

SUPPORTING INFORMATION

Geochemical Weathering Increases Lead Bioaccessibility in Semi-Arid Mine Tailings

Sarah M. Hayes¹, Sam M. Webb², John R. Bargar², Peggy A. O'Day³, Raina M. Maier¹, and Jon Chorover¹

¹Department of Soil, Water and Environmental Science, University of Arizona, Tucson, AZ
85721

²Stanford Synchrotron Radiation Laboratory, SLAC National Accelerator Laboratory, 2575 Sand
Hill Road, MS 69, Menlo Park, California 94025

³School of Natural Sciences, University of California, Merced, CA 95343, USA

7 pages

DETAILED DESCRIPTION OF MATERIALS AND METHODS

Reference materials

Twelve Pb-bearing XAS reference minerals were purchased, synthesized, or borrowed from curated reference sources (**Table S1**). Lead oxalate ($K_{sp}=8.5 \times 10^{-9}$) was synthesized by precipitation from a supersaturated solution containing PbNO_3 and 0.2 M $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ at pH=3 (Skoog et al. 1996). Compost-sorbed Pb was prepared by equilibrating 5 g of compost (UA dairy farm) with 25 g of 0.5 mM PbNO_3 solution (Sigma, lot 11715TC) for 24 h in an end-over-end mixer at 7 rpm and room temperature. Hematite ($\alpha\text{-Fe}_2\text{O}_3$; method 4) and birnessite ($\delta\text{-MnO}_2$) (McKenzie 1971; Schwertmann and Cornell 2000) were synthesized for Pb^{2+} sorption experiments. Hematite- and birnessite-sorbed Pb references were prepared by first washing 0.8 g of the respective solid twice in 0.1 M NaNO_3 background electrolyte solution that had been adjusted to pH 7 for hematite and pH 5 for birnessite. Solids were then equilibrated at the same corresponding pH values with 30 g of 0.1 M NaNO_3 solution containing 0.1 mM and 3 mM PbNO_3 for hematite and birnessite, respectively, for 24 h in an end-over-end mixer at 7 rpm. Compost and mineral sorption experiments were terminated by centrifugation, removal of supernatant solution for analysis, and preservation of the wet pellet by either refrigeration (compost, birnessite) or freeze-drying (hematite). Sorbate (Pb) concentrations, calculated on the

basis of loss from solution, were 500, 9600, and 805 mg kg⁻¹ for Pb-sorbed compost, hematite, and birnessite samples, respectively.

Sequential extraction

The sequential extraction procedure (Hayes et al. 2009) was modified after (Dold 2003). It involves addition of 1.0 g of air-dried tailings to 50 mL Teflon centrifuge tubes in triplicate followed by the following reaction sequence: (i) “**H₂O**”: 18MΩ water extraction, 25°C, 1 h that targets soluble salts such as gypsum; (ii) “**AA**”: 1.0 M ammonium acetate, pH 4.5, 25 °C, 2 h that targets sorbed species, and calcite; (iii) “**AAO 25°C**”: 0.2 M ammonium oxalate at 25°C, pH 3.0, 2 h that targets short-range-order Fe, Al and Mn (oxy)hydroxides and poorly-crystallized jarosites; (iv) “**AAO 80°C**”: 0.2 M ammonium oxalate at 80°C pH 3.0, 80 °C, 2 h) that targets long-range-order Fe, Al, and Mn (oxy)hydroxides and well-crystallized jarosites; (v) “**H₂O₂**”: 30-35% hydrogen peroxide in 1.0 M ammonium acetate (pH 4.5, 60 °C, 2 h) that oxidizes organic matter and secondary supergene sulfides; and (vi) “**Acid**”: 750 mg of KClO₃ and 15 mL 12 M HCl (25 °C, 30 min), then addition of 10 mL of 18 MΩ water followed by centrifugation and decanting the supernatant prior to reacting pellets with 25mL of 4.0 M HNO₃ (90 °C, 20 min) that targets primary sulfides. After each step, the pellets were rinsed with 30 mL of 18 MΩ water. The combined supernatant and wash solutions were then collected by centrifugation, filtered (Acrodisc, 0.22 μm), acidified to pH 2 and analyzed for metal concentrations by inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer DRCII).

