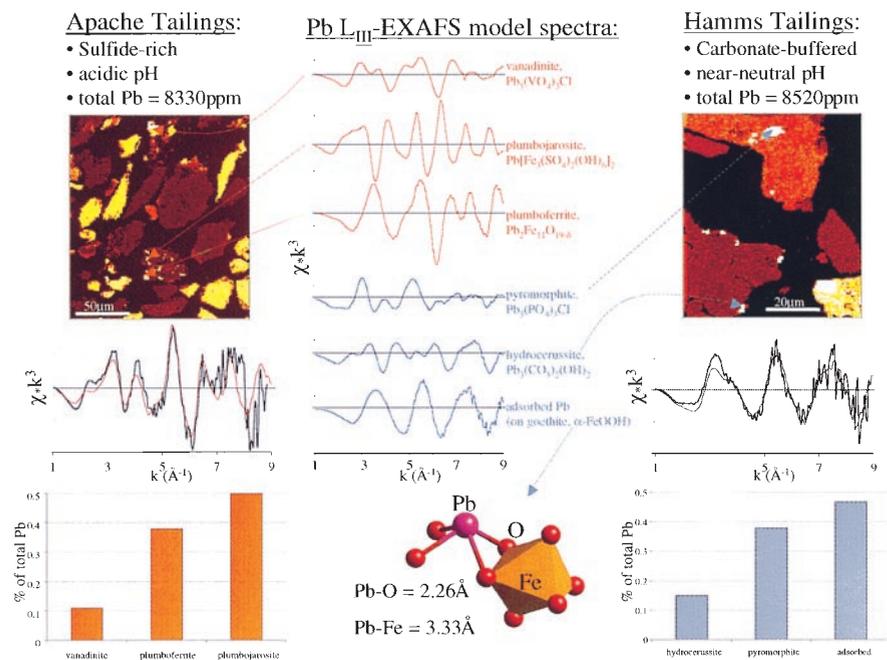
FIG. 4. Pb L_{III}-edge EXAFS data and fluorescent x-ray images for Pb-contaminated mine tailings from Leadville, CO (derived from data reported in ref. 62). EXAFS spectra of crystalline model compounds are shown in the center panel, and linear least-squares fits of EXAFS spectra of two mine tailings samples by using the model compound spectra are shown in the side panels. Bar plots of the abundance of different lead species are shown in the bottom panels on each side of the figure.

Colloquium Paper: Brown *et al.*

Proc. Natl. Acad. Sci. USA 96 (1999)   3393

form in the case of the model lead sorption systems. In each case, the sorption sample in the form of a wet paste was loaded into a Teflon sample holder sealed with Mylar windows, and XAFS spectra were collected at the Stanford Synchrotron Radiation Laboratory (SSRL) on wiggler-magnet beamlines within 2 days of sample preparation. XAFS spectra for the model sorption samples were collected in the fluorescence-yield mode by using either a Stern–Heald type gas-filled ionization chamber detector (57) or a 13-element Ge detector under ambient conditions. The XAFS spectra of crystalline model compounds were collected in transmission mode under ambient conditions. In none of these experiments was evidence found for oxidation or reduction of the sorbate ion during or after XAFS data collection, as indicated by the lack of energy shifts in the edge positions, extended x-ray absorption fine structure (EXAFS)-derived metal-oxygen bond lengths, and x-ray photoelectron spectroscopy measurements. XAFS data analysis procedures used for the powdered sorption samples are described in Bargar *et al.* (38, 39) and O'Day *et al.* (58).

