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Changes in zinc speciation with mine tailings acidification in a semi-arid weathering environment

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Abstract

High concentrations of residual metal contaminants in mine tailings can be transported easily by wind and water, particularly when tailings remain unvegetated for decades following mining cessation, as is the case in semi-arid landscapes. Understanding the speciation and mobility of contaminant metal(loid)s, particularly in surficial tailings, is essential to controlling their phytotoxicities and to revegetating impacted sites. In prior work, we showed that surficial tailings samples from the Klondyke State Superfund Site (AZ, USA), ranging in pH from 5.4 to 2.6, represent a weathering series, with acidification resulting from sulfide mineral oxidation, long-term Fe hydrolysis, and a concurrent decrease in total (6,000 to 450 mg kg⁻¹) and plant-available (590 to 75 mg kg⁻¹) Zn due to leaching losses and changes in Zn speciation. Here, we used bulk and micro-focused Zn K-edge X-ray absorption spectroscopy (XAS) data and a six-step sequential extraction procedure to determine tailings solid phase Zn speciation. Bulk sample spectra were fit by linear combination using three references: Zn-rich phyllosilicate (Zn_{0.8}talcl), Zn sorbed to ferrihydrite (Zn_{ads}FeO_x), and zinc sulfate (ZnSO₄·7H₂O). Analyses indicate that Zn sorbed in tetrahedral coordination to poorly-crystalline Fe and Mn (oxyhydr)oxides decreases with acidification in the weathering sequence, whereas octahedral zinc in sulfate minerals and crystalline Fe oxides undergoes a relative accumulation. Micro-scale analyses identified hetaerolite (ZnMn₂O₄), hemimorphite (Zn₄Si₂O₇(OH)₂·H₂O) and sphalerite (ZnS) as minor phases. Bulk and micro-focused spectroscopy complement the chemical extraction results and highlight the importance of using a multi-method approach to interrogate complex tailings systems.

1. INTRODUCTION

Mine tailings are a significant source of anthropogenic Zn in the environment because their metal-rich particles can be readily dispersed by water and wind erosion. This is particularly true in arid regions, where wind particle dispersion is a principal mechanism of contaminant transport. ¹ Revegetation of mine tailings, an effective method of reducing erosion, is hindered by their low pH, solubility of salts and toxic metals, and poor soil structure. ^{2,3} Zinc, which is commonly associated with sulfide ore-derived mine tailings, is generally soluble under acidic conditions, and can be phytotoxic at pore water concentrations

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6. SUPPORTING INFORMATION AVAILABLE

Text, tables, and figures describing sample preparation, characterization, and spectroscopic analysis. This information is available free of charge via the Internet at <http://pubs.acs.org>.

exceeding *ca.* 30 μM (2 mg L^{-1}), thereby limiting revegetation.⁴ The toxicity of Zn to plants depends on its bioaccessibility.⁵ This is a function of its molecular-scale speciation, which can be altered by geochemical weathering of the sulfide-rich tailings, particularly the near surface portion that undergoes rapid oxidation after deposition.

The oxidation of primary sulfides releases sulfate, metal cations and protons to solution. Release of protons is buffered by their consumption during dissolution of calcite and silicate minerals, but kinetic limitations of silicate weathering often lead to progressive acidification of tailings.⁶ Dissolution of tailings primary minerals may result in Zn translocation or supersaturation of pore waters with respect to secondary phases, such as sulfate salts, iron hydroxysulfates, silicates and oxides.⁷ The solids hosting trace metals in multi-component soils and sediments have long been investigated using sequential chemical extractions (SE) that target operationally-defined constituents, but such procedures suffer from shortcomings in precision of target phase dissolution.⁸ More recently these techniques have been profitably combined with direct measurement of metal speciation using X-ray absorption spectroscopy (XAS).^{9,10}

