## INVESTIGATING METAL ATTENUATION PROCESSES IN MIXED SULFIDE

### CARBONATE BEARING WASTE ROCK

by

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### Abstract

The objective of this study was to identify the trace metal/secondary mineral phase associations in a heterogeneous waste rock dump that contains carbonate bearing lithologies and a mix of metal sulfides. The identification of attenuation processes can be used to better predict the drainage chemistry from waste rock at this site and/or other sites with similar waste rock. This study also provides the opportunity to investigate metal attenuation at the largest scale of complexity and compare these observations to those made from the smaller scale tests conducted for this site and is useful for understanding scalability of the smaller scale tests.

This study shows that in carbonate bearing waste rock the predominant processes that attenuate copper (Cu) and zinc (Zn) are precipitation of hydroxycarbonate and hydroxysulfate phases and sorption onto iron oxides. Arsenic (As) and molybdenum (Mo) are associated with iron oxides, although for Mo this association was observed in only a few samples. Lead (Pb) was observed in association with iron oxides. Wulfenite observed in a few samples provides an additional attenuation process for Mo and Pb. The stability of the phases and potential for remobilization of these metals suggested from this study. can also be The hydroxycarbonate/hydroxysulfate phases are the least stable phases identified and can dissolve at pH<5. Iron oxides are considered a stable phase, as such, the As, Cu, Pb and Zn associated with these phases may also be quite stable. Sorption of Mo is limited at neutral pH but wulfenite is a stable phase that is not expected to dissolve once formed.

Geochemical modelling of seepages from the dump show that iron oxides are supersaturated and wulfenite and gypsum are at equilibrium. Two mixed Cu:Zn hydroxycarbonate phases and hydrozincite were added to the geochemical database and are supersaturated, while malachite and smithsonite were generally undersaturated. Brochantite and antlerite were also generally undersaturated, but the observations made in this study show that copper hydroxysulfates and mixed copper/zinc hydroxysulfates are precipitating. In mixed sulfide/carbonate bearing waste rock mixed of Cu:Zn hydroxycarbonate and hydroxysulfate phases may require consideration for adequate prediction of Cu and Zn concentrations in drainage.

## Preface

Chapter 2 and Chapter 3 are based on the results of my efforts to identify secondary phases and the metals associated with them. Under the supervision of Roger D. Beckie, I was responsible for the design of the experimental program, carrying out the tests and data reduction/interpretation for these chapters.

A version of Chapter 3 has been published in the proceedings from the 10<sup>th</sup> International Conference on Acid Rock Drainage (ICARD) and International Mine Water Association (IMWA) Annual Conference.

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## **Chapter 1 Introduction**

### **1.1 Problem Description**

Non-economic waste rock typically constitutes the largest volume of waste produced during mining, especially in open-pit operations. After being exhumed, waste rock is stockpiled onsite in dumps and left exposed to ambient conditions. The primary environmental concern with respect to waste rock is drainage quality, and at all stages of mining significant effort is put forth to understand the hydrologic, geochemical, and microbiological influences on the waste rock with the goal of producing accurate predictions of water quality. Initial geochemical investigations of waste rock involve assessing primary mineralogy, trace element composition and potential to generate/buffer acidity of the waste rock. However, researchers have concluded that metals associated with secondary mineral phases are more important to identify and quantify because they exert a much stronger control on water quality (Al et al., 2000; Sloot and Zomeren, 2012).

The chemistry of drainage from a mine site is the result of the competing processes of acid generation, acid neutralization, and secondary mineral production resulting in metal attenuation. The oxidation of sulfide minerals proceeds either via dissolved oxygen ( $O_2$ ) or dissolved ferric iron (Fe<sup>3+</sup>) acting as the oxidizing agents (Nordstrom and Alpers, 1999). The relative importance of oxidation by dissolved oxygen or ferric iron depends on the pH of the water and microbiology. Oxygen dominates oxidation at near-neutral conditions (Nordstrom and Alpers, 1999). Dissolved ferric iron is more effective than dissolved oxygen in oxidizing sulfide minerals, but has limited solubility in neutral pH conditions and is generally a more effective oxidizing agent at low-pH conditions (though both are active at low pH) (Nordstrom and Alpers, 1999). Typically pyrite is the most abundant sulfide mineral that oxidizes to generate acidity:

$$\mathbf{FeS}_2 + \frac{7}{2}\mathbf{O}_2 + \mathbf{H}_2\mathbf{O} = \mathbf{Fe}^{2+} + 2\mathbf{SO}_4^{2-} + 2\mathbf{H}^+$$
 1-1

$$FeS_2 + 14Fe^{3+} + H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$
 1-2

Other sulfide minerals such as pyrrhotite, sphalerite, galena, and chalcopyrite can also oxidize to produce acidity depending on the oxidizing agent. Dissolution of some carbonate minerals, such as calcite, consumes the acidity generated by sulfide oxidation:

$$CaCO_3 + H^+ = Ca^{2+} + HCO^{3-}$$
 1-3

While other carbonate minerals, such as siderite and rhodochrosite, will cause the release of acidity due to hydrolysis/precipitation of the released  $Fe^{2+}$  and  $Mn^{2+}$ . Aluminosilicate minerals can also consume acid, however, their reactivity is slower and less effective than carbonates with the exception of wollastonite and olivine (Jambor et al., 2002). It is the balance between the acidity generated by oxidation versus the dissolution of buffering minerals that determines if acid rock drainage (ARD) or neutral rock drainage (NRD) will dominate the overall drainage of the waste material. However, in a heterogeneous waste rock dump with both potentially acidgenerating (PAG) and non-acid generating (NAG) waste rock, it is possible to have acidic zones producing acidic drainage and neutral zones producing neutral drainage. Although acidity in mine drainage defines the problem, the issues are related to dissolved metals and metalloids (referred herein as metals) in the drainage for which many countries will have regulated concentrations for release. Dissolved metal concentrations differ in ARD and NRD because metal mobility is highly dependent on pH. In acidic conditions metals such as Al, Fe, Cu, Pb, Zn, Cd, and Mn are mobile, while in neutral conditions elements which are either weakly hydrolyzing, like Zn, or oxyanion forming like Mo and As are mobile (Price, 2009; Stumm and Morgan, 1995).

Studies have shown that significant metal sequestration occurs on secondary mineral surfaces due to sorption onto metal oxides (Nordstrom, 2011). The most prolific metal oxides in sulfidic mining wastes are iron oxides. In addition to sorption of metals, precipitation of secondary minerals due to solubility limitations in highly concentrated waters, or by evapo-concentration, also sequesters metals and stores them in the solid phases. Secondary phases that form as a result of precipitation from concentrated solutions are often initially amorphous and are low abundance compared to primary minerals (Bigham et al., 1996; Jang et al., 2003).

The potential for long-term storage of trace metals depends on the stability of the phase that is attenuating metals and the stability of the environment it was sequestered in. Consequently, understanding the process of attenuation gives insight into the local environment that attenuation occurred and the potential for remobilization.

### **1.2 Study Background**

Since 2006, UBC, Compañia Minera Antamina (CMA) and Teck-ART have been collaborating on a multi-scale study of the hydrology, geochemistry and microbiology of waste rock at the Antamina mine site. The field studies include five 36m x 36m x 10m tall experimental waste rock piles (Bay, 2009). Three of these piles are composed of a single waste rock class (Peterson, 2014) and two are composed of a combination of waste rock classes (Blackmore, 2015). In addition to the experimental piles, smaller scale field studies involving field barrels of the single lithology and of mixed lithologies were constructed. The mixed lithology field barrels were designed to identify attenuation of Mo and Zn (Hirsche et al., 2012). Laboratory tests were also conducted which include batch tests, humidity cell testing and mixed lithology column tests (Blackmore, 2015; Conlan et al., 2012; Dockrey et al., 2014; Hirsche et al., 2014; Hirs

al., 2012). This study was motivated, in part, by the conclusions of previous researchers using smaller scale studies at Antamina to identify attenuation mechanism and secondary phases. These conclusions are:

- Mo studies showed that wulfenite precipitation is favoured over kinetically limited powellite, however in the absence of Pb, precipitation of powellite should be the only significant attenuation mechanism for Mo in a carbonate buffered system (Conlan et al., 2012).
- Acidic micro-environments in waste rock could lead to the precipitation of iron oxides where Mo sorption is possible (Dockrey et al., 2014).
- Attenuation of Mo was observed when Mo leaching waste rock was placed over Pb bearing waste rock (Hirsche et al., 2012)
- 4) Zn attenuation was suggested to occur via precipitation of a carbonate or hydroxide phase or may be incorporated into crystalline structure of phyllosilicate clay minerals such as clinochlore (Hirsche et al., 2012). Hirsche et al. (2012) also suggested from modelling that the precipitation of smithsonite could not account for all of the Zn attenuated in his studies.
- 5) In one of the experimental waste rock piles a blue precipitate consisting of gypsum, malachite and mostly amorphous phases in which X-ray absorption spectroscopy (XAS) showed that Cu in the amorphous material was bound primarily to sulfates in the form of brochantite and to some carbonates in the form of malachite (Peterson, 2014).

The primary objective of this study is to identify metal attenuation processes in the full scale waste rock dump and hypothesizes that the processes identified at this scale will be similar to what was identified at the smaller scales of investigation.

### **1.3** Site Description

The Antamina deposit is a large copper-zinc-molybdenum skarn deposit with smaller quantities of silver, bismuth and lead that formed by the intrusion of a quartz monzonite body into limestones (Lipten & Smith, 2004; Love, Clark, & Glover, 2004; Redwood, 1999). The Antamina mine is located approximately 270km NE of Lima, Peru in the department of Ancash (Figure 1.1). It is situated in the Andes, at an elevation ranging between 4200 and 4700masl. Antamina receives approximately 1200-1300mm precipitation per year, 80% of which falls as rain during the region's wet season (October – April). The mean annual temperature at the mine site is ~5.0°C measured at the meteorological station at Punto B.

The East Dump receives both potentially acid-generating (PAG) waste rock and non-acid generating/acid-buffering (NAG) waste rock from a range of lithologies, i.e., limestone, marble, hornfels, exo- endo- skarn and intrusive, and is thus considered geochemically heterogeneous. At the time of drilling (November 2012 – February 2013), the deepest material in the East Dump had been in place for over 10 years, while the shallowest material for more than 5 years. Two holes were drilled at two sites, Site 1 and Site 3, on the East Dump (Figure 1.2). The holes were drilled using air-driven reverse circulation (RC) using a Casagrande C8 drill. Drilling fluids were not used to minimize the alteration of secondary phases. As part of the drilling program drill cuttings were logged by the Antamina Geology Department; these logs are presented in Appendix A. The size fraction selected for testing was <2mm, based on work conducted by

Strömberg & Banwart (1999) which identified that particles with diameters smaller than 0.25mm contribute to approximately 80% of the sulfide and silicate dissolution, and carbonate minerals larger than 5–10mm react too slowly to neutralize the acid produced from sulfides. Thus, the <2mm material was selected for this study with the expectation that these size fractions would host the secondary minerals that form coatings on grains as a result of sulfide oxidation and carbonate neutralization.

### 1.4 Method

The observations made in this study are from a suite of geochemical and mineralogical tests. Figure 1.3 presents the experimental framework used for this study. X-ray diffraction (XRD) and total digests were used to characterize the mineralogy and total elemental content of the samples, respectively. Sequential extractions (SEP) were used to leach metals out of operationally defined "pools" representative of secondary minerals/phases. The results of these tests were then used to select a smaller number of samples to be prepared into thin-sections and undergo a more detailed mineralogical investigation. The detailed mineralogical investigation involved using transmitted and reflected light microscopy and scanning electron microscopy to identify secondary coatings on primary mineral surfaces. Energy dispersion x-ray spectroscopy (EDS) was used to obtain a semi-quantitative analysis of metal content of the secondary phases by focusing the beam on spot locations.

Aqueous chemistry of seepages located downslope of the drill sites (also shown in Figure 1.2) was analysed using PhreeqC (Parkhurst and Appelo, 2013) to obtain saturation indices (SIs) of potential controlling phases.

#### **1.4.1** Sequential Extraction Procedure Used

It has only been in the last few decades that SEPs have been used to investigate metal attenuation (metal mobility and metal partitioning) in mine waste materials. Most of these studies have been focused on tailings (Carlsson et al., 2002; Dold, 2003; Fanfani et al., 1997, 1997; Hall et al., 1996); and only a few studies have conducted SEPs on waste rock (Jeong and Lee, 2003; Singh and Hendry, 2012; Stockwell et al., 2006). In this study, sequential extractions were used to suggest what phases metals were associated with and to identify samples in which high concentrations of elements might allow for visual identification of these phases in thin-section. Sequential extraction procedures also provide a way of obtaining useful information concerning the stability of the metals and associated phases. SEPs are "operationally" defined meaning that different extraction reagents can be used depending on the metals of interest and the expected secondary phases. Accordingly, multiple SEPs have been proposed. The main criticisms of SEPs are the lack of selectivity due to the wide range of secondary minerals possible (especially in mining wastes) and the potential to dissolve non-targeted phases causing difficulty in the interpretation of results. Two SEP methods were identified in the literature and were both suitable for this study because they accounted for the secondary minerals expected in this waste rock environment (i.e., water soluble phases, carbonate phases, and iron oxides). These two methods were investigated in Chapter 2 of this thesis to determine if there was a difference in the results obtained between the two methods and, if so, to what those difference could be attributed. A sub-set (N=8) of East Dump waste rock samples were selected for this study. SEP leachate results were paired with XRD scans of the unreacted material and of the residues after each extraction step, in order to compare the concentrations of metals leached with the minerals dissolved or precipitated during each step.

### 1.5 Thesis Structure

This thesis is written in a paper-based format. It consists of four chapters: an introduction, two papers and a conclusion. The two papers are self-contained – each with an introduction, methods, results, discussion sections. The first paper (Chapter 2) presents the investigation of the two sequential extraction procedures conducted on samples from the East Dump. The second paper (Chapter 3) uses the results of the experimental framework described above to discuss the attenuation of As, Cu, Pb, Mo, and Zn in mixed sulfide/carbonate bearing waste rock collected from East Dump, Antamina Mine, Peru.

## Figures



Figure 1.1 Location of the Antamina Mine in Peru, South America (inset). From (Conlan, 2009).



Figure 1.2 The Antamina Mine site, inset plan of the East Dump and pre-mining topography showing drill site locations and seeps downslope of drill sites



Figure 1.3 Experimental framework

# Chapter 2 Comparison of Two Sequential Extraction Procedures Using Waste Rock Material Collected from the East Dump, Antamina Mine, Peru

### 2.1 Introduction

Sequential extraction procedures (SEPs) were first proposed in mineral exploration because they allowed for the distinction between primary and secondary metal bearing minerals, the latter of which was used to infer "signals" of hidden deposits (Gatehouse et al., 1977; Sondag, 1981; Tessier et al., 1979). SEPs were also developed to understand metal retention and mobility in contaminated environments (Chao and Zhou, 1983; Wenzel et al., 2001). In the last few decades SEP methods have been proposed and used on mine wastes, mainly tailings (Carlsson et al., 2002; Dold, 2003; Fanfani et al., 1997, 1997; Hall et al., 1996) while only a few studies have focused on waste rock (Jeong and Lee, 2003; Singh and Hendry, 2012; Stockwell et al., 2006). SEPs are ideal for determining metal retention in secondary phases that cannot be identified via instrumental methods because they are either too low in concentration (<1%), or nano-crystalline/amorphous or sorbed onto other mineral phases. SEPs consist of a sequence of leaching steps each of which targets specific phases. All SEPs are operationally defined, meaning that the reagent used in each step is optimized to target, or select, metals retained by specific phases. The main criticism of SEPs is that they are not selective essentially dissolving more than the intended phase, particularly in mine waste which contains a wide range of primary and secondary minerals. Another criticism is that there is potential for redistribution of metals during the procedure such that metals are incorrectly associated with phases and consequently the contributions of specific phases to metal attenuation can be over- or underestimated. Many of the SEP methods recommend the use of other mineralogical techniques in parallel to improve

phase identification (Caraballo et al., 2009; Dold, 2003; Hall et al., 1996; Ryan et al., 2008; Tessier et al., 1979). Several studies on a variety of natural and synthetic samples have shown that SEPs are never ideally selective, particularly for steps that target amorphous and crystalline iron oxides (Caraballo et al., 2009; Chao and Zhou, 1983; Dold, 2003; Hall and Pelchat, 1999; Larios et al., 2012). For example, Chao and Zhou (1983) found that the presence of magnetite in a sample catalyzed the dissolution of crystalline iron oxides during the amorphous iron oxide step when using oxalate as a reagent. The study concluded that an acidified hydroxylamine hydrochloride solution was the most desirable reagent for use on amorphous iron oxides due the close agreement with the results of extraction using oxalate (Chao and Zhou, 1983). The study also showed that Mn oxides are dissolved during the Fe oxide steps (Chao and Zhou, 1983). Caraballo et al. (2009) showed that Al hydroxides were also dissolved together with iron oxides when using oxalate as a reagent (Caraballo et al., 2009). Hall et al. (1996) proposed using hydroxylamine hydrochloride for the dissolution of both amorphous and crystalline iron oxides instead of oxalate because of the lack of selectivity of oxalate in the presence of magnetite when dissolving amorphous iron oxides, as described by Chao and Zhou (1983), and because the UV light set-up required for oxalate dissolution of crystalline iron oxides was considered to be too cumbersome. Dold (2003) compared hydroxylamine hydrochloride and oxalate in darkness for the dissolution of amorphous Fe oxides and Mn oxides concluding that both mineral phases were dissolved by these two reagents, but proposed oxalate for oxides in Cu-bearing sulfide tailings. Broadhurst et al. (2009) qualitatively compared the SEP proposed by Hall et al. (1996) to the method proposed by Dold (2003) using tailings material. Their results showed that there was relative consistency between the leachate results of the two SEPs; however, the study did not attempt to identify the minerals dissolved during the different steps or identify the phases from

which the elements leached and concluded that more research was required to identify the phases and mechanisms. While there is no doubt that oxides are excellent scavengers for trace metals in mine impacted sediments and tailings in the presence or absence of carbonates, studies involving carbonate waste rock where there is a focus on determining the potential for metal attenuation via precipitation of metal carbonates or sorption onto carbonate mineral phases have not been carried out. This is partly because SEPs are typically designed such that metals extracted via carbonates and cation exchange/weak sorption are assessed in a single step, although these are two very different attenuation mechanisms.

The objective of this study was to identify selectivity issues in two SEPs in weathered waste rock containing As, Fe, Cu, Pb, Zn, and Mo bearing sulfides and carbonates. The two methods used, Method 1 and Method 2, were modified from Hall et al. (1996) and Dold (2003), respectively. These two published SEPs were selected for this study as they targeted the same phases, in the same order, using different reagents, and because the methods could be modified to include supplementary steps to address additional expected attenuation mechanism for carbonate bearing waste rock material. The criteria used to evaluate the two SEPs were:

- 1) Selectivity (i.e., the ability of a reagent to dissolve only the intended phases); and,
- 2) Retention of metals in the extraction solution (i.e., minimal confounding effects due to secondary mineral formation with the extraction reagents).

Our study used heterogeneous waste rock material with a range of acid generating and acid neutralizing potentials and a range of leaching potentials for As, Cu, Pb, Mo, and Zn to compare two SEP methods modified from published SEPs. These SEPs were designed to separate metals attenuated by secondary water soluble phases, cation exchange/weak sorption, weak-acid soluble phases (targeting carbonates), metals sorbed to amorphous iron oxides and metals sorbed to crystalline iron oxides from metals associated with primary silicate and sulfide minerals. Using observed leachate chemistry in tandem with mineralogical analyses of the residuals after each step, our study identified not only selectivity issues with respect to oxide phases but also with respect to phases that are weak-acid soluble.

### 2.2 Site and Sample Collection

The Antamina Mine is located approximately 270km North of Lima, Peru. The climate at Antamina is bimodal with two distinct annual seasons; a wet season and a dry season. During the wet season approximately 80 - 90% of the total annual precipitation (~1200-1300mm) occurs. During the dry season, rainfall is limited and evaporation is high (Peterson, 2014). The mine exploits Cu-Zn-Mo (Bi, Pb and Ag) from a skarn deposit hosted in limestone (Lipten and Smith, 2004; Love et al., 2004; Redwood, 1999) and exhumes limestone, marble, hornfels, skarn, and intrusive waste rock with a range of neutralization/acid-generating potentials and metal contents during the mining process. The waste rock samples used in this study were collected from boreholes drilled in the East Dump, one of the operating waste rock dumps at the mine. Although Antamina segregates waste rock into specific dumps based on reactivity and metal content the East Dump is designed to accept all types of waste rock, and diverts seepage from the dump into the tailings pond where it is treated as part of the water quality management program. Figure 2.1 shows the drilling locations that provided the samples for this study (Site 1 and Site 3). At the time of drilling, the deepest material had been in place for over ten years, and the shallowest material for more than 5 years. A total of four boreholes (2 per site) were drilled using air-driven reverse circulation drilling, in which no drilling fluids were used to minimize the potential for alteration/dissolution of secondary phases. At each site, waste rock was collected from a deep
hole (>100m) and a shallow hole (~20m). To obtain the waste rock material, the drill casing was advanced in 1.5m intervals and waste rock drill cuttings were blown up the hole by compressed air and collected in trays. The drill cuttings from each 1.5m interval were sieved using a 2mm (#10) mesh and 500g of the passing material was saved for this study. Table 2.1 lists the eight samples selected for this study along with lithology, visible sulfide mineralization, and visible secondary minerals. Prior to testing, the samples were air dried at room temperature in a fume hood for several days. The dried sample was then ground to a fine powder in a swing mill for ~30s to further homogenize the samples before application of the SEPs. Rao et al. (2008) presented a review on the effects that sample pre-treatment had on extraction results, summarizing that air-drying at low temperature had a minimal impact on the results of extractions. Grinding may have an effect on metal extractability by increasing the availability of phases; however, in this study this was not investigated.

