

TRACE METAL SUBSTITUTION IN AND RELEASE FROM SECONDARY IRON (OXY)HYDROXIDES

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INTRODUCTION

Cobalt (Co) is a trace metal that is deemed critical to society because it is essential to our modern infrastructure and clean energy future (Slack et al., in press). The Blackbird Mining District located in the Idaho Cobalt Belt (near Salmon, ID) contains the largest known reserve of cobalt ore in the United States, with about 6.5 million tons grading at 0.55 % Co (Bennet, 1977). The Blackbird Mine produced nearly 14 million pounds of Co between 1939 and 1968 (Johnson et al., 1998). Like many metal mines, this site contains sulfide minerals that oxidize to produce acid mine drainage (AMD) and high dissolved metal concentrations. In order to remediate acidity, active pH neutralization began in 1981 (USEPA, 2008) and by 1987, pH values in Blackbird Creek, which drains the mine site, ranged from 5 to 7, yet untreated spring water near the mine was pH ~ 3 (McHugh et al., 1987). Today, one of the remaining issues is copious precipitation of secondary Fe solids that coat the streambed of Blackbird Creek (Fig. 1). Like many mine sites, these Fe precipitates are expected to include amorphous hydrous ferric oxide (HFO), semicrystalline ferrihydrite and schwertmannite, and crystalline jarosite and goethite, depending on the pH (Fig. 2). When these secondary Fe (oxy)hydroxide solids form, trace metals may coprecipitate and be incorporated into the amorphous or crystalline structure. The occurrence of trace-metal-substituted (TMS) secondary minerals in surface environments is well known (Levy et al., 1997; Jamieson et al., 1999; Schroth and Parnell, 2005; Sidenko and Sherriff, 2005; Carmona et al., 2009; Peretyazhko et al., 2009; Groeger et al., 2011).



Figure 1. Photos of Blackbird Creek downstream of the Blackbird Mine (within the Idaho Cobalt Belt), showing the view looking up at the closed mine site (a), students collecting and filtering stream water (b and c), and Lena Goss collecting stream sediments for microbiological characterization (d). From left to right, students in (b) are Jason Anthony, Samantha Schonberger, and Shanti Penprase. Photos taken by Bryn Kimball.

Adding base to AMD in order to raise the pH and precipitate dissolved metals has been a common form of remediation for decades. This treatment is expensive, and the long-term stability of coprecipitated trace metals is largely unknown. Because this process will impact the dissolved concentrations of trace metals, it will also have some control on the bioaccessibility of trace metals to aquatic organisms. Many studies have focused on trace metal sorption-desorption with secondary Fe precipitates, but relatively few studies have documented trace metal

coprecipitation-dissolution. As a result, the purpose of this work was to: (1) document Co substitution in and dissolution from synthesized schwertmannite (Swt), jarosite (Jr), and goethite (Gt); and (2) compare the mineralogy, morphology, and chemical composition of natural ochreous precipitates from Blackbird Creek to the synthesized minerals.

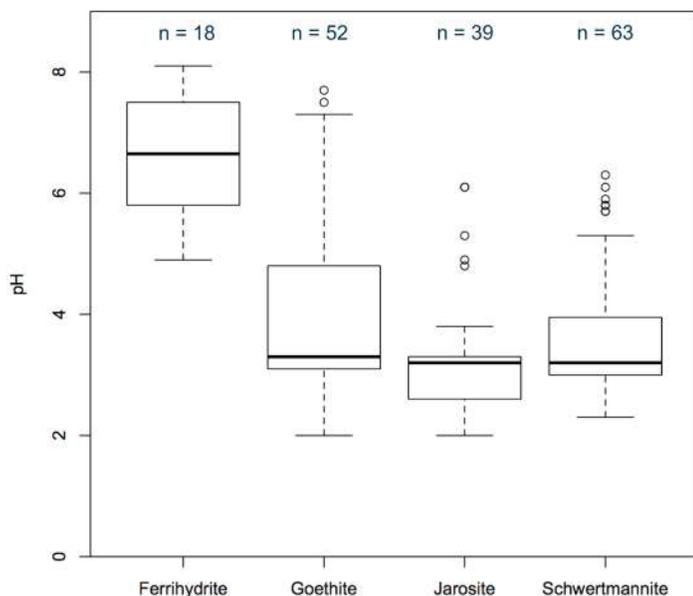


Figure 2. Occurrences of secondary Fe minerals in mining environments at various pH values. Data were compiled from multiple sources (Murad and Rojik, 2005; Bigham et al., 1992; Kimball et al., 2016; Courtin-Nomade et al., 2009; Peretyazhko et al., 2009; Sidenko and Sherriff, 2005; Hochella et al., 1999; Valente and Gomes, 2009; Bigham et al., 1996a).