XAS has been used to investigate Zn speciation in several natural sedimentary systems, including dredged sediments prior to and during phytostabilization,^{11,12} soils contaminated by galvanized power line tower runoff,^{13–15} smelting impacted soils,^{10,16,17} and sulfide mine tailings.^{9,18} Schuwirth et al. combined SE and XAS to examine Zn speciation in temperate sulfide mine tailings in the northern Rhineland of Germany.⁹ Zn-rich phyllosilicates, adsorbed Zn species, and Zn coprecipitated with goethite were evident in both oxidized surface (pH 5.5) and reduced subsurface (pH 7.2) tailings, along with sphalerite in subsurface samples. Zn-rich phyllosilicates have been reported in previous studies,^{12,16} where Zn substitution occurs in the octahedral sheet of a 2:1 talc-like clay mineral, with the extent of substitution depending on aqueous phase Zn concentration. Zn phyllosilicates precipitated in the laboratory have a distinctive EXAFS feature at 5.2 $\text{\AA}^{-1}$ from silicon and aluminum backscattering atoms in the surrounding tetrahedral sheets.¹⁹ Iron(III) and Mn(IV)-(oxyhydr)oxides are also high affinity sorbents for Zn in natural systems,^{9,12,18} and XAS indicates that, when present at low concentration, Zn sorbs preferentially via inner-sphere tetrahedral coordination to ferrihydrite and birnessite.^{20–22}

In prior research at the Klondyke State Superfund (AZ, USA) site we observed near complete depletion of parent sulfide minerals along with a large gradient in pH (8 to 2.6) across the top 0.6 m of a 50 year old Zn-rich tailings pile, and concluded that this pH gradient corresponds to a weathering sequence leading to progressive tailings acidification.²³ In separate experiments, we assessed the influence of Klondyke tailings pH and chemistry on the germination and growth of a range of native desert plant species, including plant metal uptake into above- and below-ground biomass.²⁴ In those studies, we found that plant growth was enhanced in acidic (pH 3.9) relative to more circumneutral (pH 5.4) tailings,²⁴ and we hypothesized that this was due to changes in metal speciation that accompany tailings acidification. In the current study, we employed chemical extractions, XAS, and micro-focused X-ray fluorescence ($\mu\text{-XRF}$) to test the hypothesis that a trend in Zn speciation accompanies progressive tailings acidification.

2. EXPERIMENTAL

2.1 Sample collection and preparation

Flotation mill tailings derived from low temperature hydrothermal and breccia deposits of lead and zinc sulfide ores from the Aravaipa mining district (Graham County, AZ)²⁵ were collected from the Klondyke State Superfund site (AZ, ID # 1236). Four samples, ranging in pH from 2.6 to 5.4 (pH denoted by subscript in sample names), were chosen for in-depth

study. After collection, the tailings were sieved to isolate the fine earth (< 2 mm) fraction and air dried for two weeks. Air-dried samples were used for bulk XAS analysis and a 2.5 cm diameter thin section of each sample was prepared for micro-focused work by impregnation with EPOTEC 301-2FL epoxy under vacuum, and cured for three days before thin sectioning to 30 μ -m, polishing on both sides, and mounting on quartz slides at Spectrum Petrographics (Vancouver, WA). Reference phases were obtained from repositories or synthesized (Zn-rich talc, Zn sorbed to hematite, ferrihydrite, and acid birnessite) in the laboratory (see Supplementary Information [SI]).

2.2 Chemical analysis

Tailings pH was measured in the supernatant solution derived from a saturated paste (1:1 solid-solution mass, 1 h reaction time) after centrifugation and decantation to separate the solid. Triplicate diethylenetriaminepentaacetic acid (DTPA) extractions were performed as described in SI to assess “plant bioavailable” Zn and related metal pools. A six step SE was used to quantify Zn (plus Fe, Mn, and Si) in operationally-defined target phases.²⁶ The procedure includes the following steps and target metal species: (i) “ H_2O ”: water extraction of soluble salts; (ii) “*AA*”: ammonium acetate extraction of exchangeable ions and calcite; (iii) “*AAO 25°C*”: ammonium oxalate at 25°C extraction of short-range-order Fe, Al and Mn-(hydr)oxides and poorly-crystalline jarosite; (iv) “*AAO 80°C*”: ammonium oxalate at 80°C extraction of crystalline Fe, Al, and Mn (hydr)oxides and jarosites; (v) “ H_2O_2 ”: hydrogen peroxide oxidative extraction of organic matter and secondary supergene sulfides; and (vi) “*Acid*”: concentrated HCl and HNO₃ extraction of primary sulfides. The Zn content of the “*Residual*” was then determined by bulk X-ray fluorescence (see SI) and the total metal mass was calculated as the sum of the six extracts plus residual.