#### 2.3 Methods

#### 2.3.1 X-Ray Diffraction (XRD) Mineralogy of Samples

X-ray diffraction (XRD) was used to identify the most abundant crystalline minerals in the samples prior to the SEPs and in residues collected after the application of each step of the SEPs. To prepare the samples for XRD analysis, the samples were ground into a powder-slurry using a mortar and pestle and ethanol. The slurry was then smeared onto a glass slide. XRD data were collected using a Bruker D8 Focus Diffractometer with a scanning step of 0.029° 20 and counting time of 100.1s over a range of 3-80° 20. Mineral phases in the X-ray diffractograms were matched to mineral phases using the International Centre for Diffraction Database PDF-4 and Search Match software by Bruker.

#### 2.3.2 Total Elemental Composition

Total elemental composition of each sample was determined by 4-acid digestion of an approximately 0.26g of sample (after homogenization and weighing) and analysis by inductively-coupled plasma – optical emission spectroscopy (ICP-OES) and inductively-coupled plasma – mass spectroscopy (ICP-MS) at SGS, Burnaby, Canada. Sulfur speciation and total inorganic carbon were analysed at ALS, Peru.

#### 2.3.3 Sequential Extraction Procedures and Comparison

For both SEP methods, each sample was prepared in the same manner: Eight splits of the sample were taken; 3 splits to be leached using the full SEP to calculate an average leachate chemistry for each step and 5 splits to be leached using a "parallel" extraction method to obtain post-step residues to be analysed using XRD. The "parallel" extractions were designed such that the first of the five splits would undergo only the first step and its residue analysed using XRD, the second of the five splits would only undergo the first and second step and its residue analysed using XRD, and so on for the rest of the splits/steps. The residues were air dried and prepared for XRD analysis as described above.

The two methods, referred herein as Method 1 (modified from Hall et al., 1996) and Method 2 (modified from Dold, 2003), are presented in Table 2.2. The main differences between the two methods are the reagents used to dissolve weak-acid soluble phases (Step 3) and amorphous and crystalline iron oxides (Step 4 and Step 5, respectively), as well as the reaction time and temperature used for these steps. The two SEPs were modified by including additional steps, but no modifications were made to the specific steps prescribed by each method. The SEPs were modified based upon previous metal attenuation studies at Antamina (Hirsche, 2012; Peterson, 2014): 1) to include a water-soluble phase extraction step in Method 1; and, 2) to use two steps instead of one to separate metals attenuated by weak sorption/cation exchange and weak-acid soluble phases, which are typically extracted together, in both SEPs. The reasons for the modifications are based on anticipated attenuation mechanisms, which were:

- Precipitation of water soluble sulfates Equilibrium geochemical modelling of seep water from locations downslope of the drilling sites indicate that gypsum is at equilibrium (Laurenzi, Chapter 3). Studies of waste rock in semi-arid to arid climates where evaporation is high show that the formation of efflorescent water soluble metal salts is possible (Carbone et al., 2013a; Smuda et al., 2007). Accordingly, a water soluble step would provide support for the model-predicted gypsum equilibrium and identify if additional water-soluble metal salts precipitated.
- 2) Attenuation via weak sorption/cation exchange or carbonates Cation exchange onto clay minerals was proposed as a potential attenuation mechanism for Zn in Antamina waste rock (Hirsche, 2012). Smithsonite (ZnCO<sub>3</sub>) was identified using XRD with Rietveld refinement on waste rock collected from a field barrel after 1 year of weathering (Dockrey, 2010). Equilibrium geochemical modelling of seep water from locations downslope of the drilling sites indicate that copper-sulfates such as brochantite (CuSO<sub>4</sub>·3Cu(OH)<sub>2</sub>) and antlerite (Cu<sub>3</sub>(SO<sub>4</sub>)(OH)<sub>4</sub>) are generally undersaturated and supersaturated at times when the pH is between 7 and 5. The geochemical modelling also shows that malachite and smithsonite are undersaturated. Furthermore, a blue, mostly amorphous, precipitate containing some malachite and gypsum was observed associated with an experimental test pile composed of intrusive material (Peterson, 2014). Using synchrotron-based X-ray adsorption near-edge structure analysis (XANES), copper in the amorphous precipitate was determined to be bonded predominantly with sulfate in the

form of brochantite and some carbonate in the form of malachite (Peterson, 2014, personal communication M. Lindsay, Univ. Saskatchewan). Accordingly, a separate extraction step that removed metals bound by weak electrostatic forces and cation exchange (Step 2) was added to distinguish between this attenuation mechanism and metals associated with carbonates (Step 3). The extraction reagent (MgCl<sub>2</sub>) used for Step 2 was based on established methods documented in the literature (Tessier et al., 1979).

Step 6 of each SEP was conducted by a commercial lab (SGS, Burnaby) using the four-acid digest method as described previously for total elemental composition.

All reagents were prepared the day of, or one day prior to, testing. Approximately 1g of solid was weighed in a 50ml Falcon <sup>TM</sup> tube and reacted in the sequence prescribed by the methods, see Table 2.2. After the reaction time was complete, the tube was centrifuged at ~2500RPM and the leachate was decanted into a syringe and filtered using a 0.45 $\mu$ m filter. The residue was rinsed with 5ml of de-ionized water (DI) and centrifuged again; the rinse water was then added to the leachate. The rinse step was then repeated. The leachates were analysed for Al, As, Ca, Cu, Fe, Mn, Mo, Pb, S, Si, and Zn by ICP-OES. Since the ICP-OES reports chemistry in mg/L of liquid and because the steps of the SEPs use different liquid:solid ratios, leachate concentrations were converted to ppm. The detection limits of the ICP-OES are generally 0.2mg/L; however, based on the volume of reagent used in each extraction step this resulted in varying detection limits in ppm (presented in Table 2.2). Element concentrations below the detection limits are reported herein as <DL. The average leachate chemistry for each step was calculated from the leachate concentrations (ppm) of the three splits of each sample that underwent the full extraction sequence. For each average leachate chemistry calculation, when

the detection limit was encountered a zero value was used. Relative percent difference (RPD) (USEPA, 2010) was used to compare the average leachate chemistries between the two SEPs, using the equation:

$$\operatorname{RPD} = \frac{||\mathbf{x}_1 - \mathbf{x}_2||}{\bar{\mathbf{x}}} \times 100$$
 2-1

Where  $x_1$  and  $x_2$  are the average leachate chemistry for a particular step in Method 1 and Method 2, respectively, and  $\bar{x}$  is the average of the two. RPD is typically used in two ways; to calculate the precision from duplicate measurements and to compare two measured values when an exact (true) value is not known (USEPA, 2010). In this study it was used based on the assumption that if the two methods are targeting the same attenuation mechanism/secondary phases per step then the leachate chemistries between the two methods should be similar. If they are not, then either additional minerals are being dissolved or precipitated or there is carry-over of metals between steps due to the reagent used or incomplete dissolution of target phases. In this study an RPD of greater than 30% was used as an indication that there was a significant difference in the leachate chemistry of the steps being compared.

The first two steps of both methods were identical in reagent, and leach time, thus comparison of the leachate results was also used as an indication that sampling biases were minimal in the splitting of samples to make replicates for the investigation; this is discussed further in the results section.

#### 2.3.4 Method Quality and Inter-sample Variability and Sample-split Variability

Appendix B presents measurements that were taken during the extraction steps to ensure solids were not lost during the manipulations of the SEPs (mass loss) and that the pH of the

carbonate extraction step (Step 3) remained at the targeted pH (pH drift). Calculation of cumulative leached versus total metal concentration were made to also determine if mass was conserved during the SEPs. Relative standard deviation (RSD) for the triplicate analyses for Al, As, Cu, Fe, Mg, Mn, Mo, Pb, Si and Zn were made to determine sample/split variability.

#### 2.4 Results

#### 2.4.1 XRD Mineralogy of Samples

Table 2.3 lists the initial, pre-SEP sample mineralogy identified from the XRD diffractograms. The minerals found in the samples are consistent with the lithologies noted in the drill logs (Appendix A) and the mineralogies reported previously in "fresh" waste rock (Peterson, 2014). Most samples were mineral mixtures typical of the dominant rock type noted in the drill logs and the other lithologies also noted in the drill logs. The primary minerals in marble samples were predominantly calcite, but they also contained quartz, orthoclase, albite and biotite from igneous intrusive rock. The igneous intrusive samples contained quartz, orthoclase, albite, biotite, muscovite, pyrite, chalcopyrite, and molybdenite as well as calcite from marble and limestone. The primary minerals of the exoskarn waste rock were the garnet minerals hibschite and andradite, vesuvianite and wollastonite along with quartz, orthoclase, albite, biotite and calcite from igneous intrusive and limestone/marble waste rock, respectively. The secondary minerals that were identified in the samples were gypsum, hemimorphite, smithsonite, and wulfenite. It should be noted that while hemimorphite and smithsonite are possible secondary minerals that can form from the oxidation of zinc-bearing sulfide minerals, at Antamina these minerals are also associated with the supergene mineralization of the deposit (Personal communication 2013, L. Plascencia) and therefore may have been placed in the dump during construction rather than have been formed in the dump as a secondary phase. Hemimorphite was also noted in "fresh" skarn material (Peterson, 2014), further suggesting that it may have been present pre-mining.

#### 2.4.2 Bulk Elemental Analysis

The results of the bulk chemistry from the four-acid digestions of the samples are presented in Table 2.4. The samples contained total Cu ranging between 1020 ppm – 18600 ppm. Total Zn contents in the samples ranged between 473 ppm – 8290 ppm. Arsenic ranged between 45 ppm – 193 ppm and Mo between 24.5 ppm – 331 ppm. Lead concentrations in the samples ranged between 50.1 ppm – 874 ppm.

Sulfur speciation and total inorganic carbon (TIC) content are presented in Table 2.5 along with the calculated acid-potential and carbonate neutralization potential of each sample. Samples that were composed of primarily igneous intrusive waste rock contained between 2.9 and 14.9 % total sulfur and between 1.3 and 1.8% TIC. The samples that were composed of primarily marble contained between 0.3 - 0.6% total sulfur and between 3.6 - 9.6% TIC. The sample that contained primarily marble diopside had 1.5% total sulfur and 2.9% TIC and the green garnet exoskarn sample had 0.8% total sulfur and 4.9% TIC. For all of the samples, greater than 86% of the total sulfur was in the form of sulfide. Of the eight samples, five would be characterized as non-acid generating, one (BH3-2) would be characterized as uncertain and two (BH1-2 and BH3-4) would be characterized as potentially acid generating (Price, 2009).

#### 2.4.3 Sequential Extractions and XRD Mineralogy

In this section, the average Ca, Fe, Cu, Pb, Zn, As and Mo leachate results for each step of Method 1 and Method 2 for select samples are compared qualitatively using % leached figures, quantitatively using calculated RPD for all samples, and XRD analysis of post-step residues on select samples. In each XRD analysis figure, the bottom diffraction pattern is the untreated sample and the above diffraction patterns correspond to Step 1 through Step 5, in order. Appendix C presents the % leached Al, Ca, Fe, Mn, As, Cu, Mo, Pb, and Zn for all samples as well as the XRD analyses for both methods for all samples.

Generally, from the figures indicating the % leached it appears that there is relative consistency between Methods 1 and 2 with respect to the % leached Fe (Figure 2.2), and, As and Mo (Figure 2.3). Figure 2.2, shows that there are notable inconsistencies with % leached Ca specifically during Step 4 and Step 5, where Ca is found in the leachates from Method 1 and not Method 2. It also appears that there are inconsistencies with % leached Cu, Pb, and Zn (Figure 2.4) during Step 3 and Step 4, where more metals are leached from Method 1. In-line with the conclusions of Broadhurst et al. (2009), from this qualitative assessment it is not possible to attribute the inconsistencies in Ca, Cu, Pb, and Zn to selectivity issues. Thus, these inconsistencies are partially addressed in the sections below using direct comparison of the leachate chemistries aided by XRD mineralogy of the residuals. The focus of the comparison is on Step 3 through Step 5 in which the reagents, reaction time, and temperature differ between methods.

#### 2.4.3.1 Extraction Results Step 1 – Water Soluble Phases

The water-soluble extraction leachate concentrations, shown in Table 2.6, were similar between both methods, with all RPD values less than 15%. The concentrations of most elements were low or below detection limit. There was measurable Ca, Si and S (S not presented) in most samples; however, Si was very close to the detection limit in most samples. Ca and S made the bulk of the leached elements and were calculated to have an approximate 1:1 molar ratio, which is consistent with the dissolution of gypsum.

Samples BH1-1, BH1-3, and BH3-1 leached the lowest concentration of Ca during this step and gypsum was not detectable in the XRD patterns for these samples. The rest of the samples leached higher Ca in this step and had detectable gypsum in their XRD patterns. It can be seen for sample BH1-4 in Figure 2.5 and Figure 2.6 for Method 1 and Method 2, respectively, that after Step 1, gypsum was no longer detected in the residues suggesting that gypsum was successfully removed during this step.

# 2.4.3.2 Extraction Results Step 2 – Metals Bound by Weak Electrostatic Forces and Cation Exchange

The MgCl<sub>2</sub> reagent used in this step is meant to remove only those elements that are bound by weak electrostatic forces and cation exchange, and is not intended to dissolve a solid phase. Table 2.7 shows the average leachate concentrations for both SEPs and calculated RPDs for Step 2. RPD values were generally less than 30%. RPD values greater than 30% were due to values at or near the detection limits of the ICP-OES where error is high. The concentrations of elements in the leachates from this step were generally near or below detection limit, with the exception of Ca, Mn, Si, Cu, and Zn in most samples, and Mo, and Pb in a few samples.

#### 2.4.3.3 Extraction Results Step 3 – Weak Acid Dissolvable Phases

From Table 2.2, the reagents used for Method 1, Na-CH<sub>3</sub>COO – sodium acetate at pH 5.0, and Method 2, NH<sub>3</sub>-CH<sub>3</sub>COO - ammonium acetate at pH 4.5, differ in pH, counter ion and leach time. Table 2.8 presents the average leachate concentrations for the two SEPs and the calculated RPDs. The RPDs for calcium, manganese and copper were good, below 30%, which is an indication that both methods dissolved similar weak-acid soluble Ca, Mn, and Cu bearing phases. However, the RPDs for Fe, Si, Pb, and Zn were greater than 30% for many samples, while Mo and As were below detection.

For both methods, XRD analysis of the residuals of the step showed that calcite was successfully dissolved from each sample. Also noted in the XRD pattern was the dissolution of hemimorphite ( $Zn_4Si_2O_7(OH)_2 \cdot H_2O$ ) during this step during application of both methods, Figure 2.5 and Figure 2.6, respectively. Also seen in Figure 2.5 and Figure 2.6, after the dissolution of the carbonate fraction in Step 3, the relative proportion of the remaining mineral phases increased, allowing for the identification of the scapolite mineral meionite ( $Ca_4Al_6Si_6O_2*4CO_3$ ) in a sample where scapolite was noted in the drill logs, merwinite ( $Ca_3Mg(SiO_4)_2$ ), and wollastonite ( $CaSiO_3$ ), which is part of the Antamina porphyry-skarn assemblage (Lipten and Smith, 2004). It is unlikely that these minerals were precipitated during the extractions.

#### 2.4.3.4 Extraction Results Step 4 – Amorphous Reducible Phases

Generally, the concentrations of elements extracted by the two methods at this step were not similar and the RPDs were >30%, with the exception of Fe (See Table 2.9). However, the concentrations of Fe in the leachates from this step were generally higher in Method 1 than in Method 2, which could be due to the enhanced dissolution of Fe oxides during Step 3, when using Method 2, as discussed above.

XRD diffractograms for residues from both methods showed that wollastonite was dissolved or partially dissolved in this step, Figure 2.7 and Figure 2.9 for Method 1 and Figure 2.8 and Figure 2.10 for Method 2. After Step 4 of Method 2, the post-step residue XRD patterns for BH1-1 (Figure 2.8), BH1-2, BH1-3 (Figure 2.10), BH1-4 (Figure 2.6), and BH3-3 showed three peaks at 17.347, 17.746 and 29.263 (20), that were not identified in the Method 1 post-step residues. The mineral was identified as whewellite (CaC<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O – calcium oxalate). The identification of a Ca-oxalate precipitate suggested the potential for precipitation of other metal oxalates but at concentrations too low to be identifiable with XRD, the possibility of which is

examined in the discussion section. Since both methods dissolved calcite in the previous step, dissolution of wollastonite is considered the main source of Ca in the leachates at this step. A nearly 1:1 Ca:Si molar ratio calculated in the Step 4 leachates from Method 1 is used as a proxy to support this assumption, with the exception of BH1-1 and BH1-3 which had Ca:Si molar ratios of 16 and 13, respectively, suggesting that other processes may have played a role in the case of these samples. Close examination of the XRD results did not provide conclusive information on the dissolution or formation of other mineral phases.

### 2.4.3.5 Extraction Results Step 5 – Crystalline Reducible Phases

Table 2.10 presents the average leachate concentrations for both methods and the calculated RPDs for the comparison of this step. Similar to the results of Step 4, the leachate concentrations were not comparable and most RPDs were >30%.

The only observed changes in the mineralogy of the post-step residues from this step were found in the samples that underwent Method 2. The whewellite peaks became more prominent in the samples previously noted to have precipitated whewellite and whewellite was detected in BH3-4 (shown in Appendix C) indicating that additional precipitation of this phase occurred during Step 5. A nearly 1:1 Ca:Si molar ratio calculated in the Step 5 leachates from Method 1 is used as a proxy to support the assumption that dissolution of wollastonite during this step supplies the Ca for the precipitation of whewellite as was observed in samples treated by Method 2.

#### 2.4.3.6 Cumulative Extraction Results for Steps 1 - 5

The sum of concentrations for Step 1 through Step 5, for each method, and the calculated RPDs for these sums are presented in Table 2.11. The RPDs for Al, Ca, Fe, Mg, Mn, Pb, Si, and Zn were generally below 30%. The elemental releases of Cu, Pb, Zn were generally higher for

Method 1 and the elemental releases for As and Mo were higher for Method 2. The low-moderate RPDs in the cumulative analysis indicated that each method dissolved similar total amounts of minerals, and suggested that the differences in the comparison of leachates is due to selectivity rather than sample variability. For example, cumulative Fe leached for both methods were similar suggesting that similar phases were dissolved but the Fe phases dissolved were distributed over Steps 3 - 5 differently for each method.

#### 2.5 Discussion

The reagents and reaction times for Step 1 and Step 2 of both methods were the same, the average leachate chemistries were characterized by low RPDs and XRD results for both extraction methods were similar, suggesting sample-split variability was low. The leachate chemistry of the extractions and XRD mineralogy showed that gypsum was the only mineral dissolved in Step 1. Based on these results, a water soluble extraction step should always be included in an SEP for carbonate bearing waste rock as gypsum is a typical mineral phase that controls the concentration of Ca and S in pore water. The leachate chemistries from Step 2 of both methods had measureable Cu and Zn in some samples but these concentrations were low compared to the concentrations leached from subsequent extraction steps. The two methods documented in the literature (Dold, 2003; Hall et al., 1996) include cation exchange/weak sorption and carbonate phases in a single step; however, our study showed through modification of these methods that in carbonate bearing waste rock, metals are more likely to be associated with weak-acid soluble phases rather than cation exchange/weak sorption. Thus, modifying each method to include a weak sorption/cation exchange step (Step 2) allowed metals bound by this attenuation mechanism to be discriminated from metals bound in weak-acid soluble phases (Step 3).

Step 3 of both methods did not selectively extract carbonates. While the RPDs for Ca, Mn and Cu were acceptable, the RPDs for Fe, Pb and Zn were >30% for most samples. Two possible reasons for Fe in the leaches are dissolution of siderite (FeCO<sub>3</sub>) and reductive dissolution of low-order amorphous iron oxides in the presence of acetate. The concentrations of Fe ranged between 75ppm and 1500ppm for Method 1 and between 220ppm and 1800ppm for Method 2, thus higher concentrations of Fe were reported in the leachates from Method 2 as compared to Method 1. Heron et al. (1994) tested whether sodium acetate at pH 5 (same as Method 1) would selectively dissolve siderite and found that siderite was not sufficiently soluble in the presence of this reagent. Caraballo et al. (2009) used ammonium acetate at pH 4.5 (same as Method 2) in an SEP to dissolve poorly crystalline Fe - phases and found that this reagent dissolved schwertmannite; however, this study did not specify if siderite was also present in the samples and if so, whether it dissolved. Based on this information, it can be concluded that the reagent used in Method 1 is unlikely to dissolve siderite, if present, and that iron oxides are more probably sources for Fe released. Method 2 has been demonstrated to dissolve iron oxides, and their enhanced dissolution may also explain the enhanced release of Fe and potentially sorbed metals. The lower pH value of this reagent may also be more favorable to promote the dissolution of siderite, if present. While siderite was not noted in the XRD patterns in the samples collected for this study, fresh waste rock samples of igneous and skarn lithologies at Antamina had between 0.1 - 0.3% siderite (Peterson, 2014). BH1-1 and BH1-3 from the current study were composed of predominantly marble and marble diopside lithologies, thus are not expected have siderite, in both cases 3x and 4x, respectively, more Fe was noted in the leachates from Method 2 than Method 1 suggesting that iron oxides or additional Fe-bearing phases are being dissolved by both reagents but more so in Method 2.