METHODS

Batch Leach Experiments

Because Fe (oxy)hydroxide precipitates in the environment tend to be mixed with other phases, it is nearly impossible to obtain pure samples. Therefore, we synthesized pure and Co-substituted minerals according to the methods described by students on this project. Batch leach experiments were conducted with synthesized pure or Co-substituted minerals and dilute ultrapure HCl (pH= 3.6). Blank samples were identical, but lacked any minerals. Samples were placed on a shaker at room temperature (23 ± 2.5 °C), which we could not control. Duplicate samples were harvested at 0, 0.2, 1, 3, 6, 10, and 20 days.

At each sampling time, solids were separated from liquids using filtration (0.2 μm), and solids were dried overnight at room temperature. Unleached and leached synthesized minerals were then characterized with a microfocused X-ray diffractometer (Xcalibur Nova) with Cu K α radiation. X-ray diffraction patterns were compared to the RDB-mineral database using JADE software (version 2.8.5). Images of unleached and leached synthesized minerals were collected using scanning electron microscopy (SEM) with an FEI Quanta 250. Sample powders were mounted onto stubs with carbon tape, then either gold-coated or carbon-coated. In Gt and Jr leach experiments, SEM images were viewed in Adobe Illustrator to estimate the grain sizes of unleached and leached minerals.

Solution temperature, pH, and conductivity were measured with a calibrated pH/conductivity meter, and filtered solutions were preserved with ultrapure HNO₃ and refrigerated before further analysis with inductively coupled plasma mass spectrometry (ICP-MS). We quantified solution composition with an Agilent 7500ce quadrupole ICP-MS using matrix-matched standards. In jarosite and schwertmannite leach experiments, dissolved sulfate (SO₄) concentrations could not be measured due to instrumental interferences, so we used the geochemical equilibrium-solving program PHREEQC to calculate dissolved SO₄ by setting it to charge balance the solution. We used the minteq.v4 thermodynamic database, which was modified to include updated thermodynamic data for jarosite (Baron and Palmer, 1996) and schwertmannite (Bigham et al., 1996a).

Field Sample Collection and Analysis

Samples of Blackbird Creek (BBC) and streambed precipitates were collected from eight locations downstream from the Blackbird Mine (Fig. 3). Precipitates were collected from the upper 2 cm of sediments at the bottom of pools, where fresh precipitates were more abundant and less disturbed by stream flow. Water samples were filtered (0.2 μm) on site and subsequently measured for temperature, pH, and conductivity using a calibrated meter. Both filtered and unfiltered water samples were preserved with

concentrated ultrapure HNO_3 and kept on ice prior to returning to the laboratory for quantification with ICP-MS (Agilent 7700) at Washington State University.

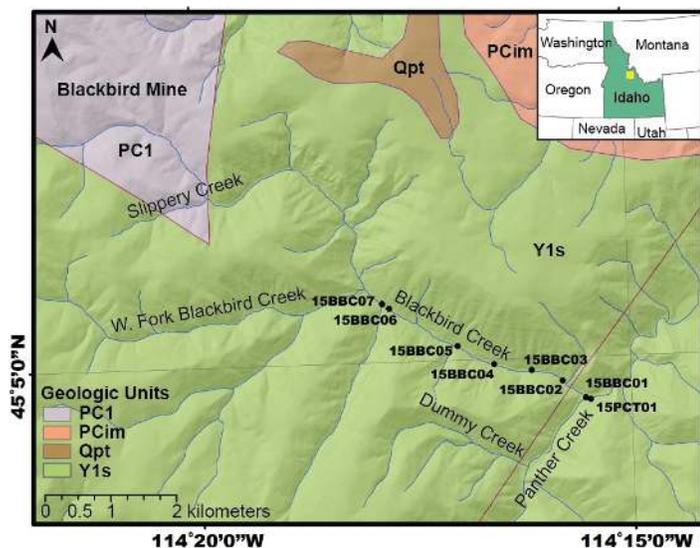


Figure 3. Site map of the Blackbird Mine area showing sampling sites on Blackbird Creek and Panther Creek. Geologic units are the following (Bond et al., 1978): Late Pleistocene till (Qpt); Middle Proterozoic prealuminous granite/orthogneiss (PCim); Middle Proterozoic gneiss/quartzite (PC1); and Middle Proterozoic quartzite/siltstone (Y1s). Map created by Lena Goss.

Field precipitates were also kept on ice until reaching the laboratory, where they were air-dried at room temperature and ground with a porcelain mortar and pestle. They were then characterized at Carleton College using XRD (Panalytical Empyrean) and SEM (Hitachi S-3000). Diffraction patterns were compared to the Crystallography Open Database (COD) using HighScore Plus software. Uncoated sample powders were mounted on stubs for SEM, which was paired with an Oxford INCA energy dispersive spectrometer (EDS) system. Because EDS does not usually detect the presence of trace elements, we also digested the stream sediment samples in ultrapure, concentrated HNO_3 and HCl , and measured acid-leachable elements using ICP-MS.