2.3 Micro-focused XRF map collection and analysis

Micro-focused XRF maps and μ -XAS spectra were collected on thin sections at Stanford Synchrotron Radiation Lightsource (SSRL) on beam lines 2-3 and 10-2 (see SI for details). Elemental mapping was performed in 2.5 μ -m steps with a 250 ms dwell time using a *ca.* 2.5 μ -m diameter beam. The thin sections were placed directly in front of an X-ray beam tuned to 13050 eV, just above the Pb L_{III} absorption edge (13035 eV). The XRF maps were analyzed using the Microanalysis Toolkit (version 0.50)²⁷ by standardizing linearly scaled maps from 0 (black) to 1000, 1000, or 7000 (white) counts for Zn, Mn, and Fe, respectively.

2.4 XAS collection and analysis

2.4.1. Data collection—Zinc K-edge X-ray absorption spectra were collected at room temperature at the Advanced Photon Source (APS) on GSECARS 13-BM and at SSRL on beam lines 10-2 and 11-2. Briefly, measurements were made using 2 mm vertical slits with transmission geometry for references and fluorescence geometry for tailings and sorbate samples, using a germanium detector. Zinc μ -XAS spectra were collected over an extended XANES region using the same beam conditions that were used for mapping. Additional details are provided in the SI.

2.4.2. Data reduction—XAS spectra were averaged and analyzed using SIXPACK (version 0.66).²⁸ Zinc energy was calibrated using a Zn foil (E_0 =9659 eV, maximum of first derivative). Fit statistics were optimized using the following background subtraction parameters: a linear pre-edge fit (−210 to −100 eV below edge) that was extended through the spectrum, a quadratic post edge fit to normalize edge step heights (above edge 150 to *ca.* 570 eV for bulk and 40 to *ca.* 150 eV for μ -XAS), low R-space reduction factor (R_{bkg} =0.9), and spline range 1 to 11.5 with no spline clamps.

2.4.3. Linear combination fitting—Fitting of Zn normalized whole-spectrum (9650 to 10050 eV, hereafter referred to as XAFS) and EXAFS (k -range 2–11 Å⁻¹; k^3 weighting) proceeded independently. Linear combination fits (LCF) to bulk Zn spectra were initially performed using the entire reference spectral library (13 spectra, Table S1, Fig. S1). Bulk fits were constrained to be non-negative, but not forced to sum to unity. The final fit components were selected after iterative fitting because they consistently resulted in best fits (based on reduced χ^2). Fits to μ -XANES spectra required the additional phases for adequate reconstruction. Sensitivity testing was performed as described in the SI.

3. RESULTS

3.1 Tailings Zn concentration and lability

Total and DTPA-extractable (proxy for plant-available) Zn decreased with decreasing pH in the samples examined, whereas the DTPA-extractable fraction ranged from 9–20% of the total Zn mass (Table 1). Sequential extraction data show that Zn shifts from dominantly labile, sorbed forms (AA- and AAO 25°C-extractable) in high pH tailings (T_{5,4} and T_{4,2}), to H₂O-soluble, AAO 80°C-extractable and Residual pools for the low pH (3.9 and 2.6) samples (Table 1). Corresponding data for Fe, Mn and Si are included for direct comparison.

3.2 Grain-scale Zn and Mn speciation

The μ -XRF images (Fig. 1A) demonstrate grain-scale elemental correlations and provide indications of stoichiometric relationships (Fig. 1B). All tailings show Zn sub-population correlation with Fe, and the higher pH samples (T_{5,4} and T_{4,2}) also show Zn correlation with Mn (Fig. 1B and Fig. S2). Micro-focused XANES of regions with high Zn concentration (i.e., “hotspots”) identified several Zn-bearing phases, including hetaerolite (ZnMn₂O₄), hemimorphite (Zn₄Si₂O₇(OH)₂·H₂O), Zn_{0.8}talca ((Zn_{0.8}Mg_{0.2})₃Si₄O₁₀(OH)₂), and several 2–3 μ -m diameter particles of sphalerite (ZnS) were observed in T_{2,6} (Fig. 1C).

