

Heavy Metal–Mineral Associations in Coeur d’Alene River Sediments: A Synchrotron-Based Analysis

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Abstract Nearly a century of mining activities upstream have contaminated Lake Coeur d’Alene and its tributaries with Pb, Zn, and other heavy metals. Heavy metal concentrations in sediments of the Coeur d’Alene watershed have been shown to be inversely proportional to the sediment size fraction; thus, analysis on a very small scale is essential to determine the mobility and stability of heavy metals in this environment. Micron-scale synchrotron-based methods were used to determine the association of heavy metals with solid phases in sediments of the Coeur d’Alene River. Bulk X-ray diffraction (XRD), extended X-ray absorption fine structure spectroscopy,

and synchrotron-based microfocused XRD combined with microfocused X-ray fluorescence mapping indicate the presence of crystalline Pb- and Zn-bearing mineral phases of dundasite [$\text{Pb}_2\text{Al}_4(\text{CO}_3)_4(\text{OH})_8 \cdot 3\text{H}_2\text{O}$], coronadite [$\text{PbMn}_8\text{O}_{16}$], stolzite [PbWO_4], mattheddleite [$\text{Pb}_{10}(\text{SiO}_4)_{3.5}(\text{SO}_4)_2\text{Cl}_2$], bindheimite [$\text{Pb}_2\text{Sb}_2\text{O}_7$], and smithsonite [ZnCO_3]. Likely phases for Zn and Pb adsorption were ferrihydrite, diaspore [$\text{AlO}(\text{OH})$], manganite [$\text{Mn}^{(\text{III})}\text{O}(\text{OH})$], muscovite [$\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH},\text{F})_2$], biotite [$\text{K}(\text{Fe},\text{Mg})_3\text{AlSi}_3\text{O}_{10}(\text{F},\text{OH})_2$], and montmorillonite [$\text{Na}_{0.3}(\text{Al},\text{Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$]. The large predominance of Fe and Mn (hydr)oxides over other

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sorbent minerals suggests that the metal sorption behavior is dominated by these (hydr)oxide phases.

Keywords Coeur d'Alene · Zinc · Lead · Sediment Characterization · XAS

1 Introduction

The waters and sediments of the Coeur d'Alene River (CdAR) in northern Idaho have been impacted by decades of mining operations within the Coeur d'Alene mining district. Lake Coeur d'Alene (LCdA) is fed at the southern portion of the lake by the St. Joe River and CdAR (Horowitz et al. 1992). These two rivers contribute approximately 94% of the influent flow into LCdA (Horowitz et al. 1995a). CdAR is composed of two main tributaries, the South Fork of the CdAR and its tributaries which flow through the Coeur d'Alene Mining district and the North Fork which joins the South Fork before continuing through an area of lateral lakes and deltas into LCdA (Horowitz et al. 1992; Balistrieri et al. 2003). The South Fork of the CdAR is of particular interest as it and its tributaries provide primary drainage for the Coeur d'Alene Mining district (Horowitz et al. 1992, 1995a).

The history of this district as well as the type of ore deposits and mineralogy has been summarized by Leach and others (Leach et al. 1985; Rosenberg and Larson 2000; Fleck et al. 2002; Mauk and White 2004; Panneerselvam et al. 2006). The mineralogy of the Coeur d'Alene Mining District consists primarily of quartz [SiO₂] and siderite [FeCO₃] veins containing deposits of galena [PbS], sphalerite [ZnS], and tetrahedrite [Cu₁₂Sb₄S₁₃] (Leach et al. 1985). Pyrite [FeS₂], chalcopyrite [CuFeS₂], and pyrrhotite [Fe_xS, x=0.8,1] are also locally abundant (Leach et al. 1985). Fe minerals including siderite, magnetite, pyrite, pyrrhotite, goethite, hematite, and ferrihydrite have been reported in sediments of LCdA and in the upstream mining district (Farrand and Harsanyi 1997; Cummings et al. 2000; Toevs et al. 2006).

Analyses of the sediment and water in the Coeur d'Alene system have been examined by others focusing on geology and geochemistry (Grieco 1981; Farrand and Harsanyi 1997; Rosenberg and Larson 2000; Fleck et al. 2002; Mauk and White 2004), as well as surface and subsurface sediment contamination and benthic transport (Maxfield et al.

1974a; Reece et al. 1978; Horowitz et al. 1992, 1995a, b; Horowitz 1993; Woods and Beckwith 1997; Harrington et al. 1998a, b; La Force et al. 1998, 1999; Winowiecki 2002; Kuwabara et al. 2003; Toevs et al. 2006). Contamination of lateral lakes adjacent to the delta (Harrington et al. 1998a; Sprenke et al. 2000; Bostick et al. 2001), CdAR and upstream tributary contamination (Maxfield et al. 1974b; Reece et al. 1978; Paulson 1997; Farag et al. 1998, 2000; La Force et al. 1998; Balistrieri et al. 2003; Box et al. 2005), and downstream of LCdA (Grosbois et al. 2001) have also been studied. Horowitz et al. (1995a) found that the CdAR and adjacent lake sediments were the most heavily contaminated. Heavy metals in the delta region of LCdA appear to be associated with an operationally defined sulfidic phase (Harrington et al. 1998b), while those elsewhere in LCdA appear to be predominantly associated with the more mobile hydroxides (Horowitz et al. 1995a; Woods and Beckwith 1997), though there is some controversy on this point (Horowitz et al. 1999).