Step 4 and Step 5 of both methods did not selectively dissolve iron oxides. The % leached Ca and leachate comparison of Ca for both steps showed that more Ca was found in the leachates from Method 1. The XRD results showed that for both methods wollastonite dissolved during these steps. A nearly 1:1 molar ratio of Ca:Si was calculated for the leachates from Step 4 and Step 5 of Method 1 for most samples, supporting the dissolution of wollastonite. However, other processes are suggested but not confirmed from samples that leached Ca:Si ratios greater than 1. In contrast to Method 1, the calcium concentrations in leachates from Step 4 of Method 2 were low as an artifact from the precipitation of whewellite (Ca-oxalate). To gain insight into the potential for precipitation of other oxalate minerals during this step, a PhreeqC (Parkhurst and Appelo, 2013) simulation was developed to mimic Step 4 of Method 2. Mineral saturation indices (SI) were investigated for metal oxalates using the solubility product constants (Ksp; at 25 °C) of calcium oxalate and other metal oxalates presented in Table 2.12. The PhreeqC input file and results are presented in Appendix D. The simulation results indicated that precipitation of Ca-oxalate and metal oxalates was possible (SI > 1). When these minerals are allowed to precipitate, in all scenarios modelled, Ca-oxalate and Zn-oxalate precipitated and in one case Cuoxalate precipitated as well. Although Ca-oxalate was the only oxalate phase noted in the XRD patterns of the residues from Step 4 and Step 5 of Method 2, the leachate concentrations and % leached Cu, Pb and Zn were generally lower in Method 2 than in Method 1, which is consistent with the geochemical modelling predictions of precipitation of trace metal oxalates during this extraction step.

While previous studies show that oxalate in the presence of  $Fe^{2+}$  can catalyze the dissolution of iron oxides, this study shows that both oxalate and hydroxylamine hydrochloride will also dissolve wollastonite, which has not been previously reported, and in the case of an

oxalate-based reagent can cause the precipitation of Ca-oxalate minerals and potentially other metal oxalates. Our study also shows that while there are relative consistencies in the leachate chemistries from each step, as was concluded by Broadhurst et al. (2009), there are instances where a non-targeted phase was being dissolved as shown by the presence of an element in the leachate of one method (i.e., dissolved Ca in Step 4 of Method 1) but masked by the precipitation of a mineral phase in the other method (i.e., precipitation of wheellite, Method 2). The use of XRD on post-step residues allowed for this determination.

Sampling biases were partially addressed above, where the leachate comparison between Step 1 and Step 2 of the two methods show low variation (high precision) suggesting that sampling biases were minimal. Thus the differences between the two methods in Step 3 are due to non-specific dissolution of iron oxides and the differences in Steps 4 - 5 are due to precipitation of metal oxalates in Method 2. Sampling biases were also addressed using a calculation of relative standard deviation (RSD) of triplicate analyses for both methods (in Appendix B). The RSDs for triplicate analyses were better for Method 1 than Method 2 but most were generally less than 10% with some between 10 % and 30%; higher RSDs (>30%) were typically elements that were low concentration and near the detection limit of the ICP-OES and in Steps 4 and 5 of Method 2 where precipitation of metal oxalates will have affected the overall chemistry of the leach solution.

#### 2.6 Conclusions

Using heterogeneous samples of waste rock collected from the East Dump at the Antamina Mine, two sequential extraction procedures were compared to identify selectivity issues, if present in the two methods, and to ultimately choose one procedure that would be appropriate for a larger study on metal attenuation. To investigate the two methods the leachate chemistries of equivalent steps of each procedure were compared using RPD to quantify if the chemistries were similar and XRD was used to identify minerals dissolved or precipitated in residues collected after each step in "parallel" designed extractions. This study shows that using both qualitative and quantitative assessments of leachate chemistry along with mineralogy of residues from extraction steps can produce a meaningful assessment of selectivity in heterogeneous waste rock samples. The results show that both methods have selectivity issues with Step3, Step 4 and Step 5. Step 3 of both methods is designed to dissolve carbonate minerals and other weak-acid soluble minerals. Both methods appear to successfully dissolve all of the calcite and similar Cu bearing phases but both methods have unresolved selectivity issues with respect to the dissolution of Fe bearing phases, specifically siderite and amorphous iron oxides. The reagent used in Step 3 of Method 1 has been shown to be insufficient to dissolve siderite which would carry over to Step 4. The reagents used in both methods may also dissolve some amorphous iron oxides in this step but from the data the reagent used in Method 2 may cause the dissolution of more iron oxides than Method 1. Step 4 and Step 5 of both methods is designed to dissolve only reducible oxide phases such as amorphous iron oxides and crystalline iron oxides, however, both reagents used also dissolved wollastonite at these steps. Although both methods have selectivity issues with the reagents used for Step 4 and Step 5, Method 1 had the following advantage over Method 2: The hydroxylamine hydrochloride used in Step 4 and Step 5 of Method 1 did not further react with the metals leached into solution as did the oxalate used in Method 2. The precipitation of whewellite in Step 4 and Step 5 of Method 2 due to the dissolution of wollastonite and the use of oxalate as the reagent is an indication that oxalate is not an appropriate reagent for samples containing wollastonite. The identification of whewellite and lower concentrations of Cu, Pb and Zn in the Step 4 and Step 5 leachates of Method 2 are an

indication that oxalates of these metals may have also precipitated, although none were noted in XRD analysis. Geochemical modelling of this system supports this hypothesis.

# Figures



Figure 2.1 View of East Dump and drilling location (Site 1 and Site 3)



Figure 2.2 Ca and Fe (% leached) SEP results for BH1-1, BH1-2, BH1-4 and BH3-3



Figure 2.3 As and Mo (% leached) SEP results for BH1-1, BH1-2, BH1-4 and BH3-3



Figure 2.4 Cu, Pb, and Zn (% leached) SEP results for BH1-1, BH1-2, BH1-4 and BH3-3



Figure 2.5 BH1-4 XRD results from Method 1



Figure 2.6 BH1-4 XRD results from Method 2



Figure 2.7 BH1-1 XRD results from Method 1



Figure 2.8 BH1-1 XRD results from Method 2



Figure 2.9 BH1-3 XRD results from Method 1



Figure 2.10 BH1-3 XRD results from Method 2

## Tables

 Table 2.1 Samples selected for this study

				Major	Minor Lithology			C
Sample ID	Borehole	From	То	Lithology (>50%)	(<50%)	Comments	Sulfides	Secondary minerals
		(m)	(m)					
BH1-1	<b>Р</b> И1 1	10.5	12	М		scapolites, some XV	Cp, Bn, Py, Po	
BH1-2	DIII-1	19.5	21	IQM	М		Cp, Mo, Py	FeOx
BH1-3	DU 14	64.5	66	М	MDP	some XV, XW, IQM	EXV, XW, Cp, Py, Po, IQM Bi	
BH1-4	DH-IU	91.5	92.4	MDP	XV	some IQM	Cp, Sp, Py, Po	FeOx, Malachite
BH3-1		1.5	3	М	IQM		Ср, Ру, Ро	FeOx
BH3-2	рп-э8	15	16.5	IQM	М		Ср, Ру, Ро	FeOx, Malachite
BH3-3		24	25.5	XV	C		Cp, Py	FeOx, Malachite
BH3-4	вн-эа	37.5	39	IQM	С		Ср, Ру	FeOx, Malachite

NOTES:

C - limestone; IQM – Igneous intrusive; M – Marble; MDP – Marble Diopside; XV – Green Garnet Exoskarn; XW – Wollastonite Exoskarn; FeOX – visible iron oxide staining; Cp – Chalcopyrite; Bn – Bornite; Py – Pyrite; Po – Pyrrhotite

Step	Phases	<b>Method 1</b> <sup>(1,4)</sup>	Method 2 <sup>(4)</sup>	ICP-OES Detection Limit ppm of solid
1	Water Soluble	50mL deionized water, shake for 1h	50mL deionized water, shake for 1h	<10 ppm
2	Weakly sorbed /Exchangeable <sup>(2)</sup>	40 mL 1M MgCl <sub>2</sub> , Shake for 1 hour at room temperature	40 mL 1M MgCl <sub>2</sub> , Shake for 1 hour at room temperature	<10 ppm
3	Carbonates	20mL 1M CH <sub>3</sub> COONa (sodium acetate) at pH 5, shake for 6h, repeat Step	20mL 1M CH <sub>3</sub> COONH <sub>4</sub> (ammonium acetate) at pH4.5, shake for 2h, at room temperature	< 6 ppm
4	Amorphous Iron Oxides	20mL 0.25M NH <sub>2</sub> OH*HCl (hydroxylamine hydrochloride) in 0.25 HCl placed in 60 <sup>o</sup> C water bath for 2h, every 30min vortex contents, repeat Step, but heat for only 30 min	20mL 0.2 M NH <sub>4</sub> -C <sub>2</sub> O <sub>4</sub> (ammonium-oxalate) at pH3.0, shake for 1h in darkness, at room temperature	<6 ppm
5	Crystalline Iron Oxides	$\begin{array}{c} 30 \text{mL of 1 M} \\ \text{NH}_2\text{OH}^*\text{HCl} \\ (hydroxylamine \\ hydrochloride) in 25\% \\ \text{CH}_3\text{COOH} (acetic \\ acid), place in 90^{0}\text{C} \\ water bath for 3h, \\ vortex every 20 min, \\ repeat Step, but heat for \\ only 1.5 hours \\ \end{array}$	30mL 0.2 M NH <sub>4</sub> -C <sub>2</sub> O <sub>4</sub> (ammonium-oxalate) at pH3.0, heat in water bath 80 °C for 2h	<8 ppm
6	Residual	Four Acid Digest <sup>(3)</sup>	Four Acid Digest <sup>(3)</sup>	

Table 2.2 Sequential extraction procedures (SEPs) used in this study

NOTES:

1) Steps 3 – 5 are repeated using the same liquid solid ratio (LSR) but extraction time was shortened. Leachates are analysed separately and the concentrations are summed.

Weakly sorbed/exchangeable step taken from (Tessier et al., 1979)

Weakly sorbed/exchangeable step taken from (ressler et al., 1979
 Residual fraction was determined at SGS, Burnaby (BC, Canada)

4) Method 1 modified from Hall et al. (1996) Method 2 Modified from Dold (2003)

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Mineral	Mineral Formula	BH1-1	BH1-2	BH1-3	<b>BH1-4</b>	BH3-1	BH3-2	BH3-3	BH3-4
Quartz	SiO <sub>2</sub>	Х	Х	Х	Х	Х	Х	Х	Х
Orthoclase	KAlSi <sub>3</sub> O <sub>8</sub>	Х	Х	Х	Х	Х	Х	Х	Х
Albite	NaAlSi <sub>3</sub> O <sub>8</sub>		Х	Х	Х	Х	Х	Х	Х
Biotite	$K(Mg,Fe)_3(AlSi_3O_{10})(F,OH)_2$	X	X	Х	Х	Х	Х	Х	X
Muscovite	$KAl_2(AlSi_3O_{10})(F,OH)_2$								Х
Calcite	CaCO <sub>3</sub>	Х	Х	Х	Х	Х	Х	Х	Х
Hibschite	$Ca_3Al_2(SiO_4)_2(OH)_4$		Х		Х			Х	
Andradite	$Ca_3Fe_2(SiO_4)_3$				Х				
Vesuvianite	$Ca_{10}Mg_2Al_4(Si_2O_7)_2(SiO_4)_5(OH)_4$		Х		Х			Х	
Wollastonite	CaSiO <sub>3</sub>	Х		Х				Х	
Actinolite	$Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$	Х	Х				Х	Х	Х
Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$				Х			Х	
Magnetite	$\mathrm{Fe}^{3+}{}_{2}\mathrm{Fe}^{2+}\mathrm{O}_{4}$						Х		
Pyrite	FeS <sub>2</sub>		Х		Х	Х	Х	Х	Х
Molybdenite	$MoS_2$					Х	Х	Х	Х
Chalcopyrite	CuFeS <sub>2</sub>				Х	Х	Х	Х	
Sphalerite	(Zn,Fe) <sub>S</sub>							Х	
Chlorite				Х	Х		Х		Х
Gypsum	CaSO <sub>4</sub>		Х		Х		Х	Х	Х
Smithsonite	ZnCO <sub>3</sub>				Х				
Wulfenite	PbMoO <sub>4</sub>							Х	Х
Hemimorphite	$Zn_4Si_2O_7(OH)_2\bullet(H_2O)$				Х				

	units	BH1-1	BH1-2	BH1-3	BH1-4	BH3-1	BH3-2	BH3-3	BH3-4
Al	%	0.55	1.92	0.94	0.58	4.95	3.11	3.06	3.23
As	ppm	46	45	65	94	98	86	193	55
Ca	%	>15	3.83	>15	10.1	10.3	8.9	24.4	5.76
Cu	ppm	1170	6360	1020	4030	1250	18600	6320	3760
Fe	%	0.63	6.74	1.07	6.15	2.05	7.78	4.88	23.4
Mn	ppm	258	744	505	1090	569	610	1850	360
Mo	ppm	24.5	50.2	42.1	107	213	124	331	154
Pb	ppm	138	293	570	874	367	50.1	700	117
Zn	ppm	1300	4600	1300	7310	1590	1090	8290	473

Table 2.4 Elemental composition of via 4-acid digestion

Table 2.5 Acid base accounting (ABA) static test results

		BH1-1	BH1-2	BH1-3	BH1-4	BH3-1	BH3-2	BH3-3	BH3-4
Major Lithology		М	IQM	М	MDP	М	IQM	XV	IQM
Minor Lithology			М	MDP	XV	IQM	М	С	С
S(T)	(%)	0.35	10	0.5	1.52	0.6	2.85	0.75	14.85
S(SO4)	(%)	0.03	0.3	0.01	0.15	0.01	0.39	0.04	0.27
S(SO4)	(%)	0.04	0.3	0.01	0.1	0.01	0.39	0.04	0.27
S(2-)	(%)	0.31	9.7	0.49	1.37	0.59	2.46	0.71	14.6
TIC	(%)	9.6	1.1	8.06	2.86	3.63	1.33	4.91	1.82
AP	kg CaCO3/t	9.7	303	15.3	42.8	18.4	76.9	22.2	456
Carb-NP	kg CaCO3/t	801	93	671	238	302	111	409	152

sample		Al_av	Ca_avg	Fe_av	Mn_avg	Si_avg	As_av	Cu_avg	Mo_avg	Pb_av	Zn_av
ID	Units	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
	Method 1	<dl< td=""><td>406.1</td><td><dl< td=""><td><dl< td=""><td>13.0</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	406.1	<dl< td=""><td><dl< td=""><td>13.0</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>13.0</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	13.0	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
BH1-1	Method 2	<dl< td=""><td>440.9</td><td><dl< td=""><td><dl< td=""><td>14.3</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	440.9	<dl< td=""><td><dl< td=""><td>14.3</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>14.3</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	14.3	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
	RPD	-	8%	-	-	10%	-	-	-	-	-
	Method 1	<dl< td=""><td>7726.9</td><td><dl< td=""><td><dl< td=""><td>15.2</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	7726.9	<dl< td=""><td><dl< td=""><td>15.2</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>15.2</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	15.2	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
BH1-2	Method 2	<dl< td=""><td>8651.4</td><td><dl< td=""><td><dl< td=""><td>16.8</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	8651.4	<dl< td=""><td><dl< td=""><td>16.8</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>16.8</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	16.8	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
	RPD	-	11%	-	-	10%	-	-	-	-	-
	Method 1	<dl< td=""><td>574.7</td><td><dl< td=""><td><dl< td=""><td>14.6</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	574.7	<dl< td=""><td><dl< td=""><td>14.6</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>14.6</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	14.6	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
BH1-3	Method 2	<dl< td=""><td>575.8</td><td><dl< td=""><td><dl< td=""><td>16.5</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	575.8	<dl< td=""><td><dl< td=""><td>16.5</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>16.5</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	16.5	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
	RPD	-	0%	-	-	12%	-	-	-	-	-
	Method 1	<dl< td=""><td>2196.3</td><td><dl< td=""><td><dl< td=""><td>38.9</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	2196.3	<dl< td=""><td><dl< td=""><td>38.9</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>38.9</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	38.9	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
BH1-4	Method 2	<dl< td=""><td>2232.2</td><td><dl< td=""><td><dl< td=""><td>37.3</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	2232.2	<dl< td=""><td><dl< td=""><td>37.3</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>37.3</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	37.3	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
	RPD	-	2%	-	-	4%	-	-	-	-	-
	Method 1	<dl< td=""><td>338.3</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	338.3	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
BH3-1	Method 2	<dl< td=""><td>346.5</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	346.5	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
	RPD	-	2%	-	-	-	-	-	-	-	-
	Method 1	<dl< td=""><td>5155.2</td><td><dl< td=""><td><dl< td=""><td>33.8</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	5155.2	<dl< td=""><td><dl< td=""><td>33.8</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>33.8</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	33.8	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
BH3-2	Method 2	<dl< td=""><td>5263.6</td><td><dl< td=""><td><dl< td=""><td>32.7</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	5263.6	<dl< td=""><td><dl< td=""><td>32.7</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>32.7</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	32.7	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
	RPD	-	2%	-	-	3%	-	-	-	-	-
	Method 1	<dl< td=""><td>936.7</td><td><dl< td=""><td><dl< td=""><td>21.8</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	936.7	<dl< td=""><td><dl< td=""><td>21.8</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>21.8</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	21.8	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
BH3-3	Method 2	<dl< td=""><td>975.6</td><td><dl< td=""><td><dl< td=""><td>25.4</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	975.6	<dl< td=""><td><dl< td=""><td>25.4</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>25.4</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	25.4	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
	RPD	-	4%	-	-	15%	-	-	-	-	-
	Method 1	<dl< td=""><td>3483.6</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	3483.6	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
BH3-4	Method 2	<dl< td=""><td>3562.6</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	3562.6	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
	RPD	-	2%	-	-	-	-	-	-	-	-