STUDENT PROJECTS

Shanti Penprase (Carleton College) Shanti experimented with pure goethite (Gt) and cobalt-substituted goethite (CoGt). Among the common secondary Fe minerals found in mining environments (Fig. 2), goethite tends not to precipitate directly

from solution, but instead forms through aging of precipitated ferrihydrite (Schwertmann and Murad, 1983), schwertmannite (Acero et al., 2006; Bigham et al., 1996a; Peretyazhko et al., 2009), and/or jarosite (Acero et al., 2006; Welch et al., 2008). Given that the leach conditions were similar to environments where goethite is often observed, we did not anticipate drastic changes in solution chemistry during leaching.

Jason Anthony (Whitman College) Jason experimented with pure jarosite (Jr) and cobalt-substituted jarosite (CoJr). Jarosite has been observed to precipitate directly from AMD (Herbert, 1997) or from aging of schwertmannite (Acero et al., 2006). Jarosite is highly crystalline and can host many trace elements within its structure (Hudson-Edwards et al., 2008; Desborough et al., 2010; Welch et al., 2007). Because jarosite has been observed to age into goethite (Acero et al., 2006; Welch et al., 2008), we anticipated that the jarosite leach experiment would exhibit moderate changes in solution chemistry over time.

Samantha Schonberger (Beloit College) Samantha experimented with pure schwertmannite (Swt) and cobalt-substituted schwertmannite (CoSwt). Schwertmannite is the least thermodynamically stable solid among the three secondary Fe minerals in this study, but it is often the most kinetically favorable solid to form. This is supported by its common occurrence in waters ranging in pH from 2 to 6 (Fig. 2). Schwertmannite tends to age into jarosite or goethite over time (Acero et al., 2006; Bigham et al., 1996a; Peretyazhko et al., 2009). Given schwertmannite's relative instability, we anticipated the most change in solution chemistry during schwertmannite leaching.

Lena Goss (Whitman College) Lena Goss was not an official participant of the Keck project, but she contributed equally to the field sample collection, and has carried out a complementary research project. Lena collected BBC precipitates in order to characterize the bacteria present using both genetic analysis and SEM imaging. The purpose of her work was to identify any Fe-oxidizing bacteria (FeOB) that may have been involved in formation of secondary Fe precipitates in BBC. Microorganisms such as FeOB play a critical role in formation of secondary

Fe precipitates at low pH (< 4) because under sterile conditions, the purely chemical oxidation of Fe^{2+} to Fe^{3+} is kinetically hindered (Singer and Stumm, 1970). Acidophilic microorganisms have evolved to catalyze Fe^{2+} oxidation at low pH for their energy needs, which leads to formation of schwertmannite and jarosite (Kawano and Tomita, 2001; Bigham et al. 1996b). Other genera of FeOB thrive at near-neutral pH conditions (Emerson and Moyer, 1997; Emerson and Weiss, 2004; Fortin and Langley, 2005). These neutrophilic FeOB are an enigma because they compete with abiotic oxidation of Fe^{2+} to Fe^{3+} that is more rapid at near-neutral pH. Identifying the microorganisms present in Fe-rich environments will help elucidate the role that they play in forming the secondary Fe precipitates that impact the concentrations of dissolved trace metals. Given the abundance of Fe in BBC, we anticipated that FeOB would be detected in BBC precipitates.

FIELD RESULTS AND DISCUSSION

Results from the batch leach experiments are described in this issue by Anthony (2016), Penprase (2016), and Schonberger (2016). Blackbird Creek pH ranged from 6.7 to 8.0 (Table 1), with values increasing from upstream to downstream. Total dissolved solids in filtered BBC water were relatively constant, ranging from 77 to 125 mg/L (Table 1). The pH and TDS values resembled remediated AMD, with near-neutral pH and low dissolved solids. Despite remediation, dissolved Co concentrations in BBC ranged from 170 to 460 $\mu\text{g/L}$ (Table 1; Fig. 4), which is above the recommendation of 23 $\mu\text{g/L}$ suggested for preventing chronic aquatic toxicity (Suter and Tsao, 1996). Dissolved [Co] decreases linearly from upstream to downstream, as pH increases (Fig. 4). Dissolved [Fe] and [Mn] also decrease from upstream to downstream (Table 1), which is consistent with an expected increase in precipitation and sorption at higher pH values. Dissolved [Co] and [Mn] show a linear relationship (Fig. 4), which is expected based on similar geochemical behavior in a range of environments (Slack et al., in press).