Of concern in the CdAR system is the potential contamination of unpolluted sediment from remobilization of heavy metals in the fine fraction. Remobilization may occur from any of the following processes: (1) physical entrainment of the small heavy-metal-laden particles from the upper sediment column into the river (Kalnejais et al. 2007), (2) adsorption of toxic metals to metal (hydr)oxides (e.g., ferrihydrite), clays, and organic compounds (e.g., humics, fulvics, citrate) followed by transport of these bound metals in the water column (Lothenbach et al. 1997; Tonkin et al. 2002; Balistrieri et al. 2003), and (3) reductive dissolution of mineral phases resulting in release of adsorbed or co-precipitated heavy metals (Fredrickson et al. 2001; Sengör et al. 2007). Additionally, micron- and smaller-scale particles are often more reactive and can be more bio-available (Oberdorster et al. 2005).

Until recently, phase association of heavy metals in sediments could only be inferred by a combination of electron microscopy, selected-area electron diffraction, and elemental analysis (Geesey et al. 2008). In the present study, we have attempted to characterize the mineral phases and geochemistry present in CdAR sediments, focusing on the micron scale, using synchrotron-radiation-based techniques in an effort to identify mineral phases at the micron scale and their potential for remobilization

2 Materials and Methods

2.1 Study Area, Sediment Sampling, and Characterization

Twenty-eight sample cores (15 cm) were taken 2.9 km (Fig. 1) upstream of Harrison, Idaho, off of East Blue Lake Road [N (47° 28' 43.8") W (116° 43' 59.6")]. Samples were collected in April 2005 using 2-in. schedule 20 polyvinylchloride (PVC) piping with plastic caps. The PVC sampler was hand-driven into undisturbed sediments under between 30 and 60 cm of water and capped while underwater. Sealed samples were placed on ice in plastic bags and transported directly to laboratories at Washington State University (WSU) where they were stored at -25°C . River water was collected at approximately 30 cm in depth from a total water depth of 60 cm in 1 L acid-washed Nalgene® containers, capped underwater to prevent head space contamination, and stored on ice. Upon arrival at WSU, water samples were stored at 4°C for 48 h until analysis.

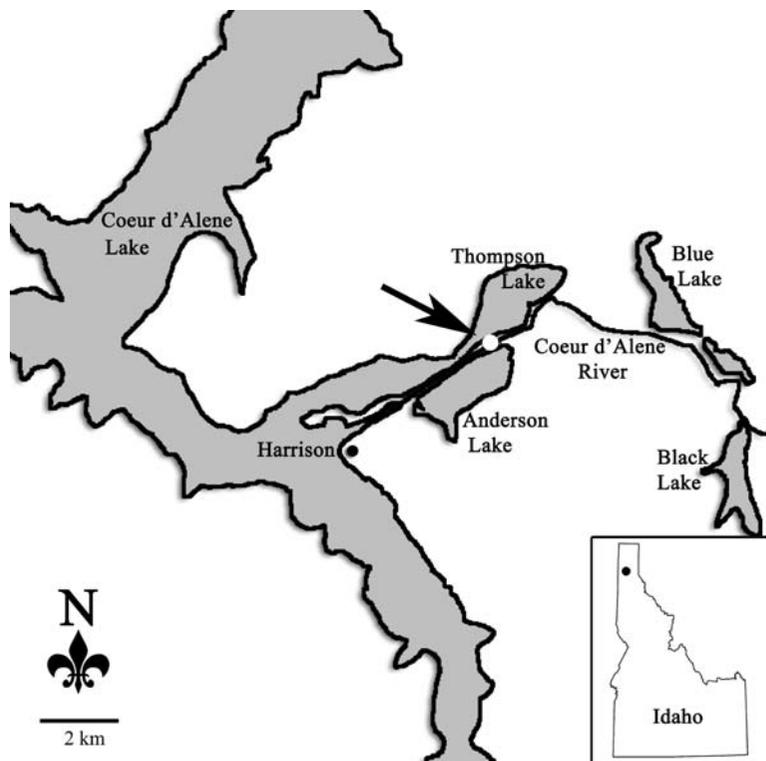
2.2 Water Analyses

The CdAR temperature was measured using an alcohol thermometer at 5.5°C . Dissolved oxygen (6.7 ppm) was measured using a portable dissolved oxygen meter (Extech Instruments Model 407510). For pore water extraction, intact (0–15 cm) frozen cores were thawed in an anaerobic chamber (Forma Scientific Inc. Model 1025), placed in acid-washed Nalgene® bottles, sealed, and centrifuged at 7,000 rpm for 20 min. The supernatant was removed in an anaerobic chamber. Samples were filtered ($0.45\ \mu\text{m}$) and acid-stabilized before being analyzed for alkalinity, total organic carbon, cations, anions, and trace metals at the Analytical Sciences Laboratory at the University of Idaho (EPA methods 200.7, 200.8, 300.0, 310.7, and 415.1).

2.3 Sediment Analyses

Visual observations of the sediment cores showed no distinct redox zones (as observed by lack of distinctly

Fig. 1 Map of study area [N (47° 28' 43.8") W (116° 43' 59.6")] on Coeur d'Alene River and adjacent area; *Inset*: State of Idaho. *Black arrow* shows the sampling site



colored zones) and appeared to be yellowish to yellowish brown, fine-grained sandy-silt, and homogeneous with the exception of occasional organic matter (primarily leaf debris) distributed within the core. Due to the homogenous nature of the sampled sediments, the cores were uniformly split in 5-cm sections for bulk analyses, starting from the sediment–water interface.