Table 2.6 Average concentrations and RPD values for Step 1

Indicates RPD >30%

<DL denotes where the minimum detection limit of the OES was reported

sample		Al_avg	Ca_avg	Fe_avg	Mn_avg	Si_avg	As_avg	Cu_avg	Mo_avg	Pb_avg	Zn_avg
ID	Units	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
	Method 1	<dl< td=""><td>3901.8</td><td><dl< td=""><td><dl< td=""><td>10.4</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>14.5</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	3901.8	<dl< td=""><td><dl< td=""><td>10.4</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>14.5</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>10.4</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>14.5</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	10.4	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>14.5</td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td>14.5</td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>14.5</td></dl<></td></dl<>	<dl< td=""><td>14.5</td></dl<>	14.5
BH1-1	Method 2	<dl< td=""><td>3683.6</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>13.1</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	3683.6	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>13.1</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>13.1</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>13.1</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>13.1</td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td>13.1</td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>13.1</td></dl<></td></dl<>	<dl< td=""><td>13.1</td></dl<>	13.1
	RPD	-	6%	-	-	-	-	-	-	-	10%
	Method 1	<dl< td=""><td>3878.8</td><td><dl< td=""><td>41.4</td><td>11.7</td><td><dl< td=""><td>29.0</td><td><dl< td=""><td><dl< td=""><td>67.0</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	3878.8	<dl< td=""><td>41.4</td><td>11.7</td><td><dl< td=""><td>29.0</td><td><dl< td=""><td><dl< td=""><td>67.0</td></dl<></td></dl<></td></dl<></td></dl<>	41.4	11.7	<dl< td=""><td>29.0</td><td><dl< td=""><td><dl< td=""><td>67.0</td></dl<></td></dl<></td></dl<>	29.0	<dl< td=""><td><dl< td=""><td>67.0</td></dl<></td></dl<>	<dl< td=""><td>67.0</td></dl<>	67.0
BH1-2	Method 2	<dl< td=""><td>3502.7</td><td><dl< td=""><td>38.7</td><td><dl< td=""><td><dl< td=""><td>31.4</td><td><dl< td=""><td><dl< td=""><td>79.7</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	3502.7	<dl< td=""><td>38.7</td><td><dl< td=""><td><dl< td=""><td>31.4</td><td><dl< td=""><td><dl< td=""><td>79.7</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	38.7	<dl< td=""><td><dl< td=""><td>31.4</td><td><dl< td=""><td><dl< td=""><td>79.7</td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>31.4</td><td><dl< td=""><td><dl< td=""><td>79.7</td></dl<></td></dl<></td></dl<>	31.4	<dl< td=""><td><dl< td=""><td>79.7</td></dl<></td></dl<>	<dl< td=""><td>79.7</td></dl<>	79.7
	RPD	-	10%	-	7%	-	-	8%	-	-	17%
	Method 1	<dl< td=""><td>3855.4</td><td><dl< td=""><td><dl< td=""><td>15.3</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>13.6</td><td>13.6</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	3855.4	<dl< td=""><td><dl< td=""><td>15.3</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>13.6</td><td>13.6</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>15.3</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>13.6</td><td>13.6</td></dl<></td></dl<></td></dl<></td></dl<>	15.3	<dl< td=""><td><dl< td=""><td><dl< td=""><td>13.6</td><td>13.6</td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>13.6</td><td>13.6</td></dl<></td></dl<>	<dl< td=""><td>13.6</td><td>13.6</td></dl<>	13.6	13.6
BH1-3	Method 2	<dl< td=""><td>3884.6</td><td><dl< td=""><td><dl< td=""><td>12.4</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>14.4</td><td>15.1</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	3884.6	<dl< td=""><td><dl< td=""><td>12.4</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>14.4</td><td>15.1</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>12.4</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>14.4</td><td>15.1</td></dl<></td></dl<></td></dl<></td></dl<>	12.4	<dl< td=""><td><dl< td=""><td><dl< td=""><td>14.4</td><td>15.1</td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>14.4</td><td>15.1</td></dl<></td></dl<>	<dl< td=""><td>14.4</td><td>15.1</td></dl<>	14.4	15.1
	RPD	-	1%	-	-	21%	-	-	-	6%	10%
	Method 1	<dl< td=""><td>4622.5</td><td><dl< td=""><td>16.0</td><td>39.2</td><td><dl< td=""><td>11.6</td><td>17.2</td><td><dl< td=""><td>29.4</td></dl<></td></dl<></td></dl<></td></dl<>	4622.5	<dl< td=""><td>16.0</td><td>39.2</td><td><dl< td=""><td>11.6</td><td>17.2</td><td><dl< td=""><td>29.4</td></dl<></td></dl<></td></dl<>	16.0	39.2	<dl< td=""><td>11.6</td><td>17.2</td><td><dl< td=""><td>29.4</td></dl<></td></dl<>	11.6	17.2	<dl< td=""><td>29.4</td></dl<>	29.4
BH1-4	Method 2	<dl< td=""><td>4165.9</td><td><dl< td=""><td>14.5</td><td>33.4</td><td><dl< td=""><td>10.9</td><td>14.5</td><td><dl< td=""><td>32.7</td></dl<></td></dl<></td></dl<></td></dl<>	4165.9	<dl< td=""><td>14.5</td><td>33.4</td><td><dl< td=""><td>10.9</td><td>14.5</td><td><dl< td=""><td>32.7</td></dl<></td></dl<></td></dl<>	14.5	33.4	<dl< td=""><td>10.9</td><td>14.5</td><td><dl< td=""><td>32.7</td></dl<></td></dl<>	10.9	14.5	<dl< td=""><td>32.7</td></dl<>	32.7
	RPD	-	10%	-	10%	16%	-	6%	18%	-	11%
	Method 1	<dl< td=""><td>4118.9</td><td><dl< td=""><td><dl< td=""><td>32.7</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	4118.9	<dl< td=""><td><dl< td=""><td>32.7</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>32.7</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	32.7	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
BH3-1	Method 2	<dl< td=""><td>3749.1</td><td><dl< td=""><td>16.0</td><td>30.6</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>16.8</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	3749.1	<dl< td=""><td>16.0</td><td>30.6</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>16.8</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	16.0	30.6	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>16.8</td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td>16.8</td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>16.8</td></dl<></td></dl<>	<dl< td=""><td>16.8</td></dl<>	16.8
	RPD	-	9%	-	-	6%	-	-	-	-	-
	Method 1	<dl< td=""><td>5459.2</td><td><dl< td=""><td>10.5</td><td>76.3</td><td><dl< td=""><td>20.1</td><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	5459.2	<dl< td=""><td>10.5</td><td>76.3</td><td><dl< td=""><td>20.1</td><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	10.5	76.3	<dl< td=""><td>20.1</td><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	20.1	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
BH3-2	Method 2	<dl< td=""><td>5278.9</td><td><dl< td=""><td>22.8</td><td>70.8</td><td><dl< td=""><td>27.4</td><td><dl< td=""><td><dl< td=""><td>12.7</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	5278.9	<dl< td=""><td>22.8</td><td>70.8</td><td><dl< td=""><td>27.4</td><td><dl< td=""><td><dl< td=""><td>12.7</td></dl<></td></dl<></td></dl<></td></dl<>	22.8	70.8	<dl< td=""><td>27.4</td><td><dl< td=""><td><dl< td=""><td>12.7</td></dl<></td></dl<></td></dl<>	27.4	<dl< td=""><td><dl< td=""><td>12.7</td></dl<></td></dl<>	<dl< td=""><td>12.7</td></dl<>	12.7
	RPD	-	3%	-	74%	7%	-	31%	-	-	-
	Method 1	<dl< td=""><td>4948.9</td><td><dl< td=""><td><dl< td=""><td>68.9</td><td><dl< td=""><td>11.9</td><td>16.1</td><td><dl< td=""><td>12.4</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	4948.9	<dl< td=""><td><dl< td=""><td>68.9</td><td><dl< td=""><td>11.9</td><td>16.1</td><td><dl< td=""><td>12.4</td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>68.9</td><td><dl< td=""><td>11.9</td><td>16.1</td><td><dl< td=""><td>12.4</td></dl<></td></dl<></td></dl<>	68.9	<dl< td=""><td>11.9</td><td>16.1</td><td><dl< td=""><td>12.4</td></dl<></td></dl<>	11.9	16.1	<dl< td=""><td>12.4</td></dl<>	12.4
BH3-3	Method 2	<dl< td=""><td>5166.7</td><td><dl< td=""><td>20.9</td><td>70.4</td><td><dl< td=""><td>18.2</td><td>22.9</td><td>5.6</td><td>26.1</td></dl<></td></dl<></td></dl<>	5166.7	<dl< td=""><td>20.9</td><td>70.4</td><td><dl< td=""><td>18.2</td><td>22.9</td><td>5.6</td><td>26.1</td></dl<></td></dl<>	20.9	70.4	<dl< td=""><td>18.2</td><td>22.9</td><td>5.6</td><td>26.1</td></dl<>	18.2	22.9	5.6	26.1
	RPD	-	4%	-	-	2%	-	41%	35%	-	72%
	Method 1	10.5	4542.0	<dl< td=""><td><dl< td=""><td>39.1</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>39.1</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	39.1	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
BH3-4	Method 2	<dl< td=""><td>4164.2</td><td><dl< td=""><td>13.1</td><td>29.9</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>15.5</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	4164.2	<dl< td=""><td>13.1</td><td>29.9</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>15.5</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	13.1	29.9	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>15.5</td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td>15.5</td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>15.5</td></dl<></td></dl<>	<dl< td=""><td>15.5</td></dl<>	15.5
	RPD	-	9%	-	-	27%	-	-	-	-	-

Table 2.7 Average concentrations and RPD values for Step 2

Indicates RPD >30%

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denotes where the minimum detection limit of the OES was reported

sample		Al_avg	Ca_avg	Fe_avg	Mn_avg	Si_avg	As_avg	Cu_avg	Mo_avg	Pb_avg	Zn_avg
ID	Units	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
	Method 1	16.3	315779.9	75.1	113.7	137.8	<dl< td=""><td>37.6</td><td><dl< td=""><td>64.6</td><td>48.3</td></dl<></td></dl<>	37.6	<dl< td=""><td>64.6</td><td>48.3</td></dl<>	64.6	48.3
BH1-1	Method 2	19.4	310419.6	220.5	148.1	60.1	8.0	29.5	<dl< td=""><td>116.1</td><td>19.9</td></dl<>	116.1	19.9
	RPD	17%	2%	98%	26%	79%	-	24%	-	57%	83%
	Method 1	326.0	17355.9	1503.3	57.9	560.0	<dl< td=""><td>1747.3</td><td><dl< td=""><td>308.0</td><td>1916.4</td></dl<></td></dl<>	1747.3	<dl< td=""><td>308.0</td><td>1916.4</td></dl<>	308.0	1916.4
BH1-2	Method 2	364.5	15017.4	1814.0	75.9	344.7	<dl< td=""><td>1312.9</td><td><dl< td=""><td>307.4</td><td>1776.3</td></dl<></td></dl<>	1312.9	<dl< td=""><td>307.4</td><td>1776.3</td></dl<>	307.4	1776.3
	RPD	11%	14%	19%	27%	48%	-	28%	-	0%	8%
	Method 1	50.9	277960.6	106.2	218.5	194.8	<dl< td=""><td>94.0</td><td><dl< td=""><td>456.5</td><td>207.6</td></dl<></td></dl<>	94.0	<dl< td=""><td>456.5</td><td>207.6</td></dl<>	456.5	207.6
BH1-3	Method 2	83.6	272885.5	409.1	300.0	144.8	<dl< td=""><td>91.7</td><td><dl< td=""><td>715.9</td><td>240.9</td></dl<></td></dl<>	91.7	<dl< td=""><td>715.9</td><td>240.9</td></dl<>	715.9	240.9
	RPD	49%	2%	118%	31%	29%	-	3%	-	44%	15%
	Method 1	116.2	64057.9	263.6	227.9	1621.5	<dl< td=""><td>2400.8</td><td><dl< td=""><td>624.2</td><td>7204.8</td></dl<></td></dl<>	2400.8	<dl< td=""><td>624.2</td><td>7204.8</td></dl<>	624.2	7204.8
BH1-4	Method 2	158.9	72539.5	448.4	212.3	1419.3	<dl< td=""><td>2148.9</td><td><dl< td=""><td>732.8</td><td>8664.1</td></dl<></td></dl<>	2148.9	<dl< td=""><td>732.8</td><td>8664.1</td></dl<>	732.8	8664.1
	RPD	31%	12%	52%	7%	13%	-	11%	-	16%	18%
	Method 1	108.7	81528.0	669.7	131.8	376.3	<dl< td=""><td>78.8</td><td><dl< td=""><td>179.2</td><td>99.6</td></dl<></td></dl<>	78.8	<dl< td=""><td>179.2</td><td>99.6</td></dl<>	179.2	99.6
BH3-1	Method 2	156.4	100577.8	1221.1	172.3	188.4	<dl< td=""><td>56.0</td><td><dl< td=""><td>282.6</td><td>54.0</td></dl<></td></dl<>	56.0	<dl< td=""><td>282.6</td><td>54.0</td></dl<>	282.6	54.0
	RPD	36%	21%	58%	27%	67%	-	34%	-	45%	59%
	Method 1	147.6	71440.2	496.7	132.4	658.9	<dl< td=""><td>1707.1</td><td><dl< td=""><td><dl< td=""><td>91.5</td></dl<></td></dl<></td></dl<>	1707.1	<dl< td=""><td><dl< td=""><td>91.5</td></dl<></td></dl<>	<dl< td=""><td>91.5</td></dl<>	91.5
BH3-2	Method 2	217.5	79562.0	824.6	140.5	414.3	<dl< td=""><td>1695.8</td><td><dl< td=""><td>25.0</td><td>128.5</td></dl<></td></dl<>	1695.8	<dl< td=""><td>25.0</td><td>128.5</td></dl<>	25.0	128.5
	RPD	38%	11%	50%	6%	46%	-	1%	-	-	34%
	Method 1	86.0	120831.9	223.9	503.1	815.6	25.3	1578.6	<dl< td=""><td>617.1</td><td>1642.3</td></dl<>	617.1	1642.3
BH3-3	Method 2	150.8	123985.2	500.5	543.7	534.1	26.5	1684.3	<dl< td=""><td>813.3</td><td>2151.2</td></dl<>	813.3	2151.2
	RPD	55%	3%	76%	8%	42%	5%	6%	-	27%	27%
	Method 1	415.1	22644.9	629.2	49.0	570.4	<dl< td=""><td>305.8</td><td><dl< td=""><td>23.8</td><td>64.9</td></dl<></td></dl<>	305.8	<dl< td=""><td>23.8</td><td>64.9</td></dl<>	23.8	64.9
BH3-4	Method 2	506.2	17852.9	818.0	72.6	342.9	<dl< td=""><td>242.9</td><td><dl< td=""><td>59.0</td><td>26.1</td></dl<></td></dl<>	242.9	<dl< td=""><td>59.0</td><td>26.1</td></dl<>	59.0	26.1
	RPD	20%	24%	26%	39%	50%	-	23%	-	85%	85%

Table 2.8 Average concentrations and RPD values for Step 3

Indicates RPD >30%

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denotes where the minimum detection limit of the OES was reported

sample		Al_avg	Ca_avg	Fe_avg	Mn_avg	Si_avg	As_avg	Cu_avg	Mo_avg	Pb_avg	Zn_avg
ID	Units	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
	Method 1	649.1	54078.2	1247.6	52.9	2356.9	15.9	117.4	<dl< td=""><td>96.1</td><td>126.9</td></dl<>	96.1	126.9
BH1-1	Method 2	60.0	14.8	673.9	7.7	305.7	10.5	17.6	<dl< td=""><td>6.0</td><td>21.4</td></dl<>	6.0	21.4
	RPD	166%	200%	60%	149%	154%	41%	148%	-	176%	142%
	Method 1	2027.3	2557.1	17802.5	110.4	2697.1	12.3	1217.0	<dl< td=""><td>395.8</td><td>2119.7</td></dl<>	395.8	2119.7
BH1-2	Method 2	839.8	60.9	13567.9	50.7	786.1	14.5	437.0	<dl< td=""><td>85.9</td><td>411.5</td></dl<>	85.9	411.5
	RPD	83%	191%	27%	74%	110%	17%	94%	-	129%	135%
	Method 1	1578.3	48327.0	1754.2	69.0	2526.5	10.1	119.5	<dl< td=""><td>355.5</td><td>268.2</td></dl<>	355.5	268.2
BH1-3	Method 2	172.2	21.3	1924.6	14.9	824.8	14.4	43.5	<dl< td=""><td>16.7</td><td>165.0</td></dl<>	16.7	165.0
	RPD	161%	200%	9%	129%	102%	35%	93%	-	182%	48%
	Method 1	1639.6	3206.0	19277.9	88.1	2506.5	8.8	1307.8	<dl< td=""><td>835.1</td><td>3095.2</td></dl<>	835.1	3095.2
BH1-4	Method 2	611.2	67.3	16098.6	67.2	1484.6	34.8	1053.7	34.4	162.0	387.5
	RPD	91%	192%	18%	27%	51%	120%	22%	-	135%	155%
	Method 1	2321.4	2305.7	4832.8	175.8	1789.8	9.1	90.9	<dl< td=""><td>224.0</td><td>307.8</td></dl<>	224.0	307.8
BH3-1	Method 2	548.2	47.1	7419.9	198.5	655.5	18.6	27.3	8.1	31.8	142.6
	RPD	124%	192%	42%	12%	93%	68%	108%	-	150%	73%
	Method 1	1533.7	1558.4	22572.5	150.0	1972.5	33.0	1512.7	<dl< td=""><td>58.9</td><td>136.1</td></dl<>	58.9	136.1
BH3-2	Method 2	770.0	54.3	20961.4	138.7	1527.2	56.0	518.4	9.7	25.4	89.4
	RPD	66%	187%	7%	8%	25%	51%	98%	-	79%	41%
	Method 1	1636.3	12749.1	4901.6	158.0	6814.8	51.0	1245.7	7.9	456.6	1404.5
BH3-3	Method 2	427.2	36.4	4852.5	51.1	2762.5	70.2	340.1	14.8	25.6	929.7
	RPD	117%	199%	1%	102%	85%	32%	114%	61%	179%	41%
	Method 1	5592.0	5217.3	5403.9	25.5	4856.6	15.9	494.4	<dl< td=""><td>93.9</td><td>101.3</td></dl<>	93.9	101.3
BH3-4	Method 2	1458.7	38.5	5817.7	25.5	1356.3	25.2	141.3	6.2	17.4	100.5
	RPD	117%	197%	7%	0%	113%	45%	111%	-	137%	1%

Table 2.9 Average concentrations and RPD values for Step 4

Indicates RPD >30%

<DL denotes where the minimum detection limit of the OES was reported

sample		Al_avg	Ca_avg	Fe_avg	Mn_avg	Si_avg	As_avg	Cu_avg	Mo_avg	Pb_avg	Zn_avg
ID	Units	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
	Method 1	194.6	611.1	659.1	3.6	256.4	<dl< td=""><td>51.2</td><td><dl< td=""><td>35.7</td><td>49.2</td></dl<></td></dl<>	51.2	<dl< td=""><td>35.7</td><td>49.2</td></dl<>	35.7	49.2
BH1-1	Method 2	438.0	25.6	1011.1	19.8	1033.8	12.2	27.5	<dl< td=""><td>26.7</td><td>38.9</td></dl<>	26.7	38.9
	RPD	77%	184%	42%	138%	121%	-	60%	-	29%	23%
	Method 1	1203.9	5075.4	5132.1	64.7	2661.9	<dl< td=""><td>546.9</td><td><dl< td=""><td>73.6</td><td>591.6</td></dl<></td></dl<>	546.9	<dl< td=""><td>73.6</td><td>591.6</td></dl<>	73.6	591.6
BH1-2	Method 2	1870.2	36.4	9428.0	93.3	3299.7	<dl< td=""><td>544.1</td><td><dl< td=""><td>131.4</td><td>1381.3</td></dl<></td></dl<>	544.1	<dl< td=""><td>131.4</td><td>1381.3</td></dl<>	131.4	1381.3
	RPD	43%	197%	59%	36%	21%	-	1%	-	56%	80%
	Method 1	659.7	1208.2	1537.8	12.3	774.8	<dl< td=""><td>45.9</td><td><dl< td=""><td>184.1</td><td>75.7</td></dl<></td></dl<>	45.9	<dl< td=""><td>184.1</td><td>75.7</td></dl<>	184.1	75.7
BH1-3	Method 2	1219.1	27.3	1519.3	24.8	1721.0	3.1	47.5	<dl< td=""><td>55.8</td><td>76.1</td></dl<>	55.8	76.1
	RPD	60%	191%	1%	67%	76%	-	3%	-	107%	1%
	Method 1	1011.9	7370.5	20792.5	58.2	3622.0	24.8	243.5	51.2	170.9	301.5
BH1-4	Method 2	1784.3	50.1	49717.3	65.2	5239.2	53.5	699.4	52.3	379.6	443.0
	RPD	55%	197%	82%	11%	36%	73%	97%	2%	76%	38%
	Method 1	628.2	1129.2	2346.4	23.1	879.6	<dl< td=""><td>37.2</td><td><dl< td=""><td>44.1</td><td>35.7</td></dl<></td></dl<>	37.2	<dl< td=""><td>44.1</td><td>35.7</td></dl<>	44.1	35.7
BH3-1	Method 2	2038.1	51.5	1762.6	56.0	3141.2	<dl< td=""><td>19.9</td><td><dl< td=""><td>40.7</td><td>39.8</td></dl<></td></dl<>	19.9	<dl< td=""><td>40.7</td><td>39.8</td></dl<>	40.7	39.8
	RPD	106%	183%	28%	83%	112%	-	61%	-	8%	11%
	Method 1	376.1	1080.2	5063.9	18.9	908.4	3.2	591.3	<dl< td=""><td><dl< td=""><td>66.1</td></dl<></td></dl<>	<dl< td=""><td>66.1</td></dl<>	66.1
BH3-2	Method 2	800.7	54.9	16258.6	81.6	3578.4	<dl< td=""><td>10.8</td><td><dl< td=""><td>28.7</td><td>15.8</td></dl<></td></dl<>	10.8	<dl< td=""><td>28.7</td><td>15.8</td></dl<>	28.7	15.8
	RPD	72%	181%	105%	125%	119%	-	193%	-	-	123%
	Method 1	1184.7	6310.7	4031.9	64.8	2943.0	11.7	445.5	<dl< td=""><td>71.4</td><td>646.6</td></dl<>	71.4	646.6
BH3-3	Method 2	2709.9	47.5	7094.6	112.5	4739.3	18.8	222.8	<dl< td=""><td>57.6</td><td>421.8</td></dl<>	57.6	421.8
	RPD	78%	197%	55%	54%	47%	46%	67%	-	21%	42%
	Method 1	1190.1	1522.7	1237.2	10.6	1392.2	<dl< td=""><td>445.1</td><td><dl< td=""><td>18.3</td><td>28.2</td></dl<></td></dl<>	445.1	<dl< td=""><td>18.3</td><td>28.2</td></dl<>	18.3	28.2
BH3-4	Method 2	5610.0	47.0	1894.9	10.1	4493.6	<dl< td=""><td>245.6</td><td><dl< td=""><td>37.3</td><td>30.9</td></dl<></td></dl<>	245.6	<dl< td=""><td>37.3</td><td>30.9</td></dl<>	37.3	30.9
	RPD	130%	188%	42%	5%	105%	-	58%	-	68%	9%

 Table 2.10 Average concentrations and RPD values for Step 5

Indicates RPD >30%

<DL

denotes where the minimum detection limit of the OES was reported
sample		Al_avg	Ca_avg	Fe_avg	Mn_avg	Si_avg	As_avg	Cu_avg	Mo_avg	Pb_avg	Zn_avg
ID	Units	ppm	ppm	Ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
	Method 1	860.0	374777.2	1981.7	170.2	2774.5	15.9	206.2	<dl< td=""><td>196.4</td><td>239.0</td></dl<>	196.4	239.0
BH1-1	Method 2	517.4	314584.5	1905.6	175.6	1413.8	30.7	74.6	<dl< td=""><td>148.8</td><td>93.3</td></dl<>	148.8	93.3
	RPD	50%	17%	4%	3%	65%	64%	94%	-	28%	88%
	Method 1	3557.2	36594.1	24437.9	274.4	5945.9	12.3	3540.3	<dl< td=""><td>777.4</td><td>4694.7</td></dl<>	777.4	4694.7
BH1-2	Method 2	3074.5	27268.7	24809.9	258.6	4447.3	14.5	2325.4	<dl< td=""><td>524.7</td><td>3648.8</td></dl<>	524.7	3648.8
	RPD	15%	29%	2%	6%	29%	17%	41%	-	39%	25%
	Method 1	2288.9	331925.8	3398.2	299.8	3526.1	10.1	259.5	<dl< td=""><td>1009.6</td><td>565.0</td></dl<>	1009.6	565.0
BH1-3	Method 2	1475.0	277394.6	3852.9	339.7	2719.6	17.5	182.7	<dl< td=""><td>802.8</td><td>497.1</td></dl<>	802.8	497.1
	RPD	43%	18%	13%	12%	26%	54%	35%	-	23%	13%
	Method 1	2767.8	81453.2	40334.0	390.2	7828.1	33.6	3963.7	68.5	1630.2	10631.0
BH1-4	Method 2	2554.5	79055.0	66264.4	359.1	8213.7	88.3	3912.8	101.2	1274.3	9527.3
	RPD	8%	3%	49%	8%	5%	90%	1%	39%	25%	11%
	Method 1	3058.3	89420.1	7848.9	330.7	3078.4	9.1	207.0	<dl< td=""><td>447.3</td><td>443.0</td></dl<>	447.3	443.0
BH3-1	Method 2	2742.7	104772.1	10403.5	442.8	4015.6	18.6	103.3	8.1	355.1	253.1
	RPD	11%	16%	28%	29%	26%	68%	67%	-	23%	55%
	Method 1	2057.4	84693.2	28133.0	311.8	3649.8	36.2	3831.2	<dl< td=""><td>58.9</td><td>293.7</td></dl<>	58.9	293.7
BH3-2	Method 2	1788.2	90213.7	38044.7	383.6	5623.4	56.0	2252.4	9.7	79.2	246.5
	RPD	14%	6%	30%	21%	43%	43%	52%	-	29%	17%
	Method 1	2907.0	145777.2	9157.4	725.9	10664.1	88.0	3281.7	24.0	1145.0	3705.8
BH3-3	Method 2	3287.8	130211.5	12447.6	728.1	8131.7	115.4	2265.3	37.7	902.2	3528.8
	RPD	12%	11%	30%	0%	27%	27%	37%	44%	24%	5%
	Method 1	7207.8	37410.5	7270.3	85.0	6858.2	15.9	1245.3	<dl< td=""><td>136.1</td><td>194.4</td></dl<>	136.1	194.4
BH3-4	Method 2	7575.0	25665.3	8530.6	121.3	6222.6	25.2	629.8	6.2	113.8	173.0
	RPD	5%	37%	16%	35%	10%	45%	66%	-	18%	12%

Table 2.11 RPD for cumulative concentrations of Step 1 through Step 5

NOTES:

Indicates RPD >30%

<DL denotes where the minimum detection limit of the OES was reported

Mineral	Formula	Ksp (at 25°C)
Calcium oxalate monohydrate	$CaC_2O_4 \times H_2O$	2.32×10 <sup>-9</sup>
Copper(II) oxalate	CuC <sub>2</sub> O <sub>4</sub>	4.43×10 <sup>-10</sup>
Lead(II) oxalate	PbC <sub>2</sub> O <sub>4</sub>	8.5×10 <sup>-9</sup>
Magnesium oxalate dihydrate	$MgC_2O_4 \times 2H_2O$	4.83×10 <sup>-6</sup>
Manganese(II) oxalate dihydrate	$MnC_2O_4 \times 2H_2O$	1.70×10 <sup>-7</sup>
Zinc oxalate dihydrate	$ZnC_2O_4 \times 2H_2O$	1.38×10 <sup>-9</sup>

### Table 2.12 Solubility product constants for metal oxalates

NOTES:

Ksp's from (Olmsted and Williams, 2007)

Chapter 3 Characterizing Trace Metal Attenuation and Secondary Phases in Carbonate Bearing Waste Rock Collected from the East Dump, Antamina Mine, Peru

#### 3.1 Introduction

Understanding the processes that attenuate metals is essential for reliable predictions of the quality of water emanating from waste materials (Al et al., 2000; Mayer et al., 2003). However, characterization of metal attenuation mechanisms and the identification of secondary minerals are difficult because secondary phases are often amorphous or nano-crystalline and in low abundance compared to primary minerals. In addition, attenuation mechanisms such as sorption require methods with low detection limits and smaller spatial resolution which can require time-consuming and expensive analyses.

