Characterization of Weathering Products and Controls on Metal Mobility at a Cu-Ni-PGE Deposit

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ABSTRACT

Secondary minerals and other weathering products (for example, secondary sulfates, carbonates, oxides, and amorphous coatings) can serve as an important control on the concentration of trace metals in mine-impacted water. This becomes particularly true for mine features like waste rock stockpiles with engineered covers that are designed to minimize water flux, thereby increasing the likelihood that constituents released during mineral weathering are going to be retained within the feature. Standard methods designed to characterize constituent release rates (i.e., humidity cell tests) do not provide information on secondary mineral controls under mine site conditions due to the high water:rock ratio employed in these tests. Other types of tests that use less water may provide empirical evidence for weathering product-related controls, but, because they lack information on control mechanism or weathering product identities, it can be a challenge to extend the results to mine site conditions. Here, we report on the results of an ongoing study into controls exerted by weathering products on trace metal mobility from a magmatic sulfide Cu-Ni-PGE deposit within the Duluth Complex, located in Minnesota, USA. Key aspects of this study include: (1) utilization of weathered samples collected from outcrops on site as proxies for potential future oxidized waste rock; and (2) application of complementary analytical techniques, from both commercial and university labs, selected to achieve the chemical sensitivity and high-spatial resolution necessary to characterize secondary minerals in weathered rocks (including, but not limited to, X-ray diffraction, electron-microprobe analysis, and chemical analysis following sequential extraction). Results of this work are being used to refine the conceptual model for the mobility of trace metals that would be released during weathering of potential future waste rock.

Keywords: secondary minerals, metal attenuation, scanning electron microscope, X-ray diffraction, mineral characterization

INTRODUCTION

The Duluth Complex, Minnesota, USA, is a large composite mafic intrusion emplaced during a failed mid-continental rifting event that occurred in the region approximately 1.1 billion years ago and has been identified as one of the world's largest Cu-Ni-PGE resources (Miller et al., 2002). Multiple magmatic sulfide Cu-Ni-PGE deposits in the Duluth Complex are currently the subjects of ongoing mineral exploration, mine planning, and environmental review. While there is likely to be variability in the chemistry of mine-impacted waters from different potential future mines in the Duluth Complex, similarities in mineralogy, geology, and regional characteristics throughout the complex suggest that the following aspects of a site geochemical model may be typical for Duluth Complex deposits:

- The region has a wet, continental climate with abundant valuable water resources. Any potential future mine would likely be required to utilize engineered systems that minimize contact water as part of the mine water and waste rock management plans, for example, utilization of advanced stockpile cover systems, where appropriate.

- Oxidation of sulfide minerals is a potential source of acidity, sulfate, iron, and other metals (Lappako & Antonson, 2012; Lappako, Olson, & Antonson, 2013; Lappako, 1993). Within Duluth Complex magmatic deposits, sulfur content, as well as the sulfide mineralogy, show wide variability (Ripley & Alawi, 1986). The typical sulfide mineral assemblage includes pyrrhotite ($Fe_{(1-x)}S$), chalcopyrite ($CuFeS_2$), cubanite ($CuFe_2S_3$), and pentlandite ($(Fe,Ni)_9S_8$). Sulfide minerals may contain trace metals in addition to those indicated by the mineral formula. Whereas a larger suite of metals may be environmentally relevant for Duluth Complex rocks, this study is focused on Cu, Ni, Co, and Zn.

- Carbonate minerals are generally absent or at low concentrations in Duluth Complex rocks; instead, neutralization potential is supplied by dissolution of silicate minerals (Lappako et al., 2013). The silicate mineralogy for Duluth Complex rocks is dominated by anorthite-rich plagioclase feldspar, olivine, and pyroxene (Miller et. al 2002), of which, anorthite-rich plagioclase and olivine may provide significant neutralization potential. For rocks of sufficiently low sulfide content, this neutralization mechanism may be adequate to maintain circum-neutral conditions (Day & Kennedy, in press; Miller et al., 2010).