Well-mixed sediments from three intact cores (0–15 cm) were dried under 90% N₂/5% H₂/5% CO₂ in an anaerobic chamber, sealed under anaerobic conditions, and shipped to the Advanced Light Source at the Lawrence Berkeley National Laboratory where microfocused X-ray diffraction (μ XRD) and fluorescence (μ XRF) mapping were performed. Samples were prepared as described previously by Ginder-Vogel et al. (2005). Kapton[®] tape enclosed the sediment samples to prevent oxidation. The samples were analyzed on beamline 10.3.2 using a water-cooled Si (111) monochromator, two Si mirrors in Kirkpatrick-Baez geometry, and a Bruker X-ray charge-coupled device camera at 14,000 keV corresponding to a wavelength of 0.8856 Å. Images were processed using Fit2D (Hammersley 1997), corrected to remove background Kapton[®] tape, and interpreted using JADE[®] (Materials Data Inc. version 6.5) software. Bulk XRD was carried out using standard procedures (Borch et al. 2008) on a Rigaku Geigerflex diffractometer with Cu $\kappa\alpha$ radiation (35 kV, 15 mA). Samples were prepared for XRD analysis by pressing the powdered mineral material into a 0.5 mm depression on a Rigaku monocrySTALLINE silica XRD slide and interpreted using JADE[®] software.

A split of the well-mixed sediments was used to determine the structural environment of Fe using extended X-ray absorption fine structure (EXAFS) spectroscopy at the Stanford Synchrotron Radiation Laboratory on beamline 11-2 (26-pole wiggler), running under dedicated conditions. The EXAFS analytical procedures used here were similar to those described previously (Hansel et al. 2003; Borch et al. 2007). Energy selection was accomplished with a Si (220) monochromator, and spectra were recorded by fluorescent X-ray production using a Lytle-detector. A set of Fe reference compounds (our library contains over 20 common Fe-containing minerals) was used to perform linear combination (LC) k^3 -weighted EXAFS spectral fitting using the SixPACK interface to IFEFIT (Webb 2005). Aqueous chemistry and XRD were used to constrain the selection of mineral phases

in the LC-EXAFS fitting procedure, although reference compounds were also chosen based on their likelihood for being present in the lake sediment (Borch et al. 2007). Elemental abundances determined by XRF were used to support the presence of minerals identified by XRD and EXAFS. Similarly, aqueous chemistry was used in a supporting role to provide guidance for selection of mineral phases (e.g., high carbonate concentration might suggest the presence of carbonate minerals such as siderite).

Grain size distributions were derived from five frozen cores cut into 5-cm sections and classified into three groups originating from sediment–water interface to 5, 5–10, and >10 cm. These sections were dried at 100°C for 12 h. The grain size distribution of each section was obtained using dry separation of US sieve sizes 16, 30, 60, 100, 140, and 200. Each sieve tray was washed and weighed prior to separation. Sieves were stacked and shaken to separate solids, then removed and weighed to determine grain size fractions in each.

Sections from the sediment–water interface to 5, 5–10, and >10 cm were oven-dried (80°C) and analyzed for elemental composition at the WSU Geo Analytical Laboratories using XRF. Ten grams of each section were finely ground using a tungsten carbide bowl and weighed with the addition of a lithium tetraborate flux (2:1 lithium tetraborate–sediment). Sediments were then heated to 1,000°C in a muffle furnace to drive off volatile compounds and fuse with the flux. After heating, the vitrified sample was reweighed to determine loss of volatile compounds. Total elemental analysis was carried out on an automated ThermoARL Advant'XP+ sequential X-ray fluorescence spectrometer. Standard reference materials were obtained from the National Institute of Standards and Technology and pure quartz controls were run to determine grinding bowl contamination.

3 Results and Discussion

3.1 Aqueous Chemistry

The measured chemical compositions of CdAR and pore water samples are presented in Table 1. These data are compared to analyses reported in Balistrieri et al. (2003) and are within the range of historically observed measurements from the US Geological Survey database (monitoring site 12413860 near

Table 1 Composition of Coeur d'Alene River and pore water

Species	Units	This study		Balistrieri et al. (2003)		
		April 2005		November 2000		
		River water	Pore water	River water	Pore water ^a	MDL
Temperature	°C	5.5	–	–	–	
pH		7.2	6.4	7.21	6.56	
Alkalinity	Equivalent mequiv/L	0.38	1.14	0.54	5.25	0.06
Total Organic Carbon	mg/L	1.6	170	0.7	41	0.5
Fluoride	mg/L	– ^b	1.7	–	–	0.15
Chloride	mg/L	0.7	2.8	18	0.5	0.2
Nitrite-N	mg/L	ND	0.81	–	–	0.05
Nitrate-N	mg/L	ND	6.8	–	–	0.05
Sulfate	mg/L	5.6	59	19	269	0.2
Calcium	mg/L	5.5	25	10	4	0.05
Potassium	mg/L	– ^b	5.2	21	2	0.5
Magnesium	mg/L	2.1	7.3	4	56	0.02
Iron	mg/L	0.03	– ^b	0.01	89	0.02
Manganese	mg/L	0.032	27	0.1	5	0.005
Zinc	mg/L	0.16	2.7	0.5	8	0.003
Arsenic	µg/L	– ^b	9	<1	1,200	<1
Barium	µg/L	18	160	29	80	10
Cadmium	µg/L	<1	18	2	0.5	<1
Chromium	µg/L	– ^b	9	–	13	1
Cobalt	µg/L	– ^b	23	<1	22	<1
Copper	µg/L	<1	3	–	2	<1
Lead	µg/L	3	130	1	21	<1
Nickel	µg/L	<1	13	<1	34	<1
Vanadium	µg/L	– ^b	2	–	–	<1
Charge Balance		–6.41	1.07	2.10	–15.88	

Adapted from (Sengör et al. 2007)