The objective of this study is to identify processes that attenuate metals in waste rock collected from the East Dump, Antamina Mine, Peru. The East Dump at the Antamina Mine is a unique environment to study these processes because it hosts both acid-buffering and acid-producing waste rock (Dockrey, 2010; Peterson, 2014). The elements of interest in this study are arsenic (As), copper (Cu), molybdenum (Mo), lead (Pb), and zinc (Zn). Metal attenuation studies on environmentally impacted sediments and mine tailings are well documented; however, there are few studies of these processes in full-scale waste rock dumps (Carbone et al., 2013b; Smuda et al., 2007). Metal attenuation studies using waste rock from smaller-scale studies, such as humidity cells, field barrels and experimental piles are more common (Andrina, 2009; Conlan, 2009; Dockrey, 2010; Hannam, 2012; Hirsche, 2012; Peterson, 2014; Stockwell et al., 2006).

However, smaller-scale studies may not reproduce all the processes and overall complexity from full-scale heterogeneous systems. Secondary phases and metal attenuation in waste rock is commonly predicted from equilibrium modelling of leachate emanating from waste rock dumps, however, it can be challenging to compare the results from small-scale solid phase samples sourced from specific locations with results derived from leachate composition (Hochella et al., 1999; Petrunic et al., 2006). This is further complicated by the fact that thermodynamic data for complex phases that precipitate from concentrated solutions are often not well-established and as such are not included in common geochemical databases (Younger, 2000); however, identification of such phases by mineralogical analysis provides motivation for inclusion of these phases in the model database. In this study, metal attenuation is investigated at the scale of an operational dump where both geochemical and physical heterogeneity can affect the geochemical processes that attenuate metals. Processes investigated at the full scale are compared to those operating in smaller-scale experiments containing waste rock from the same site. The chemistry of leachate from seeps emanating from the dump associated with the waste rock sampling locations is set in context with the observed mineralogy from the samples collected from within the dump.

The first section of this chapter introduces the site, the sample collection and selection, and the methods used in this study. The second section describes the results from solid phase analyses and geochemical modelling. The third section provides a discussion of the results, including their significance for the study of drainage from waste rock and their relationship to previous studies. The final section concludes on the results and discussion of this chapter.

#### **3.1.1** Site Information

The Antamina mine, located approximately 270km NE of Lima, Peru in the department of Ancash, is considered one of the ten largest mines in the world (Antamina, 2015). The skarn deposit was formed by the intrusion of a quartz monzonite body into limestones and hosts copper, zinc, molybdenum, lead, silver and bismuth bearing ore minerals (Lipten and Smith, 2004; Love et al., 2004; Redwood, 1999). The deposit is situated in the Andes, at an elevation ranging between 4200 and 4700m.a.s.l. Antamina receives approximately 1200-1300mm precipitation per year, almost all as rain. 80% of the precipitation falls during the region's six to seven month wet season (October – April) while the remaining 20% falls during the months of May to September, the dry season. The mean annual temperature at the mine site is approximately 5.0°C.

#### **3.1.2** Sample Collection and Selection

The waste rock used for this study was collected by taking advantage of boreholes drilled to monitor gases within an operating waste dump. A total of four boreholes were drilled: one shallow and one deep, drilled at each of two sites (Site 1 and Site 3, Figure 3.1) on the East Dump. The waste rock collected from the boreholes is broadly representative of the different lithologies at the site, and increases in age with depth where the deepest samples would have been in the dump for approximately 10 years at the time of drilling. The deepest borehole is at Site 3 and penetrates the entire depth of the waste rock dump (145m) into the underlying bedrock.

The East Dump receives both potentially acid-generating (PAG) waste rock and non-acid generating/acid-buffering (NAG) waste rock from a range of lithologies, i.e., limestone, marble, hornfels, exo- endo- skarn and intrusive, and is thus considered geochemically heterogeneous.

All water seeping from the East Dump is diverted and captured in the tailings pond where it is treated as part of Antamina's water management plan. Air-driven reverse circulation (RC) drilling was used for all boreholes, minimizing the alteration and dissolution of secondary mineral phases that would be caused by drilling fluids. The drill casing was advanced in 1.5m intervals and the waste rock cuttings for each interval were blown out of the borehole pneumatically and collected in trays. The trays of drill cuttings from each 1.5m interval were homogenized and split for experimental testing, drill logging and acid – base accounting (ABA) tests. The samples used for the experiments in this study consisted of 500g of waste rock cuttings that had been sieved, passing a 2mm (#10) mesh (the -2mm fraction). The drill logs were produced by Antamina's Geology Department from 2kg splits of each 1.5m interval of drill cuttings (see Appendix A).

In this study, the sample naming convention is: "BH" for borehole, number of site drilled ("1" or "3"), the depth of the borehole ("s" for shallow; "d" for deep), and the interval (in meters below ground surface) from which they were collected (example ID: BH-1s (0.0 - 1.5)). Based on visual inspection of oxidation products on the cuttings and the drill logs, 32 samples (from >150 intervals) were selected for this metal attenuation study. Table 3.1 lists the samples selected for testing along with the drill-log information of major lithology (lithology making up >50% of the sample), minor lithology (lithology making up <50% of the sample), other lithologies noted in the sample, sulfides, weathering products as well as the results of ABA testing and acid-rock drainage (ARD) classification (Price, 2009) of each sample.

#### 3.2 Methods

Metal attenuation and secondary phases were investigated experimentally using both geochemical and mineralogical tests. The total elemental composition of the -2mm material

fraction was determined by inductively coupled plasma - mass spectrometry and -optical emission spectrometry (ICP-MS/-OES) analyses after sample digestion using 4-acids (i.e., HCl (hydrochloric acid), HNO<sub>3</sub> (nitric acid), HF (hydrofluoric acid) and HClO<sub>4</sub> (perchloric acid)) at SGS in Vancouver, Canada. X-ray Diffraction (XRD) was used to identify the crystalline minerals in the samples. Qualitative XRD data was collected for all samples and quantitative XRD using Rietveld refinement was collected for only two samples. Samples prepared for qualitative XRD were ground in mortar and pestle under ethanol. Samples prepared for quantitative XRD were reduced to <10µm by grinding under ethanol in a vibratory micronizing mill. XRD data were collected using a Bruker D8 Focus Diffractometer with a scanning step of 0.029° 20 and counting time of 100.1 s over a range of 3-80° 20. Mineral phases in the X-ray diffractograms were matched to mineral phases using the International Centre for Diffraction Database PDF-4 and Search Match software by Bruker. Quantitative mineralogical data was obtained using the Rietveld method with TOPAS 4.2 software package (Bruker AXS). While XRD is useful for high abundance crystalline mineral phases, it has limited ability to detect minerals below ~0.5 - 1 wt.% abundance or those that are amorphous or nano-crystalline. Accordingly, a modified sequential extraction procedure (SEP) proposed by Hall et al. (1996) (Table 3.2) was used to selectively dissolve the secondary phases from a 1g sample. The SEPs were performed on duplicates of each sample and the average leachate concentration for each step is reported. The extraction solutions were analyzed by a Varian 725-ES ICP-OES. The SEP results are reported as % leached. Values below the detection limits of the ICP-OES, generally 0.2mg/L, are reported as <DL (i.e., less than the detection limit). Table 3.2 presents the detection limits for each extraction step of the SEP in units of ppm of solid. Seven samples were examined in thin section using transmitted and reflected light microscopy to identify secondary phases.

These phases were then examined using scanning electron microscopy (SEM) and energy dispersion spectroscopy (EDS). Thin sections for the SEM were coated with evaporated carbon and examined on a Philips XL30 SEM equipped with a Bruker Quantax 200 Microanalysis system and a light element XFLASH 4010 Silicon Drift detector. Secondary phases were assumed to occur as coatings on mineral surfaces and/or rock particles, and as discrete mineral grains of phases that were not part of the primary mineral assemblage noted in "fresh" waste rock. A semi-quantitative analysis of the wt.% abundance of elements associated with these phases was determined using the EDS on spot locations.

Figure 3.1 presents the location of the drill sites on the dump, the locations of monitored seeps found at the toe of the slopes below the drill sites, and the pre-dump topography in which natural catchments are inferred for drainage from waste rock dumped at Site 1 and Site 3. These seeps drain into the tailings ponds where they are managed as part of the water quality management program. Site 1 is in the catchment in which seeps CO-41 and CO-57 were located and Site 3 is in the catchment in which seeps CO-28 and CO-56 were located. Seepage chemistry for each of these monitored locations was provided from December 2004-May 2012 for CO-28 and CO-41 and November 2011-May 2012 for CO-56 and CO-57. The seep CO-41 had a data gap between August 2008-April 2011. The saturation indices (SIs) of phases that control the seepage chemistry were determined with PHREEQC (Parkhurst and Appelo, 2013) using the WATEQ4F database modified to include Mo species data from the MINTEQ.V4 database. The database used was further modified to include the phases hydrozincite,  $Zn_5(OH)_6(CO_3)_2$  (Preis and Gamsjäger, 2001), aurichalcite, (Cu,Zn)<sub>5</sub>(OH)<sub>6</sub>(CO3)<sub>2</sub> and rosasite, (Cu, Zn)<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> (Alwan et al., 1980), taking into consideration that the mineralogical studies indicated the presence of mixed Cu and Zn phases (discussed in the sections below).

#### 3.3 Results

#### 3.3.1 Lithology and Mineralogy

Table 3.1 presents the logged lithologies, visible sulfides and secondary phases, and ABA results for the 32 samples investigated in this study. These data show that most samples were composed of a mixture of lithologies which is partly due to the drilling method used. The major lithology of most of the Site 1 samples was marble, with some samples composed mostly of marble diopside and igneous intrusive waste rock. The major lithology of most of the Site 3 samples was igneous intrusive, with a few samples that were marble, hornfels and exoskarn. Iron oxides were visible in most of the samples and a blueish mineral, logged as malachite, was visible in many of the samples (N=16). The degree of iron oxidation was qualified using a scale of 0 (none) - 4 (strong) and many of the samples had visible oxidation products. Using the ARD criteria from Price (2009), the ABA results show that most of the samples from each site were non-acid generating (NAG) (N=20); however, three samples from Site 1 were classified as potentially acid-generating (PAG) and one as uncertain while four samples from Site 3 were PAG and three uncertain.

Table 3.3 summarizes the sulfide minerals and secondary minerals identified in the waste rock samples using XRD analysis. A detailed tabulation of mineralogy and XRD patterns for all the samples is presented in Appendix E. The minerals identified in the samples were consistent with minerals previously identified using XRD in homogenous "fresh" waste rock samples by Peterson (2014). The sulfide minerals pyrite (N=29), chalcopyrite (N=18), and molybdenite (N=17) were identified in many of the samples. Sphalerite was also identified, but in fewer samples (N=3). All of the samples contained some calcite; gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) (N=23), hemimorphite (Zn<sub>4</sub>Si<sub>2</sub>O<sub>7</sub>(OH)<sub>2</sub>·H<sub>2</sub>O) (N=2), smithsonite (ZnCO<sub>3</sub>) (N=4), and wulfenite (PbMoO<sub>4</sub>) (N=8) were also identified. Aside from hemimorphite and smithsonite, these minerals were not previously reported in "fresh" waste rock samples and were considered secondary. While hemimorphite and smithsonite may be secondary minerals that formed due to the weathering of Zn-bearing sulfides, they may also have been present prior to construction of the waste rock pile considering that they were found as part of the supergene mineralization of the Antamina deposit (Personal communication 2013, L. Plascencia). As such, hemimorphite and smithsonite cannot be unambiguously considered secondary minerals that formed in the dump. Although many of the samples had a "rusty" appearance, and iron oxides were noted in the drill logs, crystalline iron oxides were not identified in the XRD patterns of any of the samples, potentially due to low abundance or because these oxide phases are actually amorphous.

#### **3.3.2** Total Elemental Composition

Table 3.4 presents the total solid phase concentrations of As, Cu, Mo, Pb and Zn in the samples. The total elemental concentrations for all elements are provided in Appendix F. Figure 3.2 presents box plots of the total metal concentrations for As, Cu, Mo, Pb, and Zn for the 16 samples from Site 1 and 16 samples from Site 3. The box plots show the median value (red line), the 25th – 75th percentile (blue box), the 9th-91st percentile (whiskers) and outliers (red crosses). The data shows that there were higher concentrations of As and Mo in the Site 3 samples and higher concentrations of Pb and Zn in the Site 1 samples. Some of the differences in total elemental composition between the sites can be explained by the distinct lithologies of the samples. The Site 1 samples contained more marble bearing waste rock which is expected to have higher Pb contents than other waste rock types (Hirsche, 2012; Lipten and Smith, 2004; Love et al., 2004). There were more samples from Site 3 that contained igneous intrusive waste rock in which Mo bearing sulfides are predominantly found (Hirsche, 2012; Lipten and Smith,

2004; Love et al., 2004). Site 1 samples contain more skarn and hornfels waste rock, known to contain higher Zn. While total Zn was generally lower in the Site 3 samples, samples from the base of the Site 3 borehole were composed mostly of hornfels and skarn and thus contained relatively high Zn.

#### 3.3.3 SEP Results

Figure 3.3 through Figure 3.9 present the SEP results as percent leached (%) Ca, Fe, As, Cu, Mo, Pb, and Zn, respectively, each figure contains an inset graph of the total metal concentration of each sample (reproduced from Table 3.4). Appendix G presents similar SEP plots for both ppm leached and % leached Al, Ca, Fe, Mn, As, Cu, Mo, Pb, Zn. The results of the SEPs indicated that weak-acid soluble phases and amorphous reducible phases contained the largest fraction of the metals of interest in this study. The highest proportion of Ca was leached during the weak-acid soluble step, Step 3 (see Figure 3.3), as was expected due to the high carbonate content of the waste rock. Ca was also leached during the water soluble extraction step, which can be attributed to gypsum dissolution. In Steps 4 and 5 Ca is attributed to the dissolution of wollastonite (see Chapter 2). Wollastonite was noted in the X-ray diffractograms of 7 samples (Appendix E) and makes up part of the exoskarn lithology (Lipten and Smith, 2004; Love et al., 2004). Jambor et al. (2002) noted that the neutralization potential (NP) of wollastonite was comparable to the NP provided by calcite, and due to its significant abundance could be an additional source of neutralization in this waste-rock pile. The highest proportion of Fe was leached during the two reductive dissolution steps that target iron oxides, Step 4 and Step 5 (Figure 3.4). The samples that leached the highest amounts of Fe in these extraction steps were generally obtained from material that was noted in the drill logs to have moderate to strong visible iron oxide alteration.

The highest proportions of extracted Cu, Pb and Zn (Figure 3.6, Figure 3.8, and Figure 3.9, respectively) were found in the weak-acid soluble and the amorphous reducible phases extraction steps. The highest proportion of extracted As (Figure 3.5) was found in the amorphous reducible phase extraction Step 4. Most Mo remained in the residual step and only a few samples (N=8) leached Mo from the secondary phases targeted by the SEP method (Figure 3.7). Mo was leached in varying concentrations during Steps 1, 2, 4 and 5 in only a few samples (N = 8) at low concentrations generally representing <10% of the total Mo with the exception of samples BH-1d (90.0 – 91.5) and BH-1d (91.5 – 92.4). These two samples leached 60 – 80% of the total Mo during Step 5 (crystalline iron oxides) but had low total Mo (~100ppm) initially.

#### **3.3.4** Optical Microscopy and SEM/BSE Imaging of Secondary Minerals

Plane-polarized microscope and SEM images were used to investigate the secondary phases that could be observed in thin section. Semi-quantitative analysis of EDS spectra from spot locations was used to determine wt.% of elements associated with the secondary phases found. Appendix H presents the full results of the microscopy and SEM/EDS imaging investigation. From the mineralogical investigation two distinct coatings on silicate, carbonate and sulfide minerals were found: a blue coating and rusty-brown coating.

Images of the "blue precipitate" are presented in Figure 3.10 and Figure 3.11 for Site 1 and Site 3 samples, respectively. Figure 3.10-A shows a calcite grain from BH-1d (19.5 - 21.0) that is coated by a blue precipitate, with high Cu, Zn, O, C and S (with Cd, Fe, Mn, Al, Si and Ca making up <1% of the phase). Figure 3.10-B and Figure 3.10-C present images and results from BH-1d (91.5-92.4), in these examples analysis of the EDS spectra showed that the mineral phase contained Cu, Zn, O and C (with Si making up <0.5% of the phase). Also in Figure 3.10-B the mineral associated with the "blue precipitate" was composed predominantly of Zn, Si and O and

was inferred to be the hemimorphite that was identified from the XRD investigation of this sample. All images in Figure 3.11 are from BH-3s (15.0 - 16.5); the analysis of these EDS spectra showed high wt.% Cu, O, C and S, with only one specimen containing 0.8 wt% Zn. Generally, other elements made up <1% of the EDS spectra except in Figure 3.11-A where volume effects of the SEM may have excited Ca in the calcite that the "blue precipitate" was coating, causing 1.8% Ca in the precipitate.

Figure 3.12 and Figure 3.13 present the plane polarized and SEM images of iron oxides found in samples from Site 1 and Site 3, respectively. Iron oxides formed as coatings around silicate minerals (Figure 3.12-B and Figure 3.13-A), and as coatings and rims around weathered sulfide minerals such as pyrite (+Zn) (Figure 3.12-A, Figure 3.12-C and Figure 3.13-C) and chalcopyrite (Figure 3.13-B). Analysis of the EDS spectra for these iron oxides showed that Cu, Zn, Pb (with 0.01% Mo in Figure 3.12-B) were associated with the samples examined from Site 1 and Cu, Zn, Pb, As and Mo were associated with the samples examined from Site 3.

#### Seepage Geochemistry

Taken together, the results of the SEPs and SEM/EDS investigations suggested that in addition to sorption onto iron oxides, Cu and Zn were precipitating as hydroxycarbonate and hydroxysulfate phases. In some samples, precipitated phases appear to contain both Cu and Zn. Prior to conducting speciation calculations on the seepage samples, thermodynamic data for aurichalcite (Cu,  $Zn_{5}(CO_{3})_{2}(OH)_{6}$  and rosasite (Cu, $Zn_{2}(CO)_{3}(OH)_{2}$  (Alwan et al., 1980) were integrated into the model database to represent the Cu and Zn-bearing blue precipitate observed in the East Dump samples. Both aurichalcite and rosasite are copper-zinc hydroxycarbonates that are found as secondary minerals in copper/zinc deposits (Frost et al., 2007a, 2007b) and are light blue to green in color. Both minerals are noted to have varying Cu:Zn ratios in natural samples

and have been synthesized with varying Cu:Zn ratios (Frost et al., 2007a, 2007b). Because hydrozincite was previously observed as a secondary phase in neutral drainage sites with high Zn contamination (Jacquat et al., 2008; Younger, 2000), it was also added to the database, even though this phase was not observed in our mineralogical investigations. Interestingly, aurichalcite is stoichiometrically similar to hydrozincite and rosasite is stoichiometrically similar to malachite, and solid solutions between each have been suggested (Yoder et al., 2011). Thermodynamic data for Cu/Zn hydroxysulfates were not available in the literature and could not be added to the database. Namuwite, (Zn,Cu)<sub>4</sub>SO<sub>4</sub>(OH)<sub>6</sub>.4H<sub>2</sub>O, which is stoichiometrically similar to brochantite (Yoder et al., 2011), has been studied for its crystalline structure and is noted to occur jointly with hydrozincite (Groat, 1996). The only documented Cu/Zn-carbonatesulfate secondary mineral naturally is schulenbergite, to occur  $(Cu,Zn)_7(SO_4,CO_3)_2(OH)_{10}\cdot 3(H_2O)$ , which was discovered at the Glücksrad mine, Germany and at the Hirao mine, Japan (Ohnishi et al., 2007), however, as with namuwite thermodynamic data for this phase are not yet available.