XAFS spectroscopic analysis of the natural soil and mine waste samples containing As, Se, and Pb was carried out by using the experimental and data analysis procedures described in Foster *et al.* (59, 60), Pickering *et al.* (61), and Ostergren *et al.* (62), for As, Se, and Pb, respectively. These natural samples were not significantly modified from their conditions in the field, except for size separation in selected cases, in an attempt to preserve the same speciation of heavy metals present in the original samples. About 100 mg of each sample was placed in a Teflon holder and covered with thin Mylar tape, and XAFS data were collected by using fluorescence-yield detection (either a Stern–Heald detector or a multielement solid state detector) at ambient temperature (298 K) and pressure [1 atm (101.3 kPa)]. In addition to the normal EXAFS spectral fitting, which yields information on the identity and arrangement of first and second neighbors around the central absorber, linear least-squares fitting of the x-ray absorption near edge structure (XANES) spectra was conducted for the As- and Se-contaminated samples, and linear least-squares fitting of the XAFS spectra was conducted for the Pb-contaminated samples. By using this approach (59, 61, 62), the quantitative speciation of the heavy metal was determined by fitting the spectrum of the contaminated sample with spectra of model compounds, including both crystalline phases and model sorption samples with the heavy element sorbed at low surface coverage on different mineral or organic substrates. This approach works well when the spectral signatures of the different models are significantly different, which is often the case. Examples of this type of fitting are given in the sections below. The amount of surface-bound heavy metals in the contaminated soil and mine waste samples was determined in this manner.

In addition to XAFS analysis of the contaminated samples, each sample was examined by powder x-ray diffraction, optical microscopy, and electron microprobe to determine the types and amounts of crystalline phases present (59, 62, 63). In addition, selected samples were examined by surface-sensitive x-ray photoelectron spectroscopy (62).

RESULTS AND DISCUSSION

As in Mine Tailings from the Mother Lode District, California. Almost 150 years of gold mining in the Mother Lode of California has resulted in significant concentrations of arsenic in mine tailings (up to 5,000 ppm), some of which have been used for housing developments in the Sierra Nevada Foothills of Central California. Because of the toxic effects of high concentrations of arsenic on humans and other organisms, there is concern about these tailings, and a number of studies are underway to determine the potential health hazard of these tailings to humans.

We have used XAFS spectroscopy to determine the oxidation state, local coordination environment (to a radius of $\approx$7 Å around As), and the relative proportion of different As species in model

compounds and three California mine wastes: a fully oxidized tailings (Ruth Mine), a partially oxidized tailings (Argonaut Mine), and a roasted sulfide ore (Spenceville Mine) (59). Analysis of the XANES spectra of these contaminated samples indicates that As(V) is the predominant oxidation state in the Ruth and Spenceville mine samples, but mixed oxidation states were observed in the Argonaut mine-waste. We obtained qualitative information about As(V) chemical speciation by fitting the XANES spectra of mine samples with a linear combination of component (model compound) spectra (Fig. 3). These analyses suggest the presence of As(V) species similar to those found in scorodite ($FeAsO_4 \cdot 2H_2O$) and As(V) adsorbed on goethite (α-FeOOH) and gibbsite [γ-Al(OH)$_3$]. Nonlinear least-squares fits of mine waste EXAFS spectra indicate variable As speciation in each of the three mine wastes. We conclude that ferric oxyhydroxides and aluminosilicates (probably clay) bind roughly equal portions of As(V) in the Ruth Mine sample. Our analysis suggests that tailings from the Argonaut Mine contain $\approx$20% reduced As bound in arsenopyrite (FeAsS) and arsenical pyrite ($FeS_{2-x}As_x$) and $\approx$80% As(V) in a ferric arsenate precipitate such as scorodite. Roasted sulfide ore of the Spenceville Mine contains As(V) substituted for sulfate in the crystal structure of jarosite [$KFe_3(SO_4)_2(OH)_6$], and sorbed to hematite surfaces. Determination of solid-phase As speciation by means of EXAFS spectroscopy is a valuable first step in the evaluation of As bioavailability, because the mobility and toxicity of As compounds vary with As oxidation state. As bound in crystalline or x-ray amorphous precipitates is generally considered to be less available for uptake by organisms than when sorbed to mineral surfaces.