Lead in the “**residual**” fraction was quantified using bulk XRF using 0.6 g of residual solid pressed into pellets with cellulose wax (3642 Cellulose binder – SPEX SamplePrep PrepAid™) for 60 s using 22 tons of pressure. The pellets were analyzed using a Polarized Energy-Dispersive X-ray Fluorescence spectrometer (EDXRF – SPECTRO XEPOS, Kleve, Germany). Measurements were conducted under Helium atmosphere and 4 secondary targets (HOPG, Mo, Al₂O₃ and Co) were used to provide different excitation conditions at different voltage and current settings, with a silicon drift detector. Acquisition time was 300 s for each secondary target. Calibration of the EDXRF was performed using 25 certified reference materials and 18 uncertified materials previously analyzed by ICP-MS following Li-metaborate fusion.

Bulk XAS collection

Lead speciation of the tailings samples and reference materials was investigated with Pb L_{III}-edge (E₀=13035eV) XAS spectroscopy. XAS spectra of the four tailings samples, the efflorescent salt, and the clay size (< 2.0 μm) fractions of T_{3,9}^S and T_{5,4}^S were collected at the Stanford Synchrotron Radiation Lightsource (SSRL) on beam lines 10-2 and 11-2 in a liquid helium cryostat (Oxford Instruments, Austin, TX) maintained at >10 K. Several reference spectra (**Table 1**), were collected at room temperature in transmission at GSE-CARS beam line 13-BM at the Advanced Photon Source (Argonne National Laboratory, IL). Measurements at SSRL were made with samples held in an Oxford liquid helium cryostat operating at < 15 K, well below the

Debye temperature for Pb oxide (145 K), thereby reducing spectral contributions from lattice vibrations (King 1958). A double-crystal monochromator with Si (220), $\phi=0$ crystals was used in conjunction with three 15 cm ion chambers with nitrogen gas and a 13- or 32-element germanium fluorescence detector. Vertical slits of 3 mm were used for all samples, and horizontal slits were adjusted between 6 and 12 mm to maximize signal without saturating the detector. Germanium and aluminum foil filters were used for fluorescence measurements to attenuate elastic and Compton scattering and Fe fluorescence. A minimum of 3 scans were collected in transmission mode (used for most reference materials) and 10-15 scans were collected in fluorescence mode (used for tailings and sorption samples). The upper end of the XAS-accessible energy range was limited by the bismuth edge at approximately $k=10 \text{ \AA}^{-1}$ (13419 eV), because Klondyke tailings samples contain Bi concentrations ranging from 48 to 96 mg kg⁻¹.

Linear combination fitting

Fitting of the EXAFS (k -range 3-9 \AA^{-1} ; k^3 -weighting) and first-derivative of the near-edge region or X-ray absorption near edge spectra (XANES; 13020 to 13070 eV) spectra proceeded independently to test for internal consistency. The linear combination fits were constrained to be non-negative, but not forced to sum to unity. Fits were initially performed using a reference library of 12 lead-bearing minerals (**Fig. S1**) that was then restricted to a smaller set of references based on fit statistics and phases identified using other techniques: Raman spectroscopy, electron microscopy, and X-ray diffraction.

During linear combination fitting, the total number of references was limited to three or fewer components for each individual fit. The statistical measure, χ^2 , was used to compare the relative “goodness” of successive fits. Previous work has suggested the detection limit of phases in XANES is roughly 10% (Foster et al. 1998), thus components fit with a fraction less than 10% were removed and the spectra were refit to determine if the addition of the low concentration phase significantly improved fit statistics, which generally was not the case. After significant iterations of independent fits for different spectral regions, three reference spectra (plumbojarosite, anglesite, and iron oxide associated Pb [$\text{Pb}_{\text{ads-FeOx}}$]) were chosen because they adequately reconstructed all bulk and micro-focused sample spectra, and the use of additional phases did not significantly improve statistics. Final fits were performed using the same three components to fit the first-derivative XANES and EXAFS portions of the spectrum, although $\text{Pb}_{\text{ads-FeOx}}$ did not improve the statistics of bulk fits.