Figure 3.14 and Figure 3.15 present the measured pH and saturation indices predicted from the chemistries of two seeps monitored at the toe of the slope below Site 1 and Site 3, respectively. An example PhreeqC input file is provided in Appendix I. The modelled geochemistry for the neutral seep associated with Site 1, CO-41, showed that goethite, Fe(OH)<sub>3(a)</sub>, rosasite, aurichalcite and calcite were supersaturated throughout the simulation period. The SI of gypsum oscillated between -1 and 0 between the wet season and dry season, respectively until the end of the wet season in 2011 after which it remained at equilibrium (SI=0). At the end of the 2011 wet season, the pH declined from 7.5 to 6.5 and the SIs of gypsum, brochantite, hydrozincite, and wulfenite increased from undersaturated values close to

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equilibrium (between -0.5 and 0.5), while the SI of calcite decreased from supersaturated values of ~1 to undersaturated (SI <-0.5). Drainage water from the neutral seep associated with Site 3, CO-28, is similar to that from the neutral seep associated with Site 1, in that goethite,  $Fe(OH)_{3(a)}$ , rosasite, aurichalcite, and calcite were supersaturated throughout the simulation period; however, hydrozincite was additionally supersaturated throughout the simulation period. Gypsum was at equilibrium. Over the time period modelled, the SI of smithsonite was always between 0 and -0.5, while the SI of wulfenite varied seasonally between -1 and 1, generally trending between supersaturated conditions in the wet season and undersaturated conditions in the dry season until after the end of the wet season in 2008 when the SI remained at equilibrium. During the wet season of 2006, 2007 and 2008 the pH at CO-28 declined to a minimum of 6.7, 5.9 and 3.8, respectively, but rebounded back to neutral at the end of each wet season. During these events the SIs of brochantite, antlerite, malachite and jarosite increased from undersaturated to supersaturated conditions with SIs > 3. In both neutral seepages, supersaturation of calcite is likely an artifact due to the degassing of CO<sub>2</sub> from the sample, prior to or at the time of the pH measurement, which tends to cause an increase in pH. If CO<sub>2</sub> degassing had taken place, it would also cause an over-prediction of the SIs for the hydroxide, hydroxycarbonate and hydroxysulfate phases. The modelled geochemistry of the acidic seeps associated with Site 1 (CO-57) and Site 3 (CO-56) are similar in that jarosite and goethite are supersaturated with SIs > 1 and gypsum is at equilibrium over the simulation period.

#### 3.4 Discussion

From the mineralogical and geochemical investigations used in this study it is possible to distinguish two predominant attenuation processes active in the waste-rock dump: precipitation of hydroxycarbonate and hydroxysulfate phases that attenuate Cu and Zn and sorption or co-

precipitation onto precipitating iron oxides that attenuate As, Cu, Pb, and Zn. The presence of a weak-acid soluble Pb-bearing phase (such as cerrusite,  $PbCO_3$ ) is inferred from the SEP results but is neither supported by the geochemical modelling of seepage chemistry, nor is it identified in the mineralogical examinations. From the data, the predominant attenuation mechanism for Mo cannot be conclusively identified; however, the data suggest that Mo is attenuated by sorption onto iron oxides in only a few samples at low concentrations and by the precipitation of wulfenite.

#### 3.4.1 Hydroxycarbonate and Hydroxysulfate Phases

Blue colored coatings on primary minerals identified in the thin sections containing variable Cu, Zn, C and S, likely represent the phases that leached Cu and Zn in the weak-acid soluble step of the SEP. The abundance of Cu, Zn, C and S associated with these phases appear to be influenced by the rock types present in the sample and the ARD classification of the material. The "blue precipitate" found in the Site 1 samples contained both Cu and Zn and is likely due to the higher total Zn concentrations present in Site 1 samples (from marble waste rock) as compared to Site 3 samples. The presence or absence of S in these phases appears to be related to the ARD character of the samples where S is present in samples that were characterized as PAG and uncertain, but not in samples that were identified as NAG. From the mineralogical investigation it is clear that a complex assortment of secondary hydroxycarbonate and hydroxysulfate mineral phases is present in the dump, potentially owing to the heterogeneous geochemical/lithological nature of the waste rock. In an experimental pile study of PAG waste rock at Antamina (Peterson, 2014) a "blue precipitate" that had formed from drainage emanating from the pile was collected and using XRD determined that the precipitate was mostly amorphous in nature containing some gypsum and malachite. X-Ray absorption spectroscopy (XAS)–fine structure (XAF) and near edge structure (XANES) was then used to show that much of the copper in the sample was bonded to sulfate. Using EDS, Peterson (2014) also showed that the precipitate contained Zn, Cu, Si, Al, Mn, Mg, S, and C, but did not quantify the relative abundance of these elements.

Without the addition of aurichalcite, rosasite, and hydrozincite to the geochemical database, speciation modeling would fail to confirm hydroxycarbonates as sinks for Cu and Zn, as malachite and smithsonite were, for the most part, undersaturated in the drainage chemistries of the seeps. Aurichalcite and rosasite were consistently supersaturated in neutral drainage from Site 1 and Site 3, but undersaturated in the acidic seeps. Brochantite and malachite were supersaturated only when pH remained in the range between 5 and 7. Hydrozincite was shown to be supersaturated in the drainage from Site 3, but was undersaturated in the drainage from Site 1 (until the pH declined below 7, at which point it became supersaturated).

#### 3.4.2 Iron Oxides

Iron oxides are widely documented to be one of the most important sinks for both cationic and anionic metals in many mining waste and environmentally impacted sediment studies in a host of different acid-rock drainage (ARD) and neutral-rock drainage (NRD) environments (Caraballo et al., 2009; Carlsson et al., 2002; Dold and Fontboté, 2002, 2002; Segura et al., 2006; Smuda et al., 2007). During the SEPs the highest concentrations of Fe were leached during the amorphous reducible phase step (Step 4), implying that the Fe-oxides are likely amorphous or poorly crystalline, consistent with the fact that Fe-oxides were not identified in the XRD investigation. The geochemical modelling showed that goethite was supersaturated in both the acidic and neutral seeps and  $FeOH_{3(a)}$  was supersaturated in the neutral seeps. From Figure 3.4, the amount of Fe leached from the Site 1 samples was similar regardless of total iron

content, ARD classification, depth or material type, while there appears to be slight differences in Fe leached from the Site 3 samples. Also leached during Step 4 of the SEP were As, Cu, Pb and Zn and these associations were confirmed by the SEM/EDS investigations. During the SEPs Mo remained until the residual phase step of most samples. The residual phases include stable silicate phases, sulfide phases, and potentially wulfenite which is considered a very stable phase (Vlek and Lindsay, 1977). Wulfenite was identified in the XRD patterns of 8 of the 32 samples. Mo was leached from 8 non-wulfenite bearing samples during Step 1, Step 2, Step 4 and Step 5 of the SEP but at very low concentrations compared to the total Mo of the sample. This SEP result appears to suggest multiple attenuation processes for Mo; however, it is also possible that Mo is released by desorption from iron oxides which is expected to occur in pH > 5 conditions (Conlan, 2009; Geng et al., 2013), as present during Step 1 and Step 2, or desorption due to the complete dissolution of iron oxides, during Step 4 and Step 5. The samples that leached Mo during these steps, when investigated using SEM/EDS, were found to have Mo associated with iron oxides. The association of Mo with iron oxides suggests that the pore water pH in these zones may be acidic as sorption of the oxyanion Mo increases with decreasing pH. These observations are consistent with previous studies at Antamina that indicated there are two likely attenuation mechanisms for Mo: sorption onto iron oxides in acidic micro-environments (Dockrey et al., 2014) and the precipitation of wulfenite when Mo bearing pore water is in contact with Pb-bearing waste rock (Conlan, 2009; Conlan et al., 2012; Hirsche, 2012). Finally, during the weakly sorbed/cation exchange extraction step (Step 2), Cu, Pb, and Zn were detected in the leachate but at low concentrations (<3% of the total leached). Cation exchange was suggested as a potential attenuation mechanism for Zn in a stacked barrel study by Hirsche et al.

(2012), however, based on the SEP results this mechanism does not appear to be the dominant attenuation mechanism for Zn.

The sequential extractions used in this study are useful to indirectly assess the potential mobility of the metals studied in the mine waste. The hydroxysulfate and hydroxycarbonate Cu and Zn phases will be stable under neutral drainage conditions, but will tend to dissolve and release metals if acidic conditions (pH<5) arise, for example in locations of low carbonate mineral content in which carbonate minerals become depleted or passivated. Hemimorphite and smithsonite, although not conclusively determined to be secondary minerals that formed in the East Dump, should also be considered phases from which Zn could be released, if the pH decreased below 5 (see Chapter 2). The metals associated with the iron oxides are expected to be stable in neutral to slightly acidic conditions and remobilization would require the development and persistence of acidic pH conditions (pH<3) or reducing conditions to cause dissolution of these oxide phases. Mo would be the exception to enhanced metal release under low pH conditions, since sorbed Mo would be expected to become more stable, provided that dissolution of iron oxides does not occur. Mo associated with iron oxides was identified in only a few samples (N = 8) suggesting that neutral conditions currently prevail in the dump. Wulfenite observed in samples (N = 8) during the XRD investigation is considered to be a stable mineral phase in neutral conditions and may provide a very stable phase for the attenuation of Mo (Vlek and Lindsay, 1977).

#### 3.4.3 Implications

The observations made in this study support the occurrence of sorption on iron oxides as a process of metal attenuation for As, Cu, Pb and Zn (and Mo in zones that are acidic) and also suggest that Cu and Zn attenuation in carbonate-bearing waste rock needs to be accounted for

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using mixed Cu:Zn hydroxycarbonate and hydroxysulfate phases, although thermodynamic data for such phases are limited. Thermodynamic data for rosasite and aurichalcite were added to the geochemical model to represent the observed of Cu-Zn-C-O phases in the East Dump samples. While the actual phases precipitating in the dump may have different Cu:Zn ratios than those of rosasite and aurichalcite, the simulations show that these phases were supersaturated, while phases like smithsonite and malachite were generally undersaturated in the neutral drainage. Hydrozincite was not observed in the mineralogical investigations, but it was also predicted to be supersaturated by the geochemical model in one of the neutral seeps; thus, should be considered a possible attenuating phase for Zn until it can be conclusively ruled out. Thermodynamic data for mixed Cu:Zn hydroxysulfate phases were not available; however, the mineralogical investigation shows phases that contain Cu-Zn-S-O-C to be present in samples that were PAG and uncertain. The SEPs also show that a significant proportion of Cu and Zn are stored in weak acid soluble phases and that the onset of ARD may cause the release of Cu and Zn via dissolution of these phases.

Although not the focus of this study, two primary minerals have been shown to be of potential interest with respect to ARD and metal leaching. The EDS examination showed that some of the pyrite contained trace amounts of Zn (0.20 - 0.23 wt.%; Appendix H Figure H.17, Figure H.21, and Figure H.22), oxidation of pyrite with Zn impurities may be another source of Zn in solution, in addition to the oxidation of sphalerite. The dissolution of wollastonite may contribute to the neutralization potential of the waste rock (Jambor et al., 2002); however, up until now calcite has been considered the only phase to contribute to acid neutralization.

#### 3.5 Conclusions

The analysis of waste rock and seepage geochemistry from Antamina's East Dump show that precipitation of weak-acid soluble hydroxycarbonate and hydroxysulfate phases and sorption/co-precipitation onto iron oxides are the predominant attenuation processes for Cu and Zn. From the SEP data these hydroxycarbonate and hydroxysulfate phases appear to be as important as iron oxides in attenuating Cu and Zn. From the mineralogical investigation these phases can contain both Cu/Zn which may vary compositionally as a function of the relative abundances of Cu and Zn. The results of the sequential extraction procedure used in this study also suggest that weak-acid soluble and iron-oxide phases are attenuating Pb, although the SEM/EDS investigations only found Pb associated with iron oxides. The SEP results and SEM/EDS investigations show that As is associated with amorphous iron oxides. In most of the samples investigated, Mo was released predominantly during the residual step of the SEP suggesting that Mo is associated with sulfides, and stable phases such a wulfenite. Only a few samples leached Mo and the SEP and SEM/EDS investigations suggest that Mo is being released mainly by desorption from iron oxide surfaces. Since Mo associated with iron oxides was identified in only a few samples it can be suggested that neutral conditions currently prevail in the dump. Geochemical modelling of the seepage chemistry provides evidence for the type of mineral phases that might be controlling metal solubility; however, the database used required modification to capture the complexity of the secondary phases that were observed in the samples. In high carbonate waste rock with both Cu and Zn sulfides, precipitation of mixed Cu:Zn hydroxycarbonate and hydroxysulfate phases in addition to pure end-member Cu or Zn hydroxycarbonate or hydroxysulfate phases may exert significant control on the aqueous

concentrations of Cu and Zn. Thermodynamic data for these phases is limited, highlighting the need for more geochemical studies on these phases.

# Tables

Table 3.1	Samples selected fo	r metal attenuation	study

	Major	Minor				S(T)	S(2-)	TIC	AP (S2-)	Carb-NP	NPR	ARD
Sample ID	Lithology (>50%)	lithology (<50%)	Other Lithology	Primary Sulfides	Secondary minerals	(%)	(%)	(%)	kg CaCO3/t	kg CaCO3/t	-	Classification (Price, 2009)
BH-1s (1.5 - 3.0)*	М	MDP	XV	Cp, Mo, Py, Bi	FeOx (2)	0.6	0.5	4.2	16	351	22.4	NAG
BH-1s (10.5 - 12.0)	М		XV	Cp, Bn, Py, Po		0.4	0.3	9.6	10	801	82.7	NAG
BH-1s (19.5 - 21.0)	IQM	М		Cp, Mo, Py	FeOx (3)	10.0	9.7	1.1	303	93	0.3	PAG
BH-1d (1.5 - 3.0)	MDP	М	XCVC, IQM	Ср, Ру, Ро	FeOx (1)	-	-	-	-	-	-	-
BH-1d (19.5 - 21.0)*	IQM		M, BN sec	Ср, Мо, Ру,	FeOx (3), Malachite	8.6	8.0	1.4	251	117	0.5	PAG
BH-1d (25.5 - 27.0)	XCVC	MDP	M, IQM, BN	Cp, Sp, Py, Po	FeOx (4), Malachite	12.9	12.4	1.7	388	143	0.4	PAG
BH-1d (39.0 - 40.5)	М	XCVC	MDP, IQM, BN	Ср, Ру, Ро	FeOx (2), Malachite	6.6	6.4	3.5	198	287	1.5	uncertain
BH-1d (42.0 - 43.5)	MDP	М	XC	Cp, Sp, Py, Po	FeOx (1), Malachite	1.7	1.7	4.5	53	374	7.1	NAG
BH-1d (49.5 - 51.0)	MDP	XV	IQM, M	Cp, Py	FeOx (1)	2.5	2.4	2.6	76.2	213	2.8	NAG
BH-1d (54.0 - 55.5)	М	IQM	MDP, XV	Cp, Mo, Py, Po	FeOx (1)	1.3	1.3	2.1	40	178	4.5	NAG
BH-1d (64.5 - 66.0)	М	MDP	IQM, XCVC, XW	Cp, Py, Po, Bi	FeOx (1)	0.5	0.5	8.1	15.3	671	43.9	NAG
BH-1d (70.5 - 72.0)	IQM	NC	M, XW, MDP, BN	Cp, Bn, Mo, Py,	FeOx (1), Malachite	1.7	1.7	2.5	51.6	207	4.0	NAG
BH-1d (76.5 - 78.0)	М	MDP	IQM, XCVC, BN	Cp, Sp, Py,Po	FeOx (1), Malachite	1.5	1.5	5.9	46.6	491	10.5	NAG
BH-1d (81.0 - 82.5)	IQM	М	M, XCVC	Cp, Py, Po,	FeOx (3), Malachite	1.0	1.0	3.2	31	268	8.8	NAG
BH-1d (90.0 - 91.5)*	М	MDP	IQM, XV	Cp, Sp, Py, Po	FeOx (4), Malachite	1.2	1.1	4.7	34	391	11.5	NAG
BH-1d (91.5 - 92.4)	MDP	XV	M, IQM	Cp, Sp, Py, Po	FeOx (4), Malachite	1.5	1.4	2.9	43	238	5.6	NAG
BH-3s (1.5 - 3.0)	М	IQM		Cp, Py, Po	FeOx(1)	0.6	0.6	3.6	18	302	16.4	NAG
BH-3s (9.0 - 10.5)	М	MDP	IQM	Py, Po	FeOx (1),	1.6	1.5	6.2	48	517	10.8	NAG

	Major	Minor			~ -	S(T)	S(2-)	TIC	AP (S2-)	Carb-NP	NPR	ARD
Sample ID	Lithology (>50%)	lithology (<50%)	Other Lithology	Primary Sulfides	Secondary minerals	(%)	(%)	(%)	kg CaCO3/t	kg CaCO3/t	-	Classification (Price, 2009)
					malachite							
BH-3s (10.5 - 12.0)	М		IQM	Ср, Ру, Ро	FeOx (2)	1.2	1.2	5.5	37	458	12.5	NAG
BH-3s (15.0 - 16.5)*	IQM	М		Ср, Ру, Ро	FeOx (4), malachite	2.9	2.5	1.3	77	111	1.4	uncertain
BH-3s (21.0 - 22.5)	М	XV		Py, Po	FeOx (2), malachite	0.4	0.4	7.1	13	591	47.2	NAG
BH-3d (10.5 - 12.0)	С			Ру	FeOx (1)	1.3	1.3	6.9	40	576	14.5	NAG
BH-3d (24.0 - 25.5)*	XV	С		Ср, Ру	FeOx (1), Malachite	0.8	0.7	4.9	22	409	18.4	NAG
BH-3d (37.5 - 39.0)	IQM	С		Cp, Py	FeOx (2), Malachite	14.9	14.6	1.8	456	152	0.3	PAG
BH-3d (39.0 - 40.5)	IQM	С		Cp, Py	FeOx (2)	19.3	19.0	1.3	593	107	0.2	PAG
BH-3d (48.0 - 49.5)*	IQM	XCVC		Cp, Py	FeOx (1)	1.7	1.7	1.4	52	117	2.3	NAG
BH-3d (72.0 - 73.5)	XV	HG		Cp, Py		12.5	12.2	2.7	383	227	0.6	PAG
BH-3d (88.5 - 90.0)	IQM			Ру	FeOx (1)	2.9	2.8	1.2	89	102	1.2	uncertain
BH-3d (91.5 - 93.0)*	IQM	XV		Ср, Ру	FeOx (1), Malachite	4.6	4.5	1.7	141	140	1.0	PAG
BH-3d (94.5 - 96.0)	IQM	NC		Cp, Sp, Mo, Py		4.7	4.6	2.8	144	236	1.6	uncertain
BH-3d (112.5 - 114.0)	IQM	М		Cp, Py	FeOx (1), Malachite	0.5	0.5	3.1	17	259	15.6	NAG
BH-3d (121.5 - 123.0)	HG	IQM		Py, Po	FeOx (1)	0.5	0.4	5.4	13.8	450	32.6	NAG

NOTES:

\* indicates samples that were selected for SEM/BSE investigations

Acronyms used in the table are defined as such: IQM – Igneous Intrusive; M – Marble; MDP – Marble Diopside; XCVC – Brown and Green Garnet Exoskarn; XV – Green Garnet

Exoskarn; C - Limestone; NC - Brown Garnet Endoskarn; Cp - Chalcopyrite; Sp - Sphalerite; Mo - Molybdenite; Py - Pyrite; Po - Pyrrhotite; Mt - Magnetite; Bi -

Bismuthite;Bn – Bornite; FeOx – Iron Oxides (1-4 denotes intensity of oxidation; where 1 = trace, 2 = weak, 3 = moderate and 4 = strong)

Step	Phases	Method <sup>(1)</sup>	ICP-OES Detection Limit ppm of solid <sup>(4)</sup>
Weight ou	it 1g of sample and react in the prese	ribed order:	
1	Water Soluble	50 mL deionized water shake for 1h	<10 ppm
2	Weakly sorbed /Exchangeable <sup>(2)</sup>	40 mL MgCl <sub>2</sub> shake for 1h	<10 ppm
3	Weak acid soluble	20 mL CH <sub>3</sub> COONa (sodium acetate) at pH 5 shake for 6h centrifuge for 10min	< 6 ppm
		Repeat Step	
4	Amorphous reducible phases	20 mL 0.25M NH <sub>2</sub> OH*HCl (hydroxylamine hydrochloride) in 0.25 HCl place in 60 <sup>o</sup> C water bath for 2h every 30min vortex contents	<6 ppm
		Repeat Step but heat for only 30 min	
5	Crystalline reducible phases	30 mL of 1 M NH <sub>2</sub> OH*HCl (hydroxylamine hydrochloride) in 25% CH <sub>3</sub> COOH (acetic acid) place in 90 <sup>o</sup> C water bath for 3h, vortex every 20 min	<8 ppm
		Repeat Step but heat for only 1.5 hours	
6	Residual Phases (silicates, sulfides)	4 - Acid Digest <sup>(3)</sup>	

#### Table 3.2 Sequential extraction procedure (SEP) (modified from Hall, Vaive, Beer, & Hoashi, 1996)

NOTES:

1) Steps 3-5 are repeated using the same liquid solid ratio (LSR) but extraction time was shortened. Leachates are analysed separately and the concentrations are summed.