Ultimately, metal concentrations in mine-impacted water will reflect combined effect of constituent release from sulfide minerals, as well as, attenuation during weathering from mechanisms such as precipitation of secondary phases, sorption onto solid phase surfaces, and co-precipitation. In this context, the term "secondary phases" refers to minerals and other solid phases that form as a result of rock weathering after being exposed at the surface. Evidence for metal attenuation by ferric (oxy)hydroxides and related iron-rich secondary phases has been widely reported in the literature (for example, Carbone et al., 2012; Alpers et. al. 1994; Jambor & Dutrizac, 1998). With respect to Duluth Complex rocks, metal attenuation has been inferred for field leach piles with acidic pH (Kelsey et al., 1996). However, the role of attenuation by secondary phases would likely be more

significant for systems with low-sulfide waste rock where drainage maintains circum-neutral pH (Smith et al., 2013), because many of these attenuation mechanisms are pH dependent. Whereas extensive characterization has been performed on constituent release rates from Duluth Complex rock (Lappako, Olson & Antonson, 2013), relatively little work has characterized the relevant attenuation mechanisms, in particular, under circum-neutral conditions.

The following work aims to characterize weathering products and related attenuation mechanisms that could be active in mine-impacted drainage at a potential future Duluth Complex mine. Characterizing weathering products can be challenging due to the poor crystallinity and micro- to nanometer-scale size of features (e.g. thin surface coatings). To overcome some of these limitations, an assortment of high-resolution techniques, including scanning electron microscopy (SEM) methods, x-ray diffraction (XRD), and chemical sequential extraction were used, employing resources at both university and commercial labs.

METHODOLOGY

Low-sulfur waste rock piles of Duluth Complex rock are not available; therefore, weathered rock from exposures (both natural outcrops and historical railroad cuts) of Duluth Complex were collected and used as analogues for waste rock that may be produced by a potential future project. This approach has some limitations, for example, differences in time scales between natural weathering and mining, difference in surfaces, and poorly constrained drainage chemistry. Opportunistic sampling was conducted at six locations to capture the variety of visual alteration. Samples included both rock with visible weathered rinds as well as, white crusts (Figure 1). Of the six sampling locations, one captured rock from a meta-sedimentary rock that underlies the Duluth Complex. This paper focus on the Duluth Complex samples from the remaining five sampling locations. At each location, a grab sample (small clasts typically less than 1-2 inches, about 1 kg) and separate hand samples (about 1 kg) were collected.

Figure 1 Left image shows example of a field sampling location where Duluth Complex rock was exposed during construction of a railroad. Right image shows "white crust" observed at the site.

Secondary Mineral Characterization Techniques

Rietveld X-Ray Diffraction

Rietveld X-ray diffraction (XRD) was performed at the University of British Columbia. Grab samples were ground (< 10 μm) under ethanol in a vibratory McCrone Micronizing Mill for 7 minutes. Step-scan X-ray powder-diffraction data were collected over a range 3-80° 2θ with CoKα radiation on a Bruker D8 Advance Bragg-Brentano diffractometer equipped with an Fe monochromator foil, 0.6 mm (0.3°) divergence slit, incident- and diffracted-beam Soller slits and a LynxEye-XE detector. The long fine-focus Co X-ray tube was operated at 35 kV and 40 mA, using a take-off angle of 6°. The detection limit for this method is about 0.5 percent.

Qualitative powder X-Ray Diffraction

To supplement Rietveld XRD on whole rock samples, coatings on hand samples were isolated for additional analysis by XRD. Samples were viewed under a binocular microscope to identify visually distinct weathered areas. Alteration coatings were then scraped with a stainless steel pick onto a plastic weigh boat. While viewing the granular scrapings under a binocular microscope, material that appeared as primary mineral grains (i.e. unweathered materials) was removed. Samples were ground with an agate mortar and pestle and mounted on zero-background plates. Using a Phillips XPert MPD diffractometer at the University of Minnesota-Duluth with CuKα radiation source, each sample was scanned between 5° and 65° 2θ at a scan rate of 0.05 deg./min. X-rays were refined with a graphite monochromator, 1° divergence slit, incident and diffracted Stoller slits, a 10 mm mask and collected with a point scintillator detector. The X-ray tube was operated at 40 kV and 40 mA. The long collection time gave sufficient counts to match patterns from the database for some secondary phases. Diffraction data were processed with X-Pert HighScore software and compared to mineral patterns in the International Centre for Diffraction Data (ICDD) database.