3.3 Bulk Zn speciation

Extracted XAFS (full spectrum, emphasizing XANES) and EXAFS spectra were fit independently with linear combinations of three components: Zn_{0.8}talca_(s), and Zn_{ads-FeOx(s)}, and ZnSO₄·7H₂O_(s). In qualitative agreement, both XAFS and EXAFS fits require a decrease in the relative contribution of the Zn_{ads-FeOx} reference and an increase in that of ZnSO₄·7H₂O_(s) with increasing tailings acidification (Table 2, Fig. 2). The mineral phases identified by micro-focused XANES (hetaerolite, hemimorphite, sphalerite) did not significantly improve fits of bulk sample spectra. EXAFS spectra indicate local bonding environment, thus the reference spectra must be considered as proxies representing distinct Zn coordination environments, not interpreted to infer unique identities of Zn-bearing phases. The distance to the first oxygen shell in the tailings have mean Zn-O bond distances of 2.03 to 2.13 Å, indicating a mixture of tetrahedral (~1.96 Å) and octahedral (~2.10 Å) coordination (Fig. 2).^{11–17} Hence, Zn_{0.8}talca represents Zn in trioctahedral coordination as occurs in 2:1 phyllosilicates with a high degree of Zn incorporation in the octahedral sheet (Zn-O: 2.14 Å), Zn_{ads-FeOx} represents Zn adsorbed to (oxyhydr)oxide surfaces in dominantly tetrahedral, with some octahedral coordination (Zn-O: 2.03 Å) and a relatively weak second shell signal, and ZnSO₄·7H₂O represents Zn in octahedral coordination with a weak second shell contribution (Zn-O: 2.13 Å).

4. DISCUSSION

4.1 Zinc speciation in mine tailings undergoing weathering induced acidification

Our prior work indicated that the samples studied here exhibit similar physical and chemical properties across a range of parameters (aqueous electrical conductivity, cation exchange capacity, total sulfur, organic and inorganic carbon, total nitrogen, particle size distribution), but that the observed decrease in pH is concurrent with progressive mineral weathering of sulfides and primary silicates to produce metal sulfates, oxyhydroxides and secondary silicates.²³ Primary sphalerite, the original source of Zn in these tailings, underwent near complete dissolution in the top 0.6 m of tailings in 50 y since deposition.²⁵ Data from the current study indicate that during this tailings acidification process, Zn partitions from relatively labile AA- and AAO 25°C- *extractable* pools into both *H₂O-soluble* and also recalcitrant (AAO 80°C and *Residual*) pools (Table 1). The XAS LCFs indicate the tailings contain a mixture of Zn coordination environments that include those represented by (i) trioctahedral occupancy of a phyllosilicate sheet ($\text{Zn}_{0.8}\text{talc}$), (ii) tetrahedral coordination on the surface of ferrihydrite ($\text{Zn}_{\text{ads-FeOx}}$), and (iii) octahedral coordination as occurs in goslarite ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) (Table 2 and Fig. 2). EXAFS LCFs suggest progressive acidification results in predominance (> 80%) of “goslarite-like” coordination for the two most acidic samples, at the expense of “Zn-talc-like” and “ $\text{Zn}_{\text{ads-FeOx}}$ -like” coordination, whereas the XAFS LCFs suggest a lower prevalence of goslarite-like Zn and persistence of Zn-talc-like coordination through the full weathering sequence (Table 2). In support of the XAFS phase quantifications, the SE indicates that *ca.* half the Zn mass remains following all SE steps for the two most acidic samples. This residual would be expected to contain SE-recalcitrant silicates and oxides.²³ These results can be reconciled by considering the diversity of information provided by the various data sets in the context of prior research on Zn speciation.