MDL method detection limit, ND not detected, – not reported

^a Killarney pore water

^b Below method detection limit

Harrison Idaho <http://nwis.waterdata.usgs.gov/id/nwis/qw>). The concentrations of heavy metals Ba, Pb, and Cd in pore water measured in this study are approximately two, six, and 36 times greater than concentrations reported by Balistrieri et al. (2003). Sulfate and As concentrations are about five and 130 times lower, respectively, than those reported by Balistrieri et al. (2003). Historical data (1991–2007) from the US Geological Survey database show a strong positive correlation in filtered and unfiltered samples ($p < 0.0001$) between Pb and Zn and the redox active elements Fe and Mn. Fe and Mn in unfiltered samples show a negative correlation with river temperature ($p < 0.0033$ and $p < 0.0002$, respectively) and to a

lesser extent pH ($p < 0.055$, and $p < 0.0073$, respectively). This may suggest a seasonal element and may explain some of the variability between the results of this study and those of Balistrieri et al. (2003).

Iron (Fe(III) and Fe(II)) was detected at 30 µg/L in the river water; Fe was below the detection limit of 20 µg/L in the pore water. River water was filtered with a 0.45 µm filter and acidified with HNO₃ at the analysis laboratory according to the Environmental Protection Agency methods 200.7 and 200.8. Ferrihydrite can rapidly form in oxic conditions and is composed of nanocrystals that aggregate into larger structures (Schwertmann and Cornell 2000). If the aggregates were smaller than 0.45 µm, then they

could conceivably pass through a 0.45 μm filter and show Fe in the river water. The counterintuitive lack of Fe in the pore water may suggest (1) that partial oxidation of Fe occurred in the pore water due to sampling procedures, (2) that mixing of the pore water from the entire 15 cm depth generated iron concentrations below the detection limit, (3) that sediment pore water originated from oxic sediments (e.g., diffusion of oxygen into the sediments from the overlying water column or hyporheic flow of oxygen-rich river water), or (4) a combination of these effects. Rapid oxidation of sediment and pore water Fe(II) to Fe(III) hydroxides has been observed by others in this system upon exposure to oxygen after sampling (Horowitz et al. 1995b). The anoxic boundary in LCdA has been reported at the water–sediment interface (Harrington et al. 1998b), within 5 cm into the sediments (La Force et al. 1999; Toevs et al. 2006) and between 10 and 15 cm in the sediments (Horowitz et al. 1992) and this variability may exist in CdAR as well. As this study focused on sediment cores extracted from the top 15 cm, the majority of the core may have been oxic and thus contained little dissolved Fe. Additionally, cold water temperatures due to seasonal runoff at the time of sampling may contribute to overall higher oxygen concentrations due to lower aerobic microbial metabolic activity. This would result in deeper O_2 penetration into

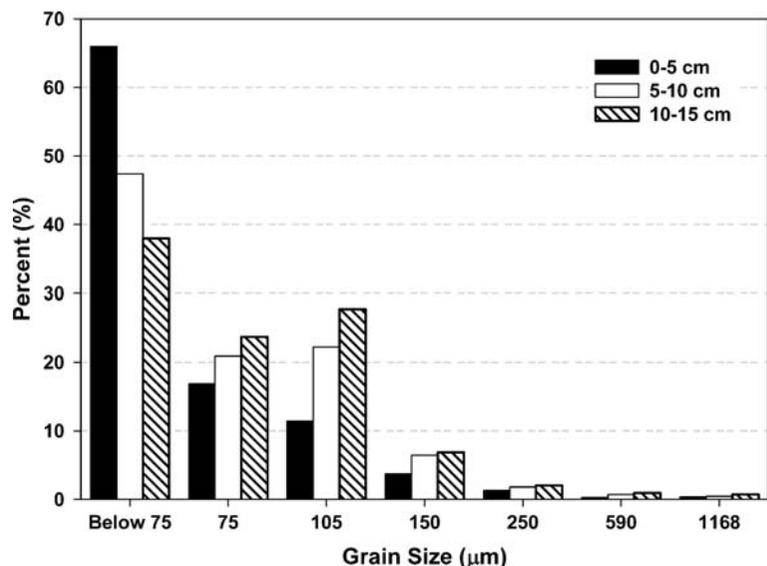
sediments causing lower pore water Fe concentrations as Fe may precipitate as ferrihydrite. The possibility that the sediments originated from the oxic sediments is further supported by microarray and clone library analysis that indicate predominantly oxygen-utilizing bacteria (Barua et al. unpublished data).

3.2 Sediment Geochemistry

3.2.1 Physical Properties

Grain size distributions of CdAR sediments are presented in Fig. 2. Dry grain size fractioning revealed that the majority, by mass, of sediment particles were in the smallest size fraction, below 75 μm (this fraction contains primarily silt (2–50 μm) and clay (<2 μm) sized particles). This distribution is most pronounced in the upper 5 cm of sediment (Fig. 2). Horowitz et al. (1992) and Grosbois et al. (2001) reported that the majority of metal contamination within LCdA is contained within the smallest fractions (<63 μm) and that metal concentration is inversely proportional to particle size. Because the majority of the smallest particles are within the top 5 cm, this may pose a potential metal remobilization issue when these sediments are disturbed by flooding, bioturbation (Atkinson et al. 2007), or anthropogenic activities, such as dredging (Kalnejais et al. 2007).

Fig. 2 Particle size distribution of sectioned bulk sediment using dry sieve technique. Adapted from (Sengör et al. 2007)



3.2.2 Elemental Analysis

Total metal content observed in this study compares well with the literature data (Reece et al. 1978; Farag et al. 1998; Paulson 2001). This site is contaminated with high levels of Zn (0.75% mass) and Pb (0.5% mass; Table 2), both of which are toxic to biota (Brim et al. 1999; Konopka et al. 1999; Sani et al. 2001; Lin et al. 2003). Although total metal content is important, the mobility, reactivity, and bioavailability of heavy metals are dictated by crystallinity, particle size, mineral phase, and associated chemistry in which these metals reside (Haus et al. 2007).