Scanning Electron Microscopy

The morphology and semi-quantitative coating chemistry were characterized using a SEM. Preparation included crushing (< 1 mm), mounting in epoxy, polishing, and carbon coating (15 nm). A JEOL JSM-6590LV scanning electron microscope, combined with an INCA X-ACT energy dispersive spectroscopy system (EDS) and complementary software, was operated at the University of Minnesota-Duluth. Operating conditions were optimized independently for imaging in backscattered mode and EDS mode; moderate accelerating voltage (15 kV) produced optimal results. EDS calibration was performed on metallic Cu and is considered semi-quantitative. Additional work was performed on a JEOL 8600 Electron Microprobe operated in EDS mode by McSwiggen & Associates, a commercial lab in St. Anthony, Minnesota. The procedure was standardless, and therefore semi-quantitative.

Chemical Sequential Extraction

A sequential extraction procedure was chosen based on a hypothesis that metals of interest could be divided into six solid phases or groupings. Groupings coincide with relative environmental stability mineral classes. One gram of pulverized material was used as the starting mass for each sample. The chemical extraction was analyzed by ICP-OES.

Table 1 Abbreviated sequential extraction procedure.

Extraction Step	Extraction Target Phase	Associated Mineral Groups	Method Reference
1	Water soluble	• Sulfate salts	Dold 2003
2	Weakly acid soluble (pH 5)	• Carbonates • Adsorption to primary and secondary Fe oxides, kaolinite and montmorillonite. • Apatite	Tessier et al. 1979
3	Weakly reducible	• Al-hydroxides • Poorly crystalline Fe-oxide/ (oxy)hydroxides	Chao and Zhou 1983
4	Strongly reducible	• Goethite • Primary Fe-oxides • Ilmenite	Chao and Zhou 1983
5	Oxidizable	• Sulfides • Pyrrhotite • Chalcopyrite	Chao and Sanzolone 1977 in Leinz et al. 2000
6	Residual	• Various silicates	

RESULTS AND DISCUSSION

X-Ray Diffraction

XRD with Reitveld analysis on powdered bulk rock samples confirmed a primary mineral assemblage consistent with typical Duluth Complex lithologies. Samples were largely composed of the primary minerals: plagioclase feldspar, olivine, pyroxene, and ilmenite. For most samples, sulfide minerals were likely below the detection limit (about 0.5 %), although chalcopyrite was detected in one sample. Results from bulk XRD did not yield secondary iron-oxide mineral identifications. This may be due to low mineral abundance and/or iron-rich coatings that were amorphous or poorly crystalline. There were isolated occurrences of the efflorescent sulfate salts alunogen and epsomite, as well as, the silicate weathering products, kaolinite and montmorillonite. Several phyllosilicate minerals (biotite, actinolite, clinochlore) were identified that may have resulted from late-stage processes associated with the igneous intrusion, such as deuteric alteration of primary silicates.

The powder XRD on the hand sample coatings provided evidence for additional weathering products. Diffraction of iron-rich material generally did not produce diffraction patterns that

allowed phase identification, suggesting the rind material structure is very poorly crystalline to amorphous. However, in one case, poorly crystalline goethite was identified and appeared to be a product of sulfide- mineral replacement (Figure 2). The presence of goethite (FeOOH) may indicate crystalline transformation of iron oxide-rich coatings (Guo & Barnard, 2013 and references therein) or *in situ* formation due to the lower pH micro-domain proximal to the primary sulfide grain undergoing alteration as suggested by Jambor, 2003. An additional efflorescent sulfate salt was identified in one sample as rozenite ($Fe(SO_4) \cdot 4(H_2O)$) (Figure 3).
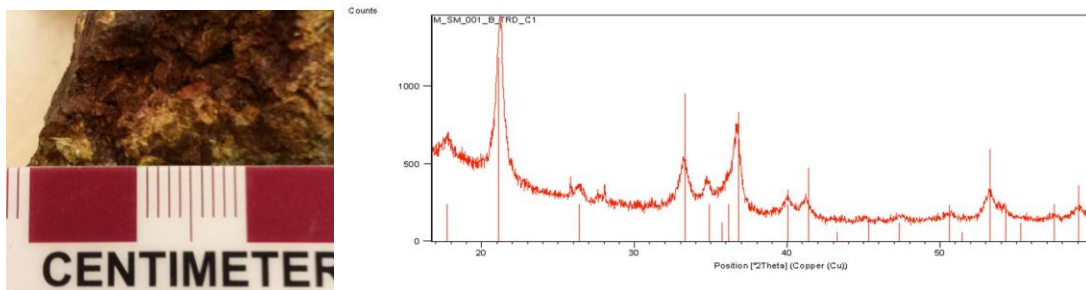