4.1.1 Zn phyllosilicate and short-range-order species in higher pH tailings—

Jacquat et al.,¹³ demonstrated that Zn-talc can be solubilized by reaction with acetic acid (used in our SE AA step, Table 1). We found that a large fraction of Zn (34–39%) was indeed liberated by AA reaction in the higher pH tailings (Table 1) where bulk and microfocused XAS data both clearly indicate such Zn coordination is prevalent (Table 2, Figs 1C, 2). The presence of Zn-talc in the two higher pH tailings is consistent with laboratory stability measurements that also suggest this phase is likely to become unstable with progressive tailings acidification ($\text{pH} < 5$).¹⁶ Incorporation of Zn in the trioctahedral sheet of secondary phyllosilicates has been previously reported to occur in a variety of circumneutral geomedias.^{9,13–15} but this is the first report of its importance in an acidic desert mine tailings system.

While the largest mass fraction of Zn in the higher pH tailings ($\text{T}_{5.4}$ and $\text{T}_{4.2}$) is solubilized during the AA SE step, the second largest fraction is released during the AAO 25°C step, when significant portions of total Fe and Mn are also released (Table 1). This step presumably dissolves short-range-order (SRO) Fe and Mn (oxyhydr)oxides that are high affinity sorbents for Zn, as has been well-documented in several laboratory^{21,22} and field^{9,12,18} studies. Prior EXAFS studies have shown that Zn sorbs to both ferrihydrite and birnessite in tetrahedral coordination (represented in this study by $\text{Zn}_{\text{ads-FeOx}}$), particularly at low aqueous Zn concentration.^{21,22} The μ -XRF maps show micrometer-scale Zn correlation with Fe and Mn, with Zn-Mn correlation being most apparent in the higher pH tailings (Figs. 1A,B, S2). Indeed, the absence of Zn-Mn association in the two low pH tailings (Fig. 1B) is coincident with a large decrease in total and AAO extractable fraction of Mn (Table 1), suggesting progressive depletion of poorly-crystalline Mn sorbent with tailings acidification. The AAO 25 °C-*soluble* fraction of Zn likewise decreases with acidification (Table 1). These patterns are consistent with bulk XAS fits showing a decrease in the fraction of sorbed

tetrahedral Zn ($Zn_{adsFeOx}$) (Table 2, Fig. 2). Zinc sorption to both ferrihydrite and birnessite exhibits strong pH dependence; sorption edges occur at pH < 5.0 and 5.5, respectively.^{29,30} Hence decreased surface charge with decreasing pH likely also contributes to the diminished relative importance of these sorbents for Zn speciation at low tailings pH.

4.1.2 Persistence of Zn in sulfate and well-crystallized oxide solids in acidified tailings—The bulk XAS analyses (Table 2, Fig. 2) indicate that, with increased tailings acidification, there is a relative accumulation of Zn in coordination environments represented in this study by reference $ZnSO_4 \cdot 7H_2O_{(s)}$. Zinc sulfate minerals – including goslarite [$ZnSO_4 \cdot 7H_2O$], bianchite [$ZnSO_4 \cdot 6H_2O$], and gunningite [$ZnSO_4 \cdot H_2O$] – have been observed to accumulate in the near-surface of tailings piles when water flux is insufficient to leach solubilized Zn to the subsurface and the precipitation of other secondary minerals is thermodynamically or kinetically unfavorable.³¹ Zinc coordination in sulfate salts is uniformly octahedral,^{33,34} and the fact that the fraction of “goslarite-like” Zn coordination in the Klondyke tailings increases with progressive weathering-induced acidification is reflected in both sets of bulk XAS data fits (Table 2, Fig. 2). This trend is consistent *qualitatively* with an increase in the fraction of *H₂O-extractable* Zn for the lowest pH tailings; relatively rapid dissolution in water is characteristic of Zn sulfate salts.³¹ However, while the EXAFS LCFs suggest a predominance (> 80%) of goslarite-like Zn coordination for the two most acidic samples, the SE data indicate that most of the Zn mass in these samples survives water extraction and nearly half remains in the *residual* fraction following all SE steps. The *Residual* Zn fraction could include SE-recalcitrant, secondary phyllosilicates; consistent with the XAFS LCF results.