Se-Contaminated Soils in the Central Valley of California. Selenium occurs naturally in sediments and soils in many parts of the Western U.S. and is assumed to be incorporated in pyrites in marine sedimentary rocks such as shales. When such soils are irrigated for agricultural purposes, this indigenous element becomes soluble and is transported in agricultural drainage waters to ponds and reservoirs where it becomes concentrated in waterborne plants and animals (up to 3,000 ppm). One result of this concentration process was discovered in the early 1980s by government scientists at the Kesterson National Wildlife Refuge in Merced County, California. Wildlife, particularly waterfowl, died or were born deformed from consumption of high levels of selenium (64). Similar problems have since been documented at nine sites in eight Western states comprising some 1.5 million acres of farmland. This problem has major financial and health implications in the San Joaquin Valley of California, a vast area that produces a significant portion of the nation's vegetables, fruits, and other crops. If farmers are prevented from draining irrigation waters in this region, the rapid buildup of salts in the soil will quickly make production of these crops impossible. About 500,000 acres of farmland in the San Joaquin Valley—one quarter of the Valley's agricultural acreage—are at stake, with an annual crop production worth about $500 million (65).

To provide molecular-level information on the chemical forms of selenium present in Se-contaminated soils from the Kesterson Reservoir area, we have carried out XAFS spectroscopy studies that showed that selenate and selenite are present in the top few cm of soil adjacent to the drainage ponds but are reduced to elemental selenium at lower soil levels (61, 66). In carefully controlled laboratory studies of soil columns to which selenate-containing solutions were added, Tokunaga *et al.* (67, 68) found that selenate is rapidly converted into elemental selenium. The reduction can occur by means of both biotic (4, 69) and abiotic (70) pathways. However, when reoxidized to the selenate form during irrigation, selenium becomes highly mobile and is transported as an aqueous complex in drainage waters. Various solutions to this problem have been proposed, including bacterial reduction, immobilization, and removal of selenium from drainage waters or the use of drainage waters to irrigate land on which salt-resistant plants such as cotton, Eucalyptus trees, and atriplex are grown. None have been adopted and some skeptics doubt that

a viable solution, which satisfies environmental, financial, and political constraints, will be found. An eventual solution to this problem will require a detailed knowledge of the redox chemistry of selenium, its speciation in soils and groundwaters, and the effect of microbial organisms and inorganic reductants on its speciation.

Pb in Mine Tailings from Leadville, CO. Pb is a ubiquitous environmental contaminant in soils because of the intensive use of Pb in batteries, paints, alloys, and solder, ammunition, gasoline additives, and other commercial products and the production of lead by mining and smelting activities. A recent study of the history of atmospheric lead deposition over the past 12,370 years, as measured in a peat bog in the Jura Mountains of Switzerland (71), has shown that the greatest lead flux (15.7 mg/m^2/yr) occurred in 1979. This level is 1,570 times the natural background value of 0.01 mg/m^2/yr. However, since the elimination of tetraethyl lead as a gasoline additive, beginning in the 1970's in the U.S. and some other countries, lead contamination levels have dropped significantly (25). They still exceed natural background levels by orders of magnitude in soils in many nonurban localities where soils have become polluted as a result of mining and smelting activities and in urban localities where paints and other anthropogenic sources of lead contaminate soils. The bioavailability of Pb is known to vary widely among different Pb species, and this fact is often cited to explain apparently dramatic variations in Pb bioavailability from site to site (e.g., ref. 10). Understanding the detailed relationship between speciation and bioavailability necessarily begins with a complete, accurate, and direct identification of Pb species in environmental media, such as soils and mine waste. Working toward this goal, researchers have recently begun applying synchrotron radiation-based x-ray absorption spectroscopic (XAS) techniques to determine the molecular-scale details of Pb speciation at contaminated sites (62, 63, 72, 73). Here we summarize the results of our work on Pb-bearing mine tailings from Leadville, CO (62). Using the unique advantages of XAS techniques, we emphasize the identification and characterization of poorly crystalline and/or fine-grained species, such as sorption complexes and poorly crystalline coprecipitates, which are likely to control Pb bioavailability and mobility in natural systems.