Sample	Stream Water						Stream Sediments				
	T °C	pH	TDS mg/L	Co $\mu\text{g/L}$	Mn $\mu\text{g/L}$	Fe $\mu\text{g/L}$	Co mg/kg	Mn mg/kg	Fe wt. %	Fe:Co ^a moles	Fe:Mn ^a moles
15BBC07a	23.9	6.7	114	460	240	2900	390	530	22	601	408
15BBC07b	-	-	-	450	240	2940	380	530	21	599	402
15BBC06a	28.3	6.9	113	430	220	2350	630	1020	18	297	170
15BBC06b	-	-	-	430	220	2360	630	1040	18	293	167
15BBC05a	25.0	7.1	76.8	340	150	240	300	220	4.3	150	191
15BBC05b	-	-	-	350	160	180	1580	1160	22	148	189
15BBC04a	19.9	7.2	125	270	120	4.5	1730	1700	17	100	95
15BBC04b	-	-	-	270	120	12	1630	1560	15	98	95
15BBC03a	27.4	7.4	116	170	62	8.1	2070	1570	20	101	124
15BBC03b	-	-	-	170	64	1.5	2430	1770	23	100	128
15BBC02a	28.2	7.9	118	170	67	8.9	1840	1870	11	64	59
15BBC02b	-	-	-	170	68	7.9	1850	1870	11	63	58
15BBC01a	19.9	8.0	118	190	68	3.1	1600	1680	8.6	57	51
15BBC01b	-	-	-	190	67	2.3	1610	1710	8.8	58	51
15PCT01a	24.4	7.8	66.6	42	18	11	700	970	3.3	50	33
15PCT01b	-	-	-	42	18	9.3	690	970	3.3	50	33

^a Replicate data not determined.
^a Ratios based on sediment digests measured by ICP-MS.

Table 1. Field parameters measured for sites along Blackbird Creek (BBC) and Panther Creek (PCT). Sites are shown in Figure 3. Stream water data are for filtered samples, and stream sediment data are for acid-digested stream precipitates. Temperature, pH, and conductivity (TDS) were measured at the time of sample collection, and all chemical data were determined later by ICP-MS at Washington State University.

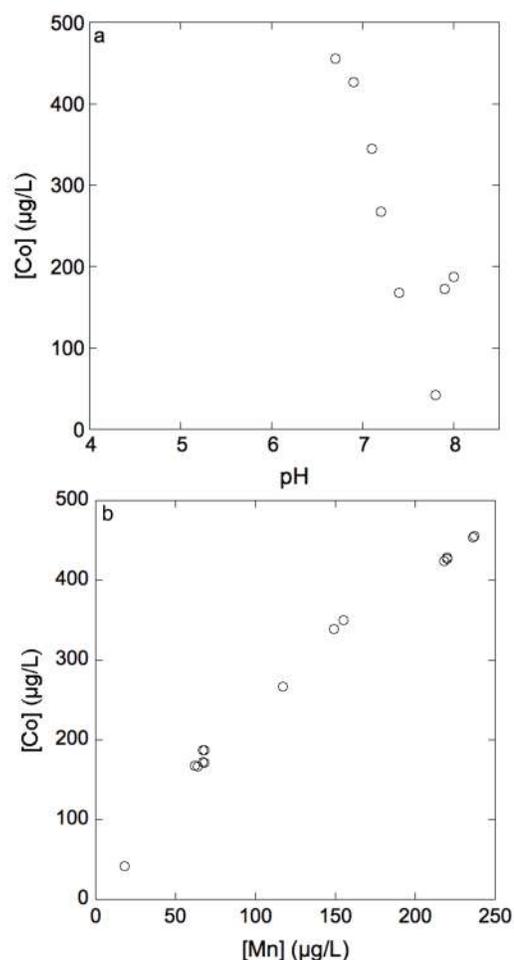


Figure 4. Dissolved [Co] versus pH (a) and dissolved [Mn] (b) for Blackbird Creek and Panther Creek water samples. The near-neutral pH values for all sites are indicative of remediated acid mine drainage. Despite remediation, the dissolved [Co] is above the recommended level for preventing chronic aquatic toxicity (see text).

As described by Penprase (2016), crystalline Fe minerals were not detected in the BBC sediments, which could have resulted from the sampling technique or difficulties detecting secondary Fe minerals using XRD. The Fe-rich precipitates contained Co ranging from 300 to 2430 mg/kg (Table 1). Our experimental results suggest that even if the secondary Fe precipitates that host this Co are stable, Co may still be released to solution. Future work will aim to better characterize the secondary Fe precipitates in BBC, and use these precipitates in batch leach experiments like those described for the synthetic minerals in this study. Our work reiterates some of the challenges involved in working with amorphous and semi-crystalline Fe solids, and highlights the need to continue doing so because these phases have some control on dissolved toxic metal concentrations in the environment.

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