For these low pH samples, it is necessary to reconcile (i) EXAFS data indicating *ca.* 80% “goslarite-like” coordination with (ii) SE mass balance data indicating that 45–46% of total Zn is recalcitrant to SE dissolution. First, we note that the Zn-hematite EXAFS spectrum (not used in the LCFs but shown in Fig. S1) is similar to that for goslarite particularly at low *k* because of octahedral coordination and weak second shell contribution. This suggests that the goslarite reference may be accounting to some extent for octahedral complexation at Fe oxide surfaces, an important mode of Zn adsorption particularly for crystalline Fe oxides such as hematite and goethite. Second, the fraction of Zn liberated by AAO 80 °C increases with decreasing pH (Table 1). This extraction includes more crystalline Fe oxides and jarosites than are solubilized in AAO 25 °C^{23,26} and also constitutes a consistently large fraction of total Fe in these tailings (Table 1). Taken together, these SE and XAS data sets suggest that the presence of other octahedral Zn coordination environments (e.g., well-crystalline oxides or phyllosilicates) could be contributing to the fraction attributed by EXAFS LCFs to $ZnSO_4 \cdot 7H_2O_{(s)}$ in $T_{3,9}$ and $T_{2,6}$. Indeed, the weathering-induced transformation of ferrihydrite to goethite in the presence of transition metals, for example, has been shown to diminish the kinetics of metal sorbate release to solution.³⁵ In any case, the *H₂O-extracted* Zn fraction (20%, Table 1) provides a conservative estimate of aqueous-labile Zn sulfates, indicating an increase in soluble sulfate salts over the course of tailings acidification. The persistence of such phases through the acidification process that accompanies tailings diagenesis in semi-arid landscapes represents an important source of readily-bioaccessible Zn.

4.2 Comparison of XAFS and EXAFS fits

XANES and EXAFS data emphasize distinct spectral features. If references selected do not replicate the precise coordination environments of the multi-component samples they are used to fit, independent LCF quantifications performed on XANES and EXAFS will diverge as was observed in the present study. Factors that contribute to divergence include similarity of spectral features among distinct references (e.g., Zn-hematite and $ZnSO_4 \cdot 7H_2O_{(s)}$ exhibit

similar EXAFS, Fig. S1), or differences between sample and reference stoichiometry (e.g., synthetic Zn-talc may be of higher Zn content than that occurring in the tailings),^{9,13,15} and/or local order (e.g., synthetic Zn-talc may have a larger second shell contribution than comparable species in tailings).

However, as shown in the present study, a multi-faceted approach that combines complementary bulk and micro-focused XAS spectroscopy with chemical extraction data helps to constrain interpretations of Zn speciation in multi-component mine tailings and reconcile XAFS and EXAFS LCFs. The SE data constrained reference choices and interpretation of the LCF XAS fits, while μ -XRF and μ -XAS were used to confirm Zn phyllosilicate and sorbed Zn populations associated with Mn and Fe (oxyhydr)oxides. Micro-focused techniques were also able to identify minor Zn-bearing minerals (hetaerolite, hemimorphite, and sphalerite) that were not identified with bulk techniques.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. Grain-scale phase identification. A) micro-probe XRF maps (beam size *ca.* 2.5 μ -m), B) Correlation plots of Zn-Mn and Zn-Fe from all pixels in each XRF map, C) Zn μ -XANES of points indicated on XRF images (numbers 1–8; fits shown in dashed lines and fit information in Table 2).

Figure 2. Linear combination fits of XAFS (XANES region shown) and k^3 -weighted EXAFS regions. Fits to the XAFS are shown in blue dash-dot and fits to EXAFS are shown in red dashed lines (fit information in Table 2).