Bulk Pb concentrations range from 6,000 to 10,000 ppm in the two tailing piles we sampled at the Leadville site. These concentrations necessarily raise human health and environmental concerns, but bioavailability and chemical lability of Pb in these materials vary dramatically and show little correlation with bulk concentrations (10). Because these samples are heterogeneous multiphase mixtures (Fig. 4), a variety of complementary analytical methods were used, including powder x-ray diffraction, scanning electron microscopy, electron probe microanalysis, x-ray photoelectron spectroscopy, and synchrotron radiation-based x-ray absorption. By using this suite of techniques, and XAS techniques in particular, in conjunction with physical and chemical separation techniques, we were able to identify and characterize a number of species not amenable to detection by conventional microanalytical techniques. In particular, we found direct spectroscopic evidence for Pb adsorbed to mineral surfaces and variations in this surface-bound component with pH as would be predicted on the basis of simplified model system studies of adsorption processes. Least-squares fitting of EXAFS spectra shows that 50% of the total Pb in selected samples of the carbonate-buffered tailings with near-neutral pH occurs as adsorption complexes on iron (hydr)oxides, whereas Pb speciation in sulfide-rich low pH samples is dominated by Pb-bearing jarosites; we find no evidence for adsorbed Pb in these latter samples. Importantly, the dominant Pb species in each of the tailing piles could not be definitively identified without the molecular-scale information provided by EXAFS analysis. Because these species likely control Pb transport and bioavailability in these environments, our results clearly illustrate the need for

molecular-scale characterization as basis for understanding the behavior of and health risks posed by Pb in natural environments.

SUMMARY AND CONCLUSIONS

The heavy metal Pb and the metalloids As and Se are among the most common environmental contaminants resulting from anthropogenic activities and the weathering of natural mineral deposits. These elements occur in a variety of chemical forms or species that can vary widely in solubility, mobility, toxicity, and bioavailability, depending on their speciation. In contaminated soils and mine tailings, for example, they can occur in primary minerals, secondary minerals formed by weathering of primary minerals *in situ*, solid precipitates formed by reactions of contaminant ions in groundwater with other aqueous ions, and adsorbed species. Although it is relatively easy to determine the types of solid phases present in a contaminated soil or mine tailings sample and the concentration levels of heavy metals and metalloids they contain by using a combination of x-ray diffraction and analytical methods, it is considerably more difficult to assess the importance of adsorbed heavy metal/metalloid species, particularly at very low surface coverages. Adsorbed species may comprise a significant fraction of the heavy metal or metalloid present, and they are often the most bioavailable fraction.

By using a combination of synchrotron-based XAFS spectroscopy and other analytical methods, the molecular-level speciation of As, Se, and Pb, including the types of sorbed species, was determined for selected mine tailings and contaminated soils. Sorbed As and Pb species were found to be major components with potentially high bioavailability in mine tailings from the Mother Lode District of California and Leadville, CO, respectively. Similar studies have shown that the most toxic and potentially bioavailable forms of selenium, Se(VI), are transformed rapidly to environmentally benign forms in contaminated soils through a combination of biotic and abiotic processes.

A detailed knowledge of molecular-level speciation of heavy metal/metalloid contaminants and the bioavailability of the different species of a contaminant element is necessary for setting maximum contaminant limits. Knowledge of speciation is also required for efficient and cost-effective remediation efforts. This point is well illustrated by cleanup efforts at the former uranium processing plant at Fernald, OH, which serves as the host for the Uranium in Soils Integrated Demonstration. This demonstration project used carbonate soil-washing procedures to remove hexavalent uranium. However, this conventional remediation procedure was not totally effective because of the presence of secondary phases containing U(IV) and U(VI), the latter being in the form of insoluble phosphates. These uranium species were detected by using a combination of XAFS, optical luminescence, Raman spectroscopy, scanning electron microscopy, and powder x-ray diffraction (74) and micro-XAFS spectroscopy (75). Changes in remediation procedures based on this type of speciation information could result in significant cost savings and more efficient cleanup of environmental contaminants, both of which should be major societal goals.

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