3.2.3 Mineral Identification

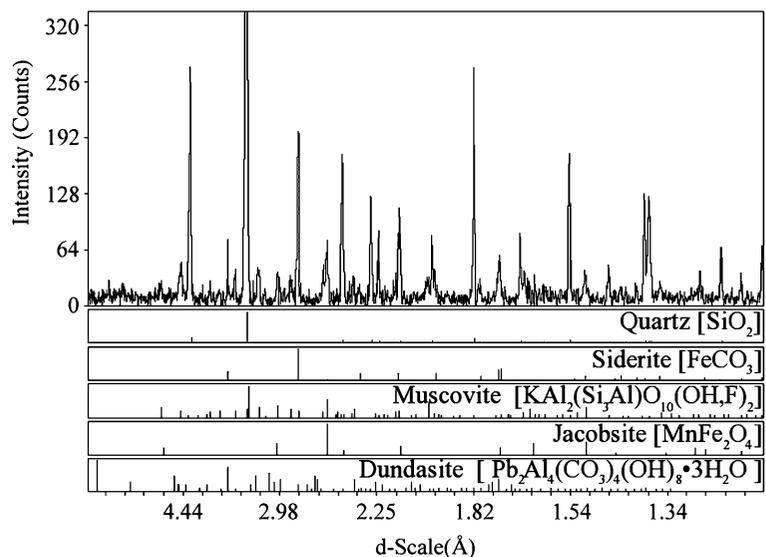
Bulk sediment analysis using XRD (Fig. 3) indicates the presence of quartz and siderite, which is in agreement with previous studies of the primary minerals in the CdAR system (Leach et al. 1985). Muscovite $[KAl_2(Si_3Al)O_{10}(OH,F)_2]$, jacobsite $[MnFe_2O_4]$, and dundasite $[Pb_2Al_4(CO_3)_4(OH)_8 \cdot 3H_2O]$; the strongest dundasite peak was, however, not obvious in the diffractogram] were also detected as likely phases in CdAR sediments. Jacobsite is often associated with hematite $[\alpha-Fe_2O_3]$ in Mn-containing sediments and forms a solid solution series with magnetite $[Fe^{(II)}Fe_2^{(III)}O_4]$ (Anthony et al. 1990), both of which are found in LCdA (Farrand and Harsanyi 1997; Cummings et al. 2000; Fig. 3). Dundasite is

often associated with cerussite $[PbCO_3]$ (Cocco et al. 1972; Anthony et al. 1990; Downs 2006), a mineral reported in the Coeur d'Alene Mining district (Melchiorre et al. 2001).

For a better understanding of the mineralogy and thus fate and transport of heavy metals in this system, it was desirable to combine both macroscale and microscale analyses. For the first time with CdAR sediments, to our knowledge, a combination of synchrotron-based μ XRD and μ XRF techniques were applied to provide high-resolution analyses of minerals and metal associations at the micron scale. μ XRF provides the means to map the distribution of toxic metals while μ XRD allows the identification of crystalline trace-metal-bearing mineral phases and/or the adsorbent to which the toxic metal may be complexed. These analyses are limited to effectively depth-averaged results but this stems from the observed apparent homogeneity of the column.

Figure 4 shows an element map of Pb, Fe, and Zn. These elements were selected for their high concentrations in CdAR sediments and biological activity and/or toxicity (Table 2). Seven spots, each approximately $5 \mu m^2$, were selected for analysis, three of which (spots A, B, and C) are included in this text due to their higher-quality diffractograms. Spot A indicates the presence of smithsonite $[ZnCO_3]$ and calcite $[CaCO_3]$ minerals (Fig. 5a), which are present in other sediments around LCdA (Bostick et al. 2001; Balistrieri et al. 2003). In the lateral lakes surrounding

Fig. 3 X-ray diffractogram of bulk sediments showing probable mineral phases of quartz $[SiO_2]$, siderite $[FeCO_3]$, muscovite $[KAl_2(Si_3Al)O_{10}(OH,F)_2]$, jacobsite $[MnFe_2O_4]$, and dundasite $[Pb_2Al_4(CO_3)_4(OH)_8 \cdot 3H_2O]$



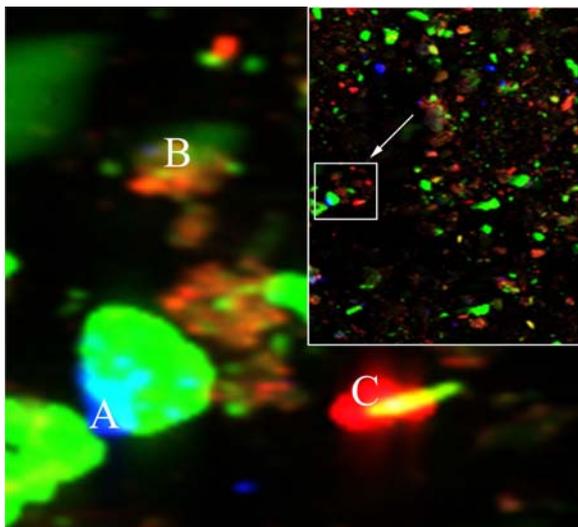


Fig. 4 Synchrotron X-ray fluorescence map (0.5×0.6 mm) with a $5\text{-}\mu\text{m}$ spatial resolution of the CdAR sediment from homogenized sediment cores (0–15 cm). The *inset* shows an overview map (3×2.5 mm; $15\text{-}\mu\text{m}$ spatial resolution). This map shows the spatial correlation between Pb (red), Fe (green), and Zn (blue)