Shell-by-shell fitting

The Pb2 site (96% of Pb atoms) in the plumbojarosite structure (Szymanski 1985) was used to create an atomic cluster of 353 atoms (using the program Atoms (Ravel 2003)) that was then employed to calculate theoretical phase shift and amplitude functions for single and multiple scattering paths from central Pb using FEFF 6 Lite (Rehr 1992). Sixpack used the theoretical functions generated by FEFF to fit the experimental plumbojarosite reference and

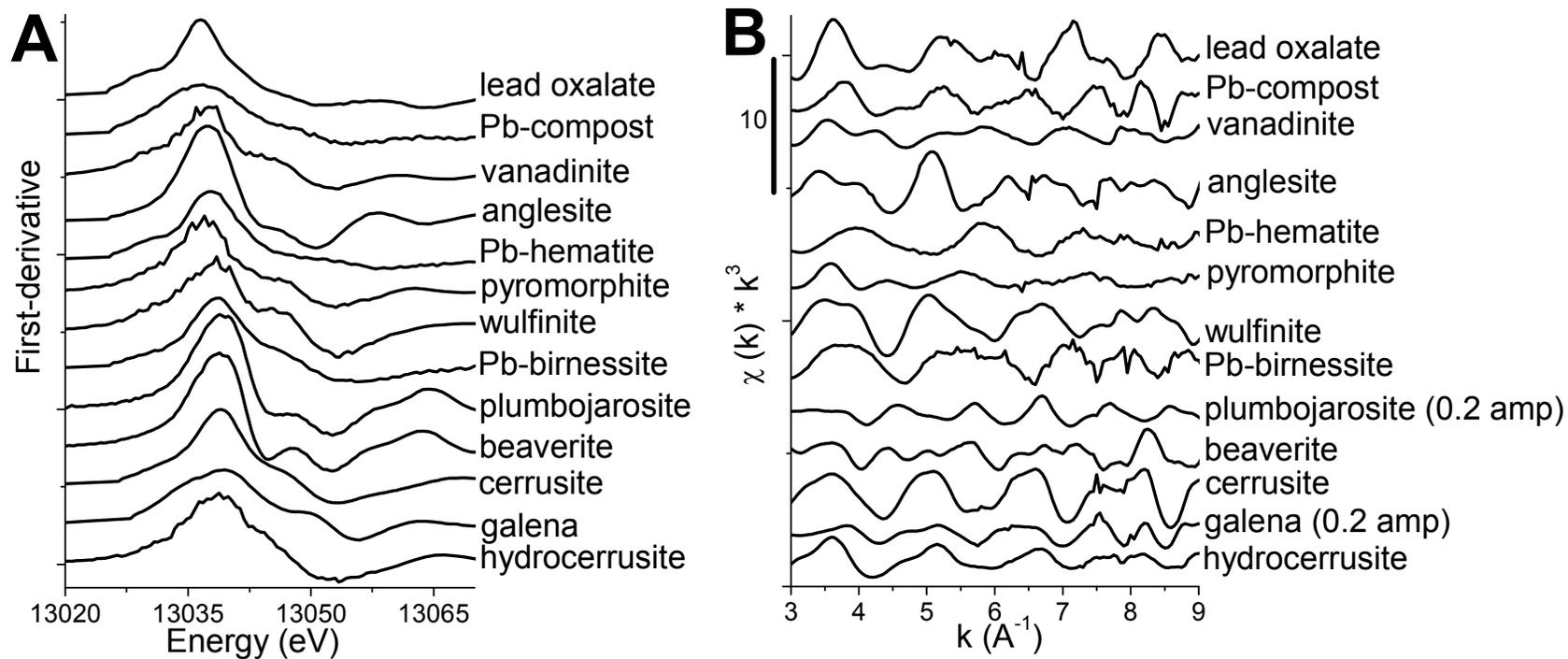
tailings EXAFS spectra over the k-range 3 to 9 \AA^{-1} with k^3 weighting. To limit the fit variables, coordination numbers were confined to values of the crystallographic structure of plumbojarosite (three shells, each with N=6) and the amplitude reduction factor (S_0^2) was set to unity. For all spectra, the fitting range had 11 degrees of freedom and seven variables. Spline error was avoided by fitting several spline functions for each sample and reference, as described above.