Table 1

Total and extractable metals in the Klondyke tailings

	Total	DTPA extractable	Sequential Extraction (percent of total)						Residual
	g kg ⁻¹	mg kg ⁻¹	H ₂ O	AA	AAO 25°C	AAO 80°C	H ₂ O ₂	Acid	
Zinc									
T _{5.4}	6.7(0.5)	590(50)	11(4)	34(5)	23(3)	9(1)	6.1(0.6)	12(1)	4.2(0.3)
T _{4.2}	4.1(0.2)	540(20)	0.6(0.1)	38(5)	34(3)	9.3(0.8)	3.6(0.5)	9(1)	5.23(0.3)
T _{3.9}	2.3(0.1)	440(20)	23(2)	3(2)	7(1)	12(6)	1.0(0.1)	8.0(0.6)	45(3)
T _{2.6}	0.42(1)	75.0(0.7)	15(2)	1.2(0.3)	1.0(0.1)	18(1)	0.8(0.4)	19(2)	46(2)
Iron									
T _{5.4}	18(1)	0.30(0.01)	0.2(0.1)	0.8(0.1)	10(2)	51(7)	3.5(0.6)	34.7(5)	>0.05
T _{4.2}	12.9(8)	1.11(0.06)	>0.05	0.45(0.03)	6.9(0.8)	64(6)	>0.05	28(4)	>0.05
T _{3.9}	9(3)	1.4(0.2)	0.3(0.1)	0.21(0.07)	18(6)	72(8)	0.07(0.01)	13(5)	>0.05
T _{2.6}	17(1)	206(9)	0.9(0.1)	2.4(0.2)	1.8(3)	39(4)	>0.05	56(6)	>0.05
Manganese									
T _{5.4}	8.5(3)	267(2)	6(2)	2.8(3)	23(2)	4.2(0.6)	1.2(0.1)	36(1)	26.9(0.9)
T _{4.2}	19.5(2)	141(3)	>0.05	1.6(0.1)	15(1)	2.1(0.2)	0.90(0.04)	3.0(0.1)	77.5(0.8)
T _{3.9}	10.23(2)	172(5)	1.80(0.05)	0.18(0.04)	1.1(0.1)	0.3(0.1)	>0.05	0.48(0.03)	96.2(0.2)
T _{2.6}	0.84(2)	200(20)	8(1)	0.4(0.1)	0.16(0.06)	0.54(0.04)	>0.05	0.40(0.05)	90(2)
Silicon*									
T _{5.4}	43.2(4)	62(4)	0.27(0.05)	2.6(0.2)	2.1(0.1)	3.3(0.2)	2.3(0.2)	5.2(0.6)	84.3(0.8)
T _{3.9}	38.8(2)	60(6)	0.08(0.01)	2.4(0.1)	0.37(0.05)	1.2(0.2)	3.0(0.2)	1.6(0.1)	96(1)

* Si data not available for T_{4.2} and T_{2.6}.

Table 2

Micro-focused XANES fits for data shown in Figure 1, and bulk whole-spectrum (XAFS) and k^3 -weighted EXAFS fits shown in Figure 2. In all cases, fraction of reference phases employed are shown as percent.

Sample	Zn _{0.8} talc	Zn _{ads} -FeOx	ZnSO ₄ ·7H ₂ O	hetaerolite	hemimorphite	sphalarite	chl ²
Micro-focused XANES							
T _{5.4}	1	95	0	0	0	0	0.8
	2	16	0	78	0	0	0.2
T _{4.2}	3	17	0	78	0	0	1.0
	4	0	0	0	95	0	1.3
	5	0	0	0	97	0	2.7
T _{3.9}	6	97	0	0	0	0	1.2
T _{2.6}	7	0	0	0	0	111	3.2
	8	0	0	0	0	110	2.2
XAFS							
T _{5.4}	53	47	0	0	0	0	0.26
T _{4.2}	60	40	0	0	0	0	0.15
T _{3.9}	56	0	44	0	0	0	1.6
T _{2.6}	52	0	46	0	0	0	2.8
k^3 -weighted EXAFS							
T _{5.4}	30	43	31	0	0	0	16
T _{4.2}	42	42	20	0	0	0	9.2
T _{3.9}	22	0	81	0	0	0	73
T _{2.6}	0	24	101	0	0	0	79