the CdAR, Bostick et al. (2001) found that seasonal changes affected the partitioning of Zn with sulfidic and carbonate phases predominating in flooded areas, while (hydr)oxides were found in oxic, drier soils, and sediments. The metal (hydr)oxide species were transformed to carbonate and sulfidic species during submersion due to reducing conditions; however, a small portion remained as metal (hydr)oxides (Bostick

et al. 2001). Samples from the present study were taken during spring runoff and could represent Zn hydroxide phases transforming to Zn carbonate. With oxidation, Zn is released and can adsorb to metal (hydr)oxides (e.g., ferrihydrite), organic phases, clays, and other minerals or remain free in solution (La Force et al. 1999). These changes illustrate the dynamic geochemical cycling of Zn in this system. Metal carbonates, such as smithsonite [ZnCO_3], may be formed biogenically by reaction of the aqueous metal with biogenically produced bicarbonate (Lloyd and Lovley 2001).

Stolzite [PbWO_4] was detected as a likely phase as shown in Fig. 5b and is often associated with cerussite and anglesite (Anthony et al. 1990; Downs 2006), both reported in the Coeur d'Alene Mining district (Bookstrom et al. 2001; Melchiorre et al. 2001). Origins of this potential mineral in this system are unknown. Analysis of spot B by μXRD supports bulk XRD data showing muscovite present (Fig. 5b). In addition, the diffractogram indicates the presence of earlshannonite [$\text{MnFe}_2(\text{PO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$] and montmorillonite [$\text{Na}_{0.3}(\text{Al},\text{Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$]. These clay minerals are known to exchange cations, such as magnesium and potassium, with other heavy metals, possibly aiding in metal sequestration (Kurek et al. 1996; Farquhar et al. 1997; Lothenbach et al. 1997). Zn was recently shown to coprecipitate with interlayer Al^{3+} cations to form a Zn-containing hydroxyl–Al layer on the basal plane of montmorillonite (Schlegel and Manceau 2007). These findings

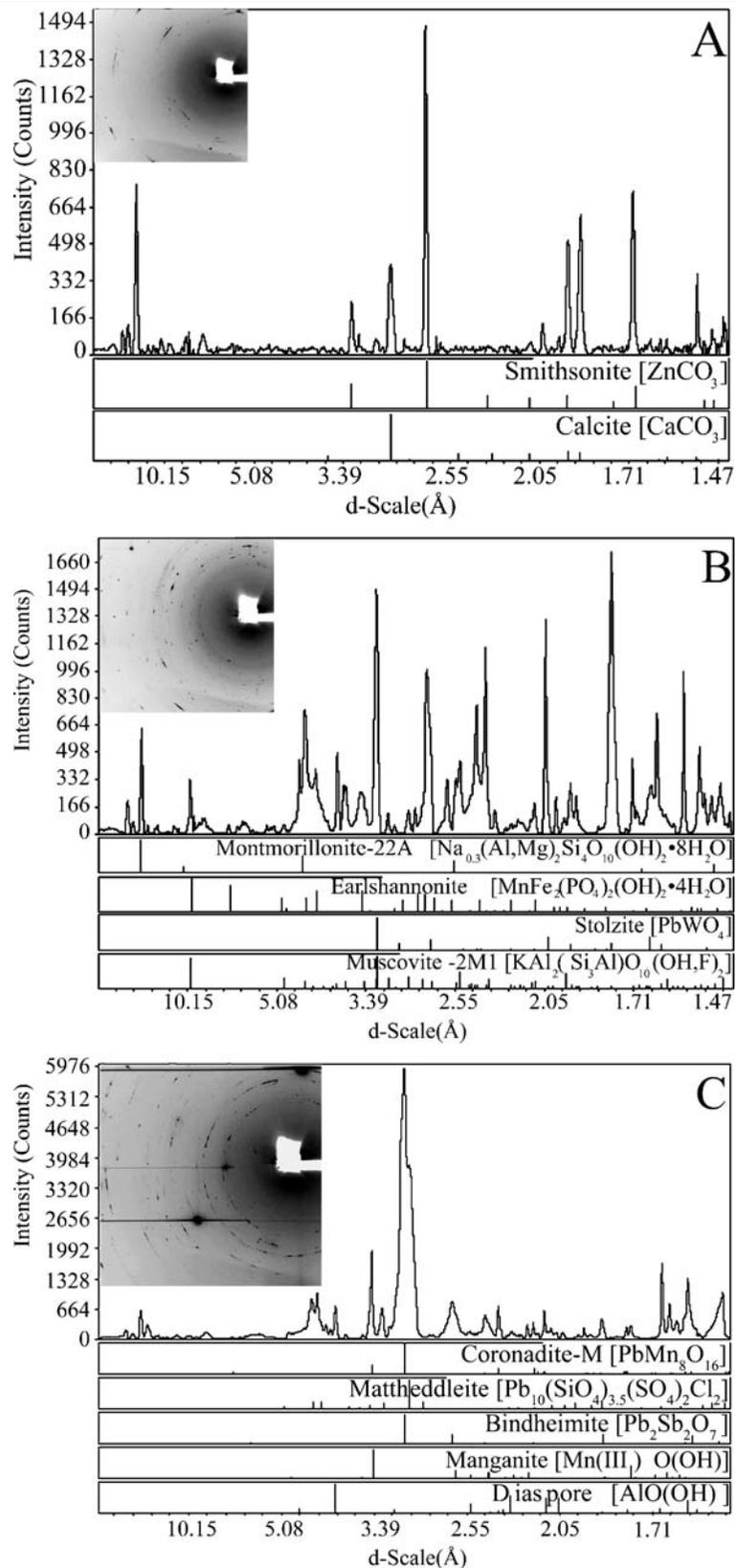
Table 2 X-ray fluorescence spectroscopic analysis of major and trace elements in CdAR sediment