2) Weakly sorbed/exchangeable step taken from (Tessier et al., 1979)

3) Residual fraction was determined at SGS, Burnaby (BC, Canada)

4) Detection limit in ppm of solid based upon detection limit of the ICP-OES (0.2mg/L) and volume of regent

Sample ID	Pyrite	Molybdenite	Chalcopyrite	Sphalerite	Gypsum	Smithsonite	Wulfenite	Hemimorphite
Mineral Formula	FeS <sub>2</sub>	MoS <sub>2</sub>	CuFeS <sub>2</sub>	ZnS	CaSO <sub>4</sub>	ZnCO <sub>3</sub>	PbMoO <sub>4</sub>	$Zn_4Si_2O_7(OH)_2\bullet(H_2O)$
BH-1s (1.5 - 3.0)*	Х	Х			Х			
BH-1s (10.5 - 12.0)								
BH-1s (19.5 - 21.0)	Х				Х			
BH-1d (1.5 - 3.0)	Х						Х	
BH-1d (19.5 - 21.0)* <sup>(1)</sup>	Х		Х		Х		Х	
BH-1d (25.5 - 27.0)	Х		Х		Х			
BH-1d (39.0 - 40.5)	Х	Х			Х		Х	
BH-1d (42.0 - 43.5)	Х			Х	Х			
BH-1d (49.5 - 51.0)	X	Х	Х		X	Х		
BH-1d (54.0 - 55.5)	X	Х						
BH-1d (64.5 - 66.0)								
BH-1d (70.5 - 72.0)	X	Х	Х		X			
BH-1d (76.5 - 78.0)	х		Х		Х			
BH-1d (81.0 - 82.5)	Х		х		Х			
BH-1d (90.0 - 91.5)*	X		Х		X			Х
BH-1d (91.5 - 92.4)	Х		Х		Х	Х		Х
BH-3s (1.5 - 3.0)	Х	Х	х					
BH-3s (9.0 - 10.5)	X	Х			X	Х		
BH-3s (10.5 - 12.0)	X		Х		Х			
BH-3s (15.0 - 16.5)* <sup>(1)</sup>	X	Х	Х		X		Х	
BH-3s (21.0 - 22.5)				Х	X			
BH-3d (10.5 - 12.0)	X				X			
BH-3d (24.0 - 25.5)*	X	X	X	Х	X		X	
BH-3d (37.5 - 39.0)	X	X			X		X	
BH-3d (39.0 - 40.5)	x	X			X			

Table 3.3 Summary of XRD identified mineralogy for East Dump waste rock samples

Sample ID	Pyrite	Molybdenite	Chalcopyrite	Sphalerite	Gypsum	Smithsonite	Wulfenite	Hemimorphite
Mineral Formula	FeS <sub>2</sub>	MoS <sub>2</sub>	CuFeS <sub>2</sub>	ZnS	CaSO <sub>4</sub>	ZnCO <sub>3</sub>	PbMoO <sub>4</sub>	$Zn_4Si_2O_7(OH)_2 \bullet(H_2O)$
BH-3d (48.0 - 49.5)*	Х	Х	х		Х			
BH-3d (72.0 - 73.5)	х	Х	х		Х		Х	
BH-3d (88.5 - 90.0)	х	х	х		Х	х		
BH-3d (91.5 - 93.0)*	х	х	х		Х			
BH-3d (94.5 - 96.0)	х	Х	Х		Х		Х	
BH-3d (112.5 - 114.0)	х	х	х					
BH-3d (121.5 - 123.0)	х							

NOTES:

\* Indicates samples that were selected for SEM/BSE investigations

(1) Indicates samples in which the Rietveld method was used to determine quantitative mineralogy

Sample ID	As	Cu	Мо	Pb	Zn
	ppm	ppm	ppm	ppm	ppm
BH-1s (1.5 - 3.0)*	104	1340	468	2080	674
BH-1s (10.5 - 12.0)	46	1170	24.5	138	1300
BH-1s (19.5 - 21.0)	45	6360	50.2	293	4600
BH-1d (1.5 - 3.0)	151	1030	27.2	800	1550
BH-1d (19.5 - 21.0)*	49	5740	104	195	4900
BH-1d (25.5 - 27.0)	68	7070	71.5	646	7660
BH-1d (39.0 - 40.5)	92	2410	169	563	2460
BH-1d (42.0 - 43.5)	48	1390	62.7	540	6550
BH-1d (49.5 - 51.0)	68	1720	103	462	3990
BH-1d (54.0 - 55.5)	28	1440	103	108	668
BH-1d (64.5 - 66.0)	65	1020	42.1	570	1300
BH-1d (70.5 - 72.0)	58	>10000	285	160	991
BH-1d (76.5 - 78.0)	67	6650	80.2	970	4190
BH-1d (81.0 - 82.5)	111	3880	215	295	857
BH-1d (90.0 - 91.5)*	118	5530	73.3	593	>10000
BH-1d (91.5 - 92.4)	94	4030	107	874	7310
BH-3s (1.5 - 3.0)	98	1250	213	367	1590
BH-3s (9.0 - 10.5)	79	3540	94.4	1800	3750
BH-3s (10.5 - 12.0)	90	4400	84.7	412	951
BH-3s (15.0 - 16.5)*	86	18600	124	50.1	1090
BH-3s (21.0 - 22.5)	152	4750	77	631	4000
BH-3d (10.5 - 12.0)	69	5510	41.8	168	850
BH-3d (24.0 - 25.5)*	193	6320	331	700	8290
BH-3d (37.5 - 39.0)	55	3760	154	117	473
BH-3d (39.0 - 40.5)	47	3180	150	74	309
BH-3d (48.0 - 49.5)*	78	6120	309	258	519
BH-3d (72.0 - 73.5)	47	2650	129	156	997
BH-3d (88.5 - 90.0)	106	5350	310	208	4370
BH-3d (91.5 - 93.0)*	151	4500	195	276	3720
BH-3d (94.5 - 96.0)	65	2900	242	294	2450
BH-3d (112.5 - 114.0)	123	2050	145	105	1950
BH-3d (121.5 - 123.0) NOTES:	90	542	16	289	1010

Table 3.4 Trace element concentration by four-acid digestion and ICP-MS finish

\* indicates samples that were selected for SEM/BSE investigations

## Figures



Figure 3.1 The Antamina Mine site, inset plan of the East Dump and pre-mining topography showing drill site locations and seeps downslope of drill sites



Figure 3.2 Box and whisker plot of total metal concentration box per site



Figure 3.3 SEP results for Ca (%) with inset total concentration (ppm)



Figure 3.4 SEP results for Fe (%) with inset total concentration (ppm)



Figure 3.5 SEP results for As (%) with inset total concentration (ppm)



Figure 3.6 SEP results for Cu (%) with inset total concentration (ppm)



Figure 3.7 SEP results for Mo (%) with inset total concentration (ppm)



Figure 3.8 SEP results for Pb (%) with inset total concentration (ppm)


Figure 3.9 SEP results for Zn (%) with inset total concentration (ppm)



Figure 3.10 Plane polarized (left)/SEM (right) images of secondary phases with semi-quantitative wt% of elements: Figure 10-A is from BH-1d (19.5 – 21.0); Figure 10-B and Figure 10-C are from BH-1d (91.5-92.4)



Figure 3.11 Plane polarized (left)/SEM (right) images of secondary phases with semi-quantitative wt% of elements: All images are from BH-3s (15.0 – 16.5)



Figure 3.12 Plane polarized (left)/SEM (right) images of secondary phases with semi-quantitative wt% of elements: Figure 3.12-A from BH-1s (1.5 – 3.0); Figure 3.12-B and -C from BH-1d (90.0 – 91.5)



Figure 3.13 Plane polarized (left)/SEM (right) images of secondary phases with semi-quantitative wt% of elements: Figure 13-A from BH-3d (24.0 – 25.5); Figure 13-B and Figure 13-C from BH-3d (48.0 – 49.5)



Figure 3.14 Equilibrium phases predicted from geochemical modelling of seeps downslope Site 1; CO-41 (top) and CO-57(bottom)



Figure 3.15 Equilibrium phases predicted from geochemical modelling of seeps downslope Site 3; CO-28 (top) and CO-56(bottom)

## **Chapter 4 Conclusions**

This research is one part of a large scale study that is aimed at understanding the hydrologic and geochemical influences on water in a neutral drainage waste rock dump that contains a mix of metal sulfides and variable carbonate content. The principal objective of this research was to identify secondary phases and characterize metal attenuation. To this end, waste rock samples were collected from a full-scale operational waste rock dump and investigated using total digestions, acid-base-accounting (ABA) tests, X-ray diffraction (XRD), sequential extraction procedures (SEPs), reflected and transmitted light microscopy, and scanning electron microscopy with electron dispersion spectroscopy (SEM/EDS). The metals of interest were arsenic (As), copper (Cu), molybdenum (Mo), lead (Pb), and zinc (Zn). This chapter summarizes the findings presented in the two main chapters of this thesis, discuss the uncertainties in the data and future research that could reduce uncertainties in the data.

#### 4.1 Summary of Key Findings

In Chapter 2 two sequential extraction procedures (SEPs) were investigated to identify selectivity and carry-over associated with geochemically heterogeneous, naturally weathered materials, the key findings of this chapter may be of interest to those investigating skarn waste rock or any other type of material consisting of silicate minerals mixed with sulfides and carbonates. The conclusions from this chapter are:

• For mixed sulfide, carbonate bearing waste rock SEPs should be designed to: 1) remove water soluble phases, such as gypsum; 2) distinguish between metals bound by cation exchange/weak sorption and metals associated with precipitation of weak acid soluble

phases, such as metal carbonate/hydroxycarbonate/hydroxysulfate phases; and, 3) distinguish metal bound by sorption onto reducible phases.

Oxalate should not be used as a reagent to dissolve iron oxides when wollastonite is present in the samples. Wollastonite dissolved in reagents that were acidified to pH < 3. The dissolution of wollastonite released Ca<sup>2+</sup> into solution which reacted with oxalate to precipitate whewellite (CaC<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O). It is postulated that the dissolution of wollastonite may have neutralized the acidity of the oxalate reagent used (Jambor et al., 2002), allowing for precipitation of whewellite. While whewellite was the only phase identified, geochemical modelling suggests that other insoluble metal oxalates (Cu-, Pb- and Zn-Oxalates) could have also formed affecting predictions of Cu, Pb and Zn release.

In Chapter 3 mixed sulfide/carbonate bearing waste rock samples collected from the East Dump were investigated to identify the phases that metals where attenuated by. The conclusions from this chapter are:

• Precipitation of blue colored weak-acid soluble hydroxycarbonate and hydroxysulfate phases are predominant attenuation processes for Cu and Zn. From the SEP data these hydroxycarbonate and hydroxysulfate phases appear to be as important as iron oxides in attenuating Cu and Zn, but are relatively less stable than iron oxides. From the mineralogical investigation these phases can contain both Cu/Zn and C/S and the variation in elemental composition may be a function of the total metal content of the waste rock as well as the total Sulfur (Stot) and Total Inorganic Carbon (TIC). The blue colored Cu/Zn hydroxycarbonate and hydroxysulfate phases observed in this study are

consistent with blue precipitates observed from an experimental pile of similar waste rock (Peterson, 2014).

- Modelling of seepage chemistry showed that most end-member Cu or Zn hydroxycarbonate and hydroxysulfate minerals were undersaturated. The observations as discussed in the bulleted point above allowed for the inclusion of mixed Cu/Zn hydroxycarbonate phases (aurichalcite and rosasite, (Alwan et al., 1980) and hydrozincite (Preis and Gamsjäger, 2002)) in the database. These phases were generally supersaturated. For future geochemical and reactive transport modelling these phases may be adequate analogues to the secondary phases observed in the East Dump samples.
- As, Cu, Pb, and Zn were leached from amorphous iron oxide dissolution steps and found associated with iron oxides in the SEM/EDS investigation. Iron oxides are well known for their ability to scavenge metals out of solution many mining waste studies (Caraballo et al., 2009; Carlsson et al., 2002; Dold and Fontboté, 2002, 2002; Segura et al., 2006; Smuda et al., 2007). From these associations sorption/co-precipitation of metals onto iron oxides is also considered a predominant attenuation process in the dump. Conceptually, these iron oxides are considered stable phases and dissolution and release of the metals associated with iron oxides would require the onset and persistence of pH<3 conditions or reducing conditions.</p>
- A Pb-bearing weak-acid soluble phase is suggested from the SEPs, although the mineralogical and SEM/EDS investigations only found Pb associated with iron oxides and the XRD investigations found wulfenite. Conceptually, this suggests that there is an "available" pool of Pb from an unknown phase from which release would require pH<5 conditions to arise.</li>

- Mo was released predominantly during the residual step of the SEP suggesting that Mo is associated with sulfides and stable phases. Only a few samples leached Mo during the SEP and the SEP and SEM/EDS investigations suggest that Mo is being released mainly by desorption from iron oxide surfaces. Mo released from the weak-sorption sites (Geng et al., 2013) and the dissolution of iron oxides in the SEP is indicative of locations in the dump in which pH<5 (Dockrey et al., 2014). The XRD investigation identified wulfenite in a few samples and Rietveld analysis of two samples show that wulfenite is present locally in low quantity (0.15 0.34 %; Appendix E Figure E.5, and Figure E.20). Wulfenite is considered a stable phase (Vlek and Lindsay, 1977) that forms quickly when Mo releasing leachate is in contact with Pb-bearing waste rock (Conlan, 2009; Conlan et al., 2012; Hirsche, 2012).</p>
- Pyrite investigated in the samples contained some Zn (0.20 0.23 wt.%; Appendix H Figure H.17, Figure H.21, and Figure H.22) oxidation of these pyrite grains would release Zn into solution. This should be considered a source of Zn, in addition to sphalerite.
- Wollastonite makes up part of the skarn lithology of the Antamina ore deposit and in the waste rock. Other researchers have shown that wollastonite may provide neutralization of acidity generated similar to that of calcite (Jambor et al., 2002). Up until now this silicate mineral has not been considered for its neutralization potential in reactive transport models at the Antamina Site.

#### 4.2 Future Work

While the SEM/study shows that Cu-Zn-C-S-O are present in varying ratios in samples, it is not able to identify the bonds between elements. These phases were potentially amorphous

and/or crystalline but low in content as to not be identifiable using XRD. Micro X-ray diffraction  $(\mu$ -XRD) or accelerated light techniques such as XAFS/XANES can be used on these phases to assess mineralogy (if possible) and bonding relationships, providing sufficient amount of this material can be collected for these techniques. Thermodynamic data for mixed Cu/Zn hydroxycarbonate phases are limited and thermodynamic data for mixed Cu/Zn hydroxysulfate phases are non-existent. Researchers show that Cu:Zn ratios for these phases are variable in natural samples (Alwan et al., 1980; Frost et al., 2007a, 2007b, 2007c; Groat, 1996). More reliable thermodynamic data for these phases would benefit geochemical and reactive transport modelling of Cu and Zn speciation and mobility in high carbonate waste rock. The scientific community at large would benefit from an increased understanding of how wollastonite contributes to the predicted neutralization potential (NP) determined via conventional acid-base-accounting methods.

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# Appendices

# Appendix A Reverse Circulation Drill Logs

This Appendix presents the Drill Logs created during drilling of the East Dump.

#### REVERSE CIRCULATION DRILLING FORM

TALAD	RO	B	41s			LO	DGU	EAD	O P	OR	TEAL	16	6d	061	sT.	AZIA		н	-	-	_	-			2			NO ES	RT	Ε.		_		-	-				Page <u>01</u> of <u>01</u>
TIPO P	ERF.	-	36	_		P	ROF	TO	TAL	-	23.	50	5			ine.	-114.		-			-			-			co	TA	1			_		_				
						Τ					Alter	atio	n					Τ	C	)TH	ER	_	V	eini	S.		_	_	_	Mir	nera	lizat	ion			I	A	G	
From	То	Graphic Log	Fm.	Lith. Rock Code (> 50%)	Sub Flock Code (< 50%)	Biotito	Sercite	Silification	K-Foldspar Vuo	PL Color	Int. Chlorite	Fluorite	Retrograde PL	Sk. Chiorte	Clay	Epidote	Calcifie	Scapolite	Fe Oxides	Secondary Cu	Gypsum	Other	Primary	Secondary	Tertiary	Sp Color	do	Bn	Sp	Mo	Py M4+	Tn	Po	8	BI	Other Trent Crimbide	And the second s	HCI Reactivity	COMMENTS:
0.00	1.5		1	M	MOP	Г										T		Т	2												1		1			1		4	> 50% MArnol PARDO (M).
																T	T																						OCNIONAL FROMMENTOS XV
1.5	3.00			M	MDE														2								1				1		1		1			4	MAYING BUDG(M)= MOP, DCALONDO
																																							Francitos XV.
3.00	4.50			M	MOP														1								1				1		1					4	Ochionoles Frantos XU.
4.50	600			Μ	MOP													2									1				1		1			1		4	
6.00	7 50				-	-		_	-	-	-		s	1	N		A	U	E	J	T	n	A	-		-	-	-		-	-	+			-	-	-	-	Wy Request 400
7.50	9,00			M														1									1				1		1				4	4	
9.00	10,50			M														2									1				1		1			1	-	4	
10,50	12,00			M														2									1	1			1		1			14	1	4	occurrente hisporter AV
12.00	16,50		-					-	1	1		-	5	1 1	N			M	U	E	5	÷	R	A	-	-	-	-		-	-	-			-		-		1 II.
16,50	18,00			Įv]	MDP														1												1	T	1			1		4	
18,00	19,50			M	IOM	1					1								2	1							1			2	2		1			1	2	3	Malapelle
19.50	21.90			18.16	M	4					1								3	14							1			2, 1	2					12		1	
21.00	22,50			IGM	M	1					1								1								1			21	1					12	3	1	
22,50	23,50	-		em.	18M	1		+	-		1	-	-	-	+	+	-		1	1	_	_		-	-	-	1	-	-	2	1	-	1		-	-	1	3	otcininale programates & y. Malage
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Figure A.1 BH-1s (0.0m - 23.50m)

REVERSE	CIRCUL	ATION	DRILLING	FORM
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Filom         To           0.00         /.50         3.00           7.50         3.00         4.50           4.50         6.00         4.50	Graphic Log	Lith Rock (Sock (Sock)	Sub Rock Code (< 50%)	olito	site	thọn spar		AH	terati	on Tail	_			_	_	_												-		_		
Fiom To 000 / 50 / 50 3 00 3 00 4/50 4 50 6 00	501 ouders	Lith Rock Code (2 50%)	Sub Rock Code (< 50%)	olito	site	filon Spar				17	_			_		OTH	ÆŔ		Ve	sins	T			N	linera	ailiza	tion	_			PAG	
000 1.50 1.50 3.00 3.00 4.50 4.50 6.00		MO		100	Bard	Silifica C-Feld	Bry	PL Color	nt. Chlorite -luorite	Retrograde I	Sk. Chlorite	ciery Epidote	Calcite	Other	Scapolite	FB-Oxides	Gypeum	Other	Primary	Secondary	Sp Colar	Cp	Bu	Mo	PY.	Mt	Po	Co	Bi	Other	Total Sulphide HCI Reactivity	COMMENTS:
1.50 3.00 3.00 4.50 4.50 6.00	-	MO	8 14			11 12	1	-		-	-		Ť	~	-	7	1		-	1		7		1	1	1	1			1	14	OCASIONAL FRAGMENTOS
3,00 450 450 600	-		M			+			-	1 1	1	+			-+'	1	1	-		1		1		1	1		1			1	14	OCASIONAL FRACHENPOSECV
4.50 600		MDI	M	-		-	++	+	-		+	+			Ľ	1	1			1		1		T	1	1	1		1		14	OCASIONAL FRACMENTOS X
1.30 0 00		M	1.6			+			1		-	-			ť	1	1			+		11	-	1	1		1	1	1		14	OCASIONAL PRACHEN 7032
601 101		M				-			-	H	+				ť		1			+	10	17		1	17	-	1		1	7	14	OCASIONAL FRACMENTOSX
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17 00 18 00	-				-	The	H		no.	15	1	0 4		-	4	-				-		1	+	1	1	1	1	t			14	SIN RECUPERACIÓN ?
1800 1950		M	Xer		-	1	H	- K	T	14	T	1	1			31				1	T	1		2	1	1	1			1	13	OCASIONAL FRACHTWOIT 10
19 50 2120		IPA		1		-	H		-	H		+	ŕ		-	3 3	2			+		Ź	-	2	Z	7	-	17			21	DEASIGNEL FRASMENTOS
210017 5	-	18M	MADO	1			H	-	-	H	+	-			-	3	2			+	1	1		12	2	-		1			22	OCASIONAL FRACKENTOS
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2002 2/50		M	MID	5		+		+	-	H	+	+			ť	1	-		-		10	1	+	1	11	1	1		H		14	JCASIONGE FARENENDS X
2150 2200		in	MAP		-	-		+	-		-	+		-	ť	1			-	-	1	4	+	-	2	1	17	+		-	27	OCASIONAL FRAGMENTOS 124 2
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40 - 42.00		M	VIV	-	-+	-		-	1		-	-	6	+	5	E			+	+		1	-	-	7	+	1	-		-	13	OCASIONAL FRAGING ITAS MON
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Figure A.2 BH-1d (0.0m - 49.50m)

REVERSE CIRCULATION DRILLING F	FORM	
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RC logging form ENE2002

Figure A.3 BH-1d (49.50m - 92.40m)

													R	EVER	SE	CIR	CUI	LATI	ON	DRIL	LIN	GFC	DRA	n										
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aco 2100	-		M	SI	ŕ		-	+	-	1	+				1		2	1	+			1	ť	1			1		1	1		1	3	tomaloguita Frontos Joh- MSP
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Figure A.4 BH-3s (0.0m – 22.50m)

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acc $bc$		Fight	То	Graphic Log	Fm.	Lith Rock Code (> 50%)	Sub Rock Code (< 50%)	Biotto	Sercite	Silfication V Extension	K-Fetdspar	PL Color	Int. Chlorite	Fluorite	Retrograde PL Sk. Chlorite	Clay	Epidote	Calcite	Other -	Scapolite	Fe Oxides	Secondary Cu	Gypsum. Other	Primatu	Seconderv	Tertiary	Sp Color	Co	Bn	Sp	Mo	Ργ	Mt	Tn	Po	S	10	Utility Yound Quantitation	BOILIDING IBIO1	HCI Reactivity	COMMENTS:
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Figure A.5 BH-3d (0.0m - 46.50m)

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Figure A.6 BH-3d (46.50m - 91.50m)

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Figure A.7 BH-3d (91.50m - 136.50m)

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Figure A.8 BH-3d (136.50m - 145.00m)

#### **Appendix B Method Quality and Inter-sample Variability (Chapter 2)**

#### B.1 Method

#### Sub-sample Precision

To identify if there was variability in the sub-sampling of each sample, precision in the leachates from the triplicate samples tested was calculated using the relative standard deviation (RSD), as follows:

where s is the standard deviation and  $\bar{x}$  is the mean. RSD is widely used in analytical chemistry to express the precision and repeatability of an assay. A low RSD was indicative of low variability in sub-samples.