Figure 2 Hand sample showing rust-colored sulfide-replacement texture (left). XRD pattern of pictured material with the matched pattern (vertical lines) from ICDD database for goethite (ID card 000080097) (right).
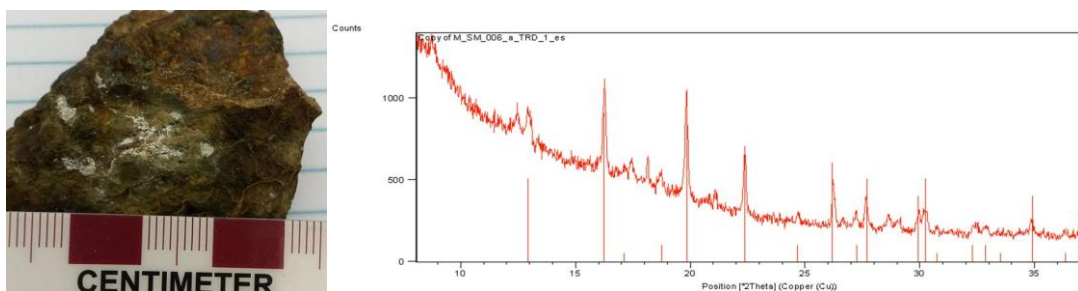

Figure 3 Hand sample showing visible weathering (left). Diffraction pattern of the white precipitate from this sample along with the pattern (vertical lines) from ICDD database for rozenite (ID card 000160699) (right).

Electron Microscope Analysis

Secondary mineral occurrences observed using back-scattered electron (BSE) images include: along fractures/ grain boundaries; as sulfide replacement; and on the exposed surfaces of mineralized rock.   Chemical composition data gathered with energy dispersive spectroscopy (SEM-EDS) performed at University of Minnesota Duluth indicate the coatings commonly contain iron and silica as major components and variable amounts of aluminum, sulfur, and metals (e.g. copper) as minor elements (Table 2). BSE images and associated chemical composition suggests variations in solution chemistry (cyclic chemical compositions) during deposition of these features.
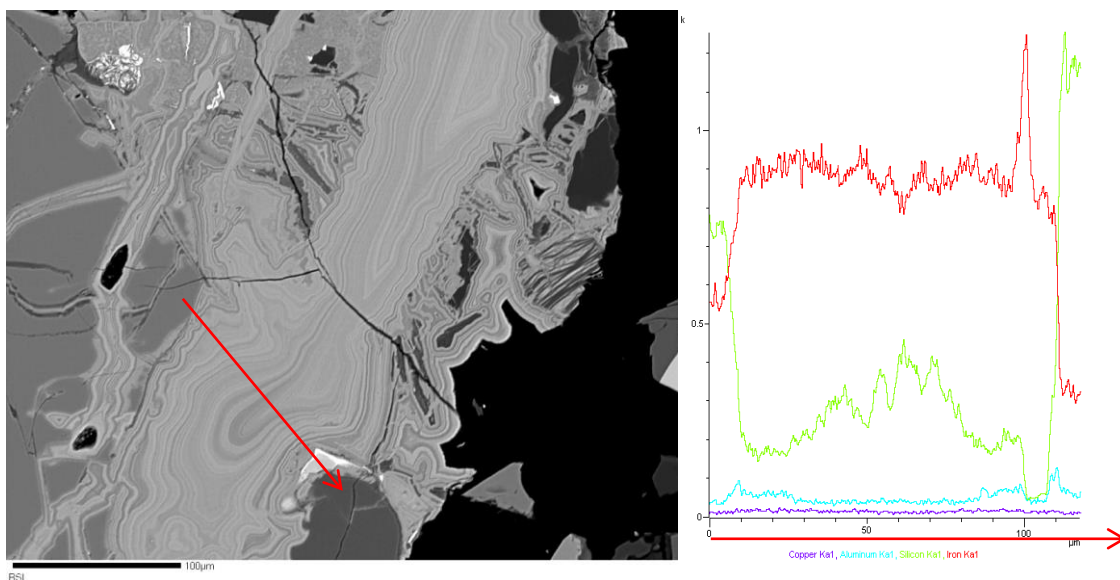
Figure 3 BSE image and location of cross-section line scan of an iron-rich coating (left). Relative chemical abundance plot Fe (red) and Si (green) Al (blue) and Cu (purple) showing variation across iron rich rind (right).