Primary sediment constituents (% mass)		SD (% mass)	Trace elements (% mass)		SD (% mass)
SiO_2	68.68	0.43	ZnO	0.747	0.014
TiO_2	0.42	0.01	PbO	0.467	0.006
Al_2O_3	7.03	0.42	BaO	0.077	0.003
Fe_2O_3	15.26	0.05	ZrO_2	0.035	0.002
MnO	1.58	0.05	CeO_2	0.021	$5.10\text{E-}04$
MgO	0.93	0.03	CuO	0.014	$6.14\text{E-}05$
CaO	0.41	0.02	Rb_2O	0.008	$3.07\text{E-}04$
Na_2O	0.48	0.06	V_2O_3	0.005	$1.70\text{E-}04$
K_2O	1.84	0.06	Y_2O_3	0.005	$2.22\text{E-}04$
P_2O_5	0.10	0.00	Nd_2O_3	0.005	$2.67\text{E-}04$
Sum	96.71		Cr_2O_3	0.004	$1.90\text{E-}04$
LOI (%)	8.52		La_2O_3	0.004	$3.02\text{E-}04$
Trace elements (%)	1.40		SrO	0.003	$2.30\text{E-}04$
			NiO	0.002	$6.94\text{E-}05$

Adapted from (Sengör et al. 2007)

SD standard deviation ($N=3$), LOI loss on ignition

Fig. 5 a XRD of spot A showing probable mineral phases of smithsonite [ZnCO_3] and calcite [CaCO_3], **b** XRD of spot B showing probable mineral phases of montmorillonite [$\text{Na}_{0.3}(\text{Al}, \text{Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$], earlshannonite [$\text{MnFe}_2(\text{PO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$], stolzite [PbWO_4], and muscovite [$\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH}, \text{F})_2$], **c** XRD of spot C showing probable mineral phases of coronadite [$\text{PbMn}_8\text{O}_{16}$], mattheddleite [$\text{Pb}_{10}(\text{SiO}_4)_{3.5}(\text{SO}_4)_2\text{Cl}_2$], bindheimite [$\text{Pb}_2\text{Sb}_2\text{O}_7$], manganite [Mn(III)O(OH)], and diaspore [AlO(OH)]. The location of each analyzed spot is shown in Fig. 4. XRD patterns were obtained with a beam size (or spot size) of $5 \mu\text{m}^2$. The CdAR sediment analyzed was obtained from homogenized sediment cores (0–15 cm)



suggest that montmorillonite can sequester Zn and other heavy metals (e.g., Ni, Cu) with similar cation–hydroxyl distances because the metal is included in the vacant octahedral sites of the gibbsite-like monolayer and may lead to permanent sequestration (Schlegel and Manceau 2007). Similarly, Zn and other cations have been observed to incorporate into the interlayer spaces of muscovite (Friedrich et al. 2006).

Likely mineral phases observed in spot C were coronadite [$\text{PbMn}_8\text{O}_{16}$], mattheddleite [$\text{Pb}_{10}(\text{SiO}_4)_{3.5}(\text{SO}_4)_2\text{Cl}_2$], bindheimite [$\text{Pb}_2\text{Sb}_2\text{O}_7$], manganite [$\text{Mn}^{(\text{III})}\text{O}(\text{OH})$], and diaspore [$\text{AlO}(\text{OH})$] (Fig. 5c). Coronadite is a Pb-containing manganese oxide which forms a tunnel structure into which the Pb is associated (Post and Bish 1989; Post 1999). Mattheddleite-like minerals have been identified as major components of blast and dross furnace dust samples from Pb smelting operations (Spear et al. 1998), such that identification of mattheddleite in this system may reflect the result of mining activities. Bindheimite is a constituent of the primary Pb–Ag ores in the Coeur d’Alene Mining district with nearly pure masses several feet in diameter (Lawson and Meyer 1964). The source of this primary mineral is likely from erosion and transport of exposed veins or mine tailings.

Manganite and diaspore detected in spot C are oxyhydroxide phases capable of adsorbing toxic metals and have been the topic of several studies in the LCdA area (Paulson and Balistrieri 1999; Tonkin et al. 2002; Balistrieri et al. 2003). Manganite is most likely the product of biological reduction of Mn followed by oxidation to form the oxyhydroxide complex (Greene and Madgwick 1991). Additionally, Mn oxyhydroxides in the CdAR system have been shown to preferentially adsorb Pb as a major component and Zn as a minor component (Bookstrom et al. 2001). Due to mineralogical heterogeneity of these sediments, it is difficult to elucidate the nature of the mineral phases in all cases, particularly on the micron scale. Small-scale analyses, especially depth-averaged analyses, are somewhat limited in extrapolating to the macroscopic sediments for more generalized hypotheses and should be interpreted cautiously.