Table S1: Lead reference compounds analyzed by XAFS.

Reference	Formula	Source ^a	ID or [Pb _{solid}]
Lead oxalate	PbC ₂ O ₄	Syn.	unknown
Pb-compost	Pb sorbed to dairy compost	Syn.	500 mg kg ⁻¹
vanadinite ^b	Pb ₅ (VO ₄) ₃ Cl	UAM	unknown
anglesite	PbSO ₄	SA	lot 10011KE
Pb- hematite	Pb sorbed to Fe ₂ O ₃	Syn.	9600 mg kg ⁻¹
pyromorphite ^b	Pb ₅ (PO ₄) ₃ Cl	DRS	unknown
wulfenite ^b	PbMoO ₄	UAM	unknown
Pb-birnessite	Pb sorbed to δ-MnO ₂	Syn.	805 mg kg ⁻¹
plumbojarosite	PbFe ₆ (SO ₄) ₄ (OH) ₁₂	UAM	5751
beaverite	PbCuFe ₂ (SO ₄) ₂ (OH) ₆	RRUFF	R060400
cerrusite	PbCO ₃	Wards	lot 1360
galena	PbS	SA	lot 00508MH
hydrocerrusite ^b	Pb ₃ (CO ₃) ₂ (OH) ₂	Wards	lot AD3017

^a Reference minerals were obtained from several sources including: Synthesized in the laboratory (syn.), University of Arizona Mineral Museum (UAM), Da Rock Shop in Tucson, AZ (DRS), Sigma-Aldrich (SA), Wards Scientific (Wards), and the RRUFF Project (RUFF) at University of Arizona. ^b XAS collected at room temperature.

Figure S1: XAS spectra of reference compounds listed in Table 1. A) First derivative of the XANES region (arbitrary units), B) normalized EXAFS. Plumbojarosite and galena EXAFS spectra are plotted with 0.2 amplitude



REFERENCES

- Dold B. 2003. Speciation of the most soluble phases in a sequential extraction procedure adapted for geochemical studies of copper sulfide mine waste. *J Geochem Explor* 80(1): 55-68.
- Foster AL, Brown GE, Tingle TN, Parks GA. 1998. Quantitative arsenic speciation in mine tailings using X-ray absorption spectroscopy. *Am Mineral* 83(5-6): 553-568.
- Hayes SM, White SA, Thompson TL, Maier RM, Chorover J. 2009. Changes in lead and zinc lability during weathering-induced acidification of desert mine tailings: Coupling chemical and micro-scale analyses. *Appl Geochem* 24(12): 2234.
- King EG. 1958. Low temperature heat capacities and entropies at 298.15-degrees-K of lead sesquioxide and red and yellow lead monoxide. *J Am Chem Soc* 80(10): 2400-2401.
- McKenzie RM. 1971. Synthesis of birnessite, cryptomelane, and some other oxides and hydroxides of manganese. *Mineral Mag* 38(296): 493-502.
- Ravel B. 2003. Atoms 3.0.1. Available:
<http://cars9.uchicago.edu/~ravel/software/aboutatoms.html> [accessed June 13, 2009].
- Rehr JJ. 1992. Ab initio multiple-scattering x-ray absorption fine structure and x-ray absorption near edge structure code. University of Washington.
- Schwertmann U, Cornell RM. 2000. Iron oxides in the laboratory: preparation and characterization. Weinheim, NY: Wiley-VCH.
- Skoog DA, West DM, Holler FJ. 1996. Fundamentals of Analytical Chemistry. New York: Saunders College Publishing.
- Szymanski JT. 1985. The crystal-structure of plumbojarosite $\text{Pb}[\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6]_2$. *Can Mineral* 23: 659-668.