Table 2 Typical range of composition for iron rich coatings, oxygen not reported.

Element	Range of values[*] observed (weight percent)
Fe	45-66
Si	4-10
Al	1-2
S	0-5
Cu	0-3

* Semi-quantitative values.

Additional energy dispersive spectroscopy (EDS) analyses, performed by McSwiggen & Associates, indicated that the iron oxide-rich layers can contain up to 6 wt% CuO. These compositions were determined using a standardless technique, and therefore were semi-quantitative. Consistent with the analyses performed at the University of Minnesota Duluth, the amount of copper contained within the iron oxide-rich layers is highly variable. For some samples, the copper content was below the detection limit of the instrument under the operating conditions described (approximately 0.1 wt.%). On-going investigations are working to resolve certainty related to Cu speciation, association, and the upper limit of trace metal concentration.

The SEM analysis indicates that the width of individual layers within the layered iron oxide-rich features ranges from approximately < 1-3 μm. Spatial resolution for the EDS analysis is on the order

of 1 μm at 15 kV. Therefore, individual EDS analyses are likely sampling multiple layers, especially when layers are not oriented parallel to the electron beam. Our analyses likely represent a composite composition of several rind layers. If this is the case, it can be expected that true variability in the chemical composition of individual layers is greater than what is suggested by EDS data. Furthermore, these techniques cannot assess the form of the Cu, for example sorbed species on Fe oxide and/or fine-grained Cu secondary minerals.

Sequential Extraction

Results from sequential extraction confirm SEM observations of trace metals associated with iron oxide-rich layers. Iron oxides are expected to report within the reducible fractions. Results from sequential extraction indicate that these fractions can contain significant copper, nickel (Table 3). Similar trends for Co and Zn were also observed. For each of these elements, up to approximately half of the total amount of that element was associated with the reducible fractions.

Table 3 Sequential extraction results for **c**opper and nickel.

Extraction (mg/kg)	Water soluble		Weakly acid soluble		Reducible*		Oxidizable		Residual	
	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni
SM1	2.2	0.3	346.5	5.0	1030.0	158.7	727.9	151.5	40.1	29.6
SM2	1.1	1.0	137.1	5.6	740.3	191.7	1302.8	135.5	18.8	31.2
SM4a**	327.0	198.2	916.2	94.2	909.5	178.7	2314.1	175.8	8.4	24.9
SM4b	22.8	28.3	201.6	47.6	832.9	220.0	5331.2	376.7	8.5	27.0
SM5	5.7	11.1	64.0	21.6	770.4	179.1	5430.9	529.1	6.3	25.5

* Both reducible extractions (step 3 and 4) summed

** SM4a contained white crusts (see Figure 1, right)

CONCLUSION

Collectively, the mineral characterization techniques employed provide evidence for attenuation of constituents released during weathering of Duluth Complex rock by means of: (1) silicate mineral alteration to clays (kaolinite, montmorillonite); (2) precipitation of sulfate salts (epsomite, alunogen, rozenite); and (3) formation of iron-oxide rich layers which also contain variable amounts of trace metals, silicon, and aluminum. Assuming that the iron-oxide layers behave similarly to hydrous ferric oxide, the degree to which iron oxide layers will attenuate copper, nickel, zinc, and cobalt from mine-impacted water will be a function of drainage pH, total iron content, trace metal content, and reactive surface area (Dzombak & Morel, 1990). Micro-scale heterogeneity may indicate the presence of micro-geochemical environments and/or temporal fluctuations in water chemistry.

ACKNOWLEDGEMENTS

NOMENCLATURE

BSE   Back-scatter electron
EDS   Energy dispersive spectrometer
ICDD   International Center for Diffraction Data
ICP-OES Inductively coupled plasma- optical emission spectrometry
SEM   Scanning electron microscope

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