Fe was the second most abundant sediment constituent identified after Si by mass (Table 2) and was selected for further spectroscopic studies by Fe-EXAFS due to its abundance and potential role as an important sorbent for toxic metals. In addition, EXAFS spectroscopy allows detection of amorphous phases which cannot be identified by XRD (Borch et

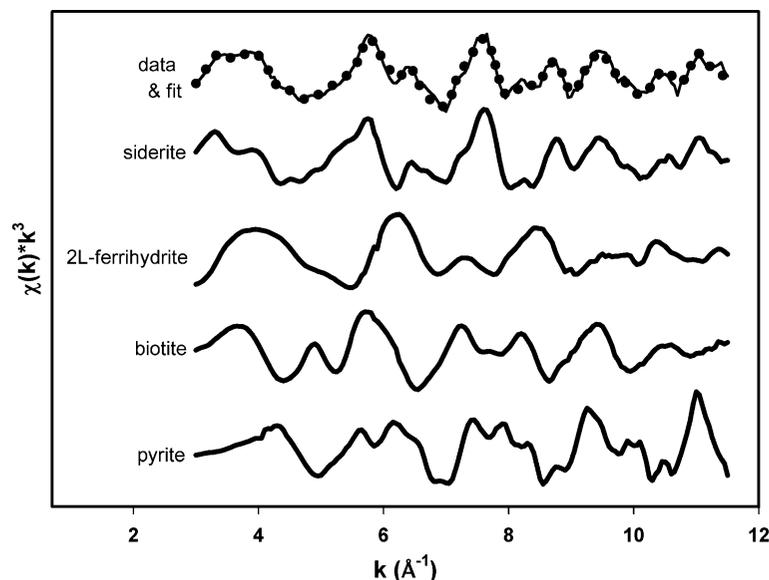


Fig. 6 k^3 weighted Fe-EXAFS spectrum (solid line; data) and linear combination fit (dotted line; fit) of the CdAR sediment from homogenized sediment cores (0–15 cm). Reference minerals used for the LC-EXAFS fitting are listed with their respective Fe-EXAFS spectra. Corresponding percents of Fe

phases (mole basis) resulting from linear combination fits were siderite (53 mol% Fe), ferrhydrite (38 mol% Fe), biotite (6 mol% Fe), and pyrite (3 mol% Fe). The concentration of pyrite was low but it significantly improved the fit. Data are $\pm 5\%$ and the detection limit is approximately 5 mol% Fe

al. 2008). Siderite (53 mol% Fe) and ferrihydrite (38 mol% Fe) were identified as the major Fe phases in CdAR sediment (Fig. 6). Biotite (6 mol% Fe) was also found, though in much smaller quantities (Fig. 6). Inclusion of pyrite (3 mol%) in the LC k^3 -weighted EXAFS spectral fitting improved the χ^2 value for the fit by 22% and was thus included in the fit despite its low concentration. The presence of pyrite has been observed in earlier studies (Toevs et al. 2006). To clearly distinguish ferrihydrite from goethite by LC-EXAFS fitting, one needs EXAFS data up to 14 k (\AA^{-1}). We fitted our data to 11.5 k due to the presence of four glitches (Comin et al. 1983) in the spectrum between 11.9 and 12.6 k. However, we did attempt to deglitch the spectrum followed by LC-EXAFS fitting to 14 k. When the EXAFS spectrum was fitted to 14 k, the fit suggested the presence of siderite (51 mol% Fe), ferrihydrite (29 mol% Fe), biotite (10 mol% Fe), goethite (7 mol% Fe), and pyrite (3 mol% Fe). However, the inclusion of goethite in the LC-EXAFS fit did not significantly improve (i.e., 3%) the χ^2 value. When goethite was not included in the fit, the ferrihydrite contribution increased to 37 mol% Fe and the other constituents (i.e., siderite, biotite, and pyrite) contributed to a similar extent as when the data were fitted to 11.5 k. This, in combination with the absence of goethite in the X-ray diffractogram (Fig. 3), indicate that goethite was most likely not present in this sample. Overall, these results are consistent with our XRD data and the reported presence of ferrihydrite by Toevs et al. (2006). Ferrihydrite is an important sorbent for many metals and nutrients such as Zn, Pb, and phosphate (Scheinost et al. 2001; Manceau et al. 2004; Borch et al. 2007; Borch and Fendorf 2008). Cations (e.g., Pb, Cd, and Cu) can bind strongly via inner-sphere complexation to biotite (Farquhar et al. 1997).

4 Conclusions

In summary, coupling macroscopic and microscopic analyses facilitates a better understanding of the geochemistry of the complex CdAR system. Micron-scale phase association of heavy metals in sediments, until recently, could only be inferred by selected-area electron diffractometry or a combination of electron

microscopy and elemental analysis. For the first time with the Coeur d'Alene River sediments, to our knowledge, both macroscopic (e.g., XRD, EXAFS) and microfocused analyses (e.g., μ XRD, μ XRF) have been applied to the study of micron-scale particles. These analyses indicate a variety of mineral phases including siderite, jacobsonite, the oxyhydroxides ferrihydrite, diaspore, and manganite, and the exchangeable clays montmorillonite, biotite, and muscovite. These mineral phases likely contribute to the sorption and sequestration of heavy metals in the CdAR system. A significant quantity of Fe and Mn (hydr)oxides was observed in this system. Metal sorption behavior may be dominated by these (hydr)oxide phases because these minerals have much higher surface areas than other observed sorbing phases. Ferrihydrite and manganite can also serve as electron acceptors for dissimilatory metal reduction, with the potential for reintroducing adsorbed metal into the environment after reductive dissolution. Of the likely toxic-metal-bearing phases identified in this study, which include smithsonite, dundasite, coronadite, bindheimite, stolzite, and mattheddleite, only dundasite would have been detected with macroscopic techniques (e.g., XRD). This study identifies the need for further study of these minerals as little is known about their solubility, toxicity, and bioavailability. Further studies are warranted to monitor seasonal variations, spatial changes in geochemistry, and biogeochemical changes in this system which may affect metal mobility and transport using the minerals identified in this study as a framework.

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