#### Percent Recovery

Percent recovery was used as a proxy for complete dissolution of all mineral phases in the samples tested. Percent recovery was calculated for each element by comparing the sum of mas extracted during all steps of the sequential extractions, including the residual step, to the total bulk elemental content determined via 4-acid digest.

#### Mass Loss

The mass of solids lost to the centrifugation, decanting and filtration of the leachates at each step was determined by weighing the syringe filter before and after use and drying. This determine that minimal solids were lost during the decanting step and that the desired liquid:solid ratio was maintained. pH Drift

To ensure that the liquid:solid ratio was sufficient to dissolve the carbonates present in the samples, the pH was monitored during the carbonate step of the SEPs (step 3). If the initial and final pH were sufficiently close, then complete dissolution of the carbonates was suggested.

#### **B.2** Results

#### **Triplicate Analyses**

Calculated RSD's for triplicate results are presented in Table B.1 and Table B.2 for Method 1 and Method 2, respectively. The RSDs for the triplicate analyses were generally better than 10%, but some were between 10 % and 30% depending on the element and the detection limit. Only a few elements had RSDs higher than 30% and were typically elements that were at low concentration or near the detection limit of the ICP-OES.

#### Percent Recovery

The calculated % recovered for Al, As, Ca, Cu, Fe, Mn, Mo, Pb, and Zn leached from Method 1 and Method 2 are presented in Table B.3. For both methods the % recovered were generally between 70% and 130%, and between methods were similar. In only a few instances was the % recovery less than 70% and in more instances was the % recovery greater than 130%. The greater amount leached versus total elemental composition is most likely due to comparing results from duplicate samples and in some of the cases for Ca is due to the results of the total digestion reported greater than the maximum detection limits of the analysis. The similarity of % recovery between methods is a good indication that both methods will dissolve the same minerals over the entirety of the sequential extraction procedure.

#### Mass Loss

Table B.4 presents the mass loss results. The maximum recorded loss was 4.18% and the minimum recorded loss was 0%, the average calculated loss was 1.52%. The mass losses were higher for the Hall method than the Dold Method. This is most likely due to the repeat analysis for steps 3-5 in the Hall method which required additional rinsing, centrifuging, and decanting steps.

#### pH Drift

Table B.5 presents the initial and final pH values for step 3 of each method. Based on the initial and final pH, both methods remained at the target pH implying that there was sufficient acid for the carbonate step.

#### **B.3** Conclusion

Each method was individually assessed by testing samples in triplicate, monitoring mass loss, pH drift and by calculating % recovery for specific elements. The calculated RSDs for both methods were low, indicating good precision in the triplicate samples. Higher mass losses were identified in Method 1 as compared to Method 2. This is expected due the higher number of manipulations of the sample prescribed by the method. A higher RPM during centrifugation of the samples would likely reduce the mass loss during decanting the leachates. The pH for Step 3 of each method remained close to the target value and thus no changes to the reagent pH are necessary. The calculated percent recoveries for specific elements were generally good for both methods and between methods were similar.

## Table B.1 Calculated RSD for triplicate analysis for Method 1

D14 4-4	1.0.0		-
BM-15	10.5	- 12	

BH-1s (10.5 - 12.0)									
RSD (N)	AI	As	Ca	Cu	Fe	Mn	Mo	Pb	Zn
Step 1		-	1	-	-	-	-	-	-
Step 2	-	-	1	-	-	-	-	-	13
Step 3	6		1	6	55	2		7	1
Step 4	2	2	22	2	19	5		4	7
Shee 5	-								
July 2	10	-		8	- 10	101			9
BH 1- (10 E - 31 0)									
BH-15 (19.5 - 21.0)									
RSD (N)	AI	As	Ca.	Cu	Fe	Mn	Mo	Pb	Zn
Step 1	-	-	4	-	-	-	-	-	-
Step 2	-	-	1	1	-	1	-	-	3
Step 3	2	-	6	4	3	6	-	5	5
Step 4	1	1	2	1	2	2	-	1	3
Step 5	2	-	2	7	2	2	-	8	1
BH 14 (64 5, 66 0)									
PSD (M)		E.	6	<i>C</i> .			N	<b>*</b>	-
the l	AI	AL	a	cu	H	MA	MO	10	40
300 p 1	-	-	2	-	-	-	-	-	-
step 2	-	-	1	-	-	-	-	19	4
step 3	0	-	4	1	5	1	-	1	2
Step 4	3	9	3	1	7	5	-	4	7
Step 5	3	-	2	9	3	2	-	4	5
BH-1d (91.5 - 92.4)									
RSD (N)	AI	Az	0	Cu	Re	Ma	Mo	Pb	Zn
Step 1	-	-	0	-	-		-		-
Step 2		-	1	0	-	1	1		5
Step 3					4	4		4	1
Step 4		1	4		12	10		-	1
Shan 5									
BH-3s (1.5 - 3.0) RSD (N)	AI	Az	0	Cu	Fe	Mn	Мо	Pb	Zn
Step 1	-	-	1	-	-	-	-	-	
									-
Step 2	-	-	2	-	-	-	-	-	-
Step 2 Step 3	- 2	-	2	- 1	17	- 2	-	- 1	-
Step 2 Step 3 Step 4	- 2 2	1	2 5	- 1 0	- 17 3	- 2	-	- 1 2	- 1 2
Step 2 Step 3 Step 4 Step 5	- 2 2 5	-	2 5 1	- 1 0 4	- 17 3	- 2 1	-	- 1 2 5	- 1 2 3
Step 2 Step 3 Step 4 Step 5 BH-3s (15.0 - 16.5)	- 2 5	-	2 5 1	- 1 0 4	- 17 3 1	2	-	- 1 2 5	- 1 2 3
Step 2 Step 3 Step 4 Step 5 BH-3s (15.0 - 16.5) RSD (%)	- 2 5 Al	- - 1 -	2 5 1 1	- 1 6 4	- 17 3 1	- 2 1 1 Mn	- - - -	- 1 2 5 Pb	- 1 2 3
Step 2 Step 3 Step 4 Step 5 BH-3s (15.0 - 16.5) RSD (%) Step 1	- 2 5 Al	- - - - - -	2 5 1 1 0 6	- 1 4 Cu	- 17 3 1 Fe	- 2 1 1	- - - - Mo	- 1 2 5 Pb	- - - - - - -
Step 2 Step 3 Step 4 Step 5 BH-3s (15.0 - 16.5) BSO (%) Step 1 Step 2	- 2 2 5 Al	- - - - - -	2 5 1 1 0	- 1 0 4 Cu -	- 17 3 1 Fe	- 2 1 1 - - 4	- - - - - -	- 1 2 5 7b -	- - 2 3 2n -
Step 2 Step 3 Step 4 Step 5 BH-3s (15.0 - 16.5) RSD (%) Step 1 Step 2 Step 3	- 2 2 5 41 	- - - - - -	2 5 1 1 6 8 6 8 7 7 8	- 1 0 4 - - 1 1	- 17 3 1 Fe - 3	- 2 1 1 - - 4 1		- 1 2 5 7b -	- 1 2 3 2 n -
Step 2 Step 3 Step 4 Step 5 BH-3s (15.0 - 16.5) RSD (%) Step 1 Step 2 Step 2 Step 4 Step 4	- 2 2 5 41  2 1	- - - - - - - - - - - -	2 5 1 1 1 0 4	- 1 0 4 - 1 1 2	- 17 3 1	- 2 1 1 - - - 4 1 1	- - - - - - -	- 1 2 5 1	- - 2 3 - - - 1 1
Step 2 Step 3 Step 4 Step 5 BH-3s (15.0 - 16.5) RSD (%) Step 1 Step 2 Step 3 Step 5	- 2 5 Al - - 2 1 3	- - - - - - - - - - 4	2 5 1 1 1 0 4 1 2	- 1 4 - - 1 1 2 4	- 17 3 1 - - - - 3 1 3	- 2 1 1 - 4 1 1 4	- - - - - - - -	- 1 2 5 	- - - - - - - - - - - - - - - - - - -
Step 2 Step 3 Step 4 Step 5 BH-3s (15.0 - 16.5) RSD (%) Step 1 Step 2 Step 3 Step 3 Step 4 Step 5 BH-3ct (24.0 - 25.5)	- 2 5 Al - - 2 1 3	- - - - - - - - - - 4 141	2 5 1 1 1 0 4 2	- 1 0 4 - 1 1 2 4	- 17 3 1 - - - 3 1 3	- 2 1 1 - - 4 1 1 4	- - - - - - - - -	- 1 2 5 - - - 1 -	- 1 2 3 - - 1 1 3
Step 2 Step 3 Step 4 Step 5 BH-3s (15.0 - 16.5) RSD (%) Step 1 Step 2 Step 2 Step 3 Step 5 BH-3d (24.0 - 25.5)	- 2 5 - 2 - - 2 1 3	- - - - - - - - - - - - - - - - - - -	2 5 1 1 0 4 1 2	- 1 0 4 - 1 1 1 2 4	- 27 3 1	- 2 1 1 - 4 1 1 4	- - - - - - - - - - -	- 1 2 5 	- - 2 3 - - - 1 1 3
Step 2 Step 3 Step 4 Step 5 BH-3s (15.0 - 16.5) RSD (%) Step 1 Step 2 Step 3 Step 4 Step 5 BH-3d (24.0 - 25.5) RSD (%)	- 2 2 5 - - - 2 1 3 3	- - - - - - - - - - - - - - - - - - -	2 5 1 1 0 4 1 2 0 6	- 1 0 4 - 1 1 2 4 - 2 4	- 17 3 1	- 2 1 1 - 4 1 1 4 4 Mm		- 1 2 5 - - - - - - - - - - - - - - - - - -	- - - - - - - - - - - - - - - - - - -
Step 2 Step 3 Step 4 Step 5 BH-3s (15.0 - 16.5) RSD (%) Step 1 Step 2 Step 3 Step 4 Step 5 BH-3d (24.0 - 25.5) RSD (%) Step 1 Step 1	- 2 2 5 - - - 2 1 3 - - 3 - - 2 1 3 -	- - - - - - - - - - - - - - - - - - -	2 5 1 1 0 4 1 2 2 6 8 1	- 1 0 4 - 1 1 2 4 - 2 4 -	- 17 3 1 3 1 3 1 Re	- 2 1 1 - - 4 1 1 4 - - 4 - - - - - - - - -		- 1 2 5 	- - - - - - - - - - - - - - - - - - -
Step 2 Step 3 Step 4 Step 5 BH-3s (15.0 - 16.5) RSD (N) Step 1 Step 2 Step 3 Step 4 Step 5 BH-3d (24.0 - 25.5) RSD (N) Step 1 Step 2	- 2 2 5 - 4 2 - 2 2 1 3 - 2 1 3 		2 5 1 1 0 4 1 2 2 5 6 9 6 9 1 2	- 1 0 4 - - 1 1 2 4 - - - - - - - - - - - - -		- 2 1 2		- 1 2 5 	- - - - - - - - - - - - - - - - - - -
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Step 2 Step 3 Step 4 Step 5 BH-3s (15.0 - 16.5) RSD (%) Step 1 Step 2 Step 3 Step 4 Step 5 BH-3d (24.0 - 25.5) RSD (%) Step 1 Step 1 Step 1 Step 1 Step 2 Step 5 Step 5 St	- 2 5 - - - - - 3 - - - 3 1 2 2 2 1 3 - - - - - - - - - - - - - - - - - -	- - - - - - - - - - - - - - - - - - -	2 5 1 1 0 4 1 2 2 5 5 3	- 1 0 4 - 1 1 2 4 - - 1 2 4 - - - - - - - - - - - - -	- 17 3 1 3 1 3 3 1 3 1	- 2 1 1 - 4 1 1 4 4 - 4 - 2 1 1 2		- 1 2 5 - - - - - - - - - - - - - - - - - -	- - - - - - - - - - - - - - - - - - -
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Step 2 Step 3 Step 4 Step 5 BH-3s (15.0 - 16.5) RSD (%) Step 1 Step 2 Step 3 Step 5 BH-3d (24.0 - 25.5) RSD (%) Step 1 Step 1 Step 5 BH-3d (24.0 - 25.5) RSD (%) Step 3 Step 4 Step 5 BH-3d (37.5 - 39.0) RSD (%)	- 2 5 5 1 1 3 4 1 - 3 1 2 2 1 3 3 2 2 2	- - - - - - - - - - - - - - - - - - -	2 5 1 1 0 4 1 2 2 6 5 3	- 1 0 4 - 1 1 2 4 - - - - - - - - - - - - -		- 2 1 1 - 4 1 1 4 - - 2 1 2 2		- 1 2 5 - - - - - - - - - - - - -	- - - - - - - - - - - - - - - - - - -
Step 2 Step 3 Step 4 Step 5 BH-3s (15.0 - 16.5) RSD (N) Step 1 Step 2 Step 3 Step 4 Step 5 BH-3d (24.0 - 25.5) RSD (N) Step 1 Step 2 Step 3 Step 4 Step 5 BH-3d (37.5 - 39.0) RSD (N)	- 2 2 5 - 2 - 2 2 1 2 1 3 - 2 3 - 3 - 3 1 2 2 2 - 4 1		2 5 1 1 0 4 1 2 2 6 5 3 3	- 1 0 4 - - 1 1 2 4 - - - - - - - - - - - - -		- 2 1 1 - - 4 1 1 1 4 - - - 2 2 1 2 2 -		- 1 2 5 	- - - - - - - - - - - - - - - - - - -
Step 2 Step 3 Step 4 Step 5 BH-3s (15.0 - 16.5) RSD (N) Step 1 Step 2 Step 2 Step 3 Step 4 Step 5 BH-3d (24.0 - 25.5) RSD (N) Step 1 Step 2 Step 3 Step 4 Step 5 BH-3d (37.5 - 39.0) RSD (N) Step 1 	- 2 2 5 - 2 1 3 - - 2 1 3 - - 3 1 2 2 - 3 1 2 - - - - - - - - - - - - - - - - - -		2 5 1 1 0 4 1 2 2 6 5 3 3 6 5 3	- 1 0 4 - - 1 1 2 4 - - - - - - - - - - - - -	- 17 3 1	- 2 1 1 2		1 2 5	- - - - - - - - - - - - - - - - - - -
Step 2 Step 3 Step 4 Step 5 BH-3s (15.0 - 16.5) RSD (%) Step 1 Step 2 Step 3 Step 3 Step 5 BH-3d (24.0 - 25.5) RSD (%) Step 1 Step 2 Step 3 Step 4 Step 5 BH-3d (37.5 - 39.0) RSD (%) Step 1 Step 5	- 2 2 5 - - - 3 3 - 1 3 - 1 2 - 3 - 1 2 - - 3 - 1 2 - - - - - - - - - - - - - - - - -		2 5 1 1 0 4 1 2 2 6 5 3 3 6 6 5 3 1 1 1 1	- 1 0 4 - - 1 1 2 4 - - - - - - - - - - - - -	- 17 3 1 3 1 3 3 1 2	- 2 1 1 - 4 1 1 4 1 1 4 - - - 2 1 2 2 1 2 - - -		- 1 2 5 	- - - - - - - - - - - - - - - - - - -
Step 2 Step 3 Step 4 Step 5 BH-3s (15.0 - 16.5) RSD (N) Step 1 Step 2 Step 3 Step 5 BH-3d (24.0 - 25.5) RSD (N) Step 1 Step 3 Step 4 Step 5 BH-3d (37.5 - 39.0) RSD (N) Step 1 Step 5 BH-3d (37.5 - 39.0) RSD (N) Step 5 Step 5	- 2 2 5 4 1 - 2 1 3 3 - 3 1 2 2 4 1 - 3 1 2 - 3 1 2 - 3 1 - 2 - 3 - 2 - 3 - 2 - 3 - 2 - 3 - 2 - 3 - - 2 - 3 - - - -		2 5 1 1 0 4 1 2 2 6 5 3 3 6 5 3 3 7 6 6 5 3 3	- 1 0 4 - 1 1 2 4 - - - - - - - - - - - - -	- 17 3 1	- 2 1 1 - 4 1 1 4 - - 2 2 1 2 - 2 - 2 - 5 5		- 1 2 5 - - - - - - - - - - - - -	- - - - - - - - - - - - - - - - - - -
Step 2 Step 3 Step 4 Step 5 BH-3s (15.0 - 16.5) RSD (%) Step 1 Step 2 Step 3 Step 4 Step 5 BH-3d (24.0 - 25.5) RSD (%) Step 1 Step 2 Step 3 Step 4 Step 5 BH-3d (37.5 - 39.0) RSD (%) Step 1 Step 5 Step 3 Step 4 Step 5 Step 4 Step 5 Step 4 Step 5 Step 3 Step 4 Step 5 Step 4 Step 5 Step 4 Step 5 Step 3 Step 4 Step 5 Step 4 Step 4 Step 5 Step 4 Step 5 Step 5 Step 5 Step 4 Step 5 Step	- 2 2 5 - 2 1 2 1 2 1 3 - - 2 2 3 - 2 2 - - 2 2 - - - 2 3 - - - -		2 5 1 1 0 4 1 2 2 6 5 3 3 0 6 5 3 3 5 5	- 1 0 4 - - 1 1 2 4 - - 3 2 1 4 - - - - - - - - - - - - -		- 2 1 1 - - 4 1 1 1 4 - - 2 1 2 2 1 2 2 - - - 5 5 2			- - - - - - - - - - - - - - - - - - -
Step 2 Step 3 Step 4 Step 5 BH-3s (15.0 - 16.5) RSD (N) Step 1 Step 2 Step 3 Step 4 Step 5 BH-3d (24.0 - 25.5) RSD (N) Step 1 Step 2 Step 3 Step 4 Step 5 BH-3d (37.5 - 39.0) RSD (N) Step 1 Step 1 Step 5 BH-3d (37.5 - 39.0) RSD (N) Step 1 Step 2 Step 3 Step 4 Step 5 BH-3d (37.5 - 39.0) RSD (N) Step 1 Step 5 Step 5	- 2 2 5 4 1 3 2 1 3 3 3 1 2 2 4 3 4 3 4 3		2 5 1 1 1 0 4 1 2 2 6 5 3 1 2 6 5 3 1 1 1 3 5 1	- 1 0 4 - - 1 1 2 4 - - - - - - - - - - - - -	- 17 3 1	- 2 1 1 2		1 2 5 Pb	- - - - - - - - - - - - - - - - - - -
Step 2 Step 3 Step 4 Step 5 BH-3s (15.0 - 16.5) RSD (%) Step 1 Step 2 Step 3 Step 4 Step 5 BH-3d (24.0 - 25.5) RSD (%) Step 1 Step 3 Step 4 Step 5 BH-3d (37.5 - 39.0) RSD (%) Step 1 Step 5 BH-3d (37.5 - 39.0) RSD (%) Step 1 Step 5 Step 5 Notes:	- 2 2 5 4 1 3 3 4 1 2 2 3 4 1 2 2 4 3 3 4 3 3		2 5 1 1 0 4 1 2 2 6 5 3 3 6 5 3 1 1 3 5 1	- 1 0 4 - - 1 1 2 4 - - 3 2 - - - - - - - - - - - - -	- 17 3 1	- 2 1 1 - 4 1 1 4 1 1 4 - - 2 1 2 2 1 2 2 - - 5 2 2 2 2			2n - - - - - - - - - - - - - - - - - - -
Step 2 Step 3 Step 4 Step 5 BH-3s (15.0 - 16.5) RSD (N) Step 1 Step 2 Step 3 Step 4 Step 5 BH-3d (24.0 - 25.5) RSD (N) Step 1 Step 2 Step 3 Step 4 Step 5 BH-3d (37.5 - 39.0) RSD (N) Step 1 Step 5 BH-3d (37.5 - 39.0) RSD (N) Step 1 Step 5 Step 5	- 2 2 5 4 1 - 2 1 3 3 - 3 1 - 3 1 2 2 - 3 1 - 3 4 1 2 - 3 - 3 1 - 3 - 3 - - 3 - - - - - - - -		2 5 1 1 0 4 1 2 2 6 5 3 3 6 5 3 1 1 1 3 5 1 1 3 5 1	- 1 0 4 - 1 1 2 4 - - - - - - - - - - - - -	- 17 3 1	- 2 1 1 - - 4 1 1 4 - - 2 2 1 2 2 1 2 2 1 2 2 2 2 2 1 2 2 2 2		- 1 2 5 Pb - - 1 - - - 3 1 1 - Pb - - - - - - - - - - - - -	- - - - - - - - - - - - - - - - - - -

Indicates 10%<RSD <30%

Indicates RSD >30%

## Table B.2 Calculated RSD for triplicate analysis for Method 2

BH-1s (10.5 - 12.0)

RSD (N)	AI	As	9	Cu .	Fe	Ma	Mo	Pb	Zn				
Step 1			1			-							
Step 2			1						11				
Step 3	7	17	1	2	5	2		2	9				
Shan A	6	4	23	6	11	2		0					
Step 5				11									
	ů.		3	44		40		40					
8H-1s (19.5 - 21.0)													
B(1-25 (25.5 - 22.0)	AI	4.	0	01		Ma	Ma	-					
films 1	~	~		<u>u</u>		80	MO	10					
Shep 2			12										
Shep 1													
Shep 4													
Shep 4			2	2	•	*		0					
such s	6	-	9	10	4	6		12	8				
BH 14 (64 E . 66 A)													
BH-10 (04.5-00.0)			~	<u></u>				-					
the l	~	~		u	He	Mn	Mo	10	<u>20</u>				
Sup 1			3										
Shee 3	-	-	1		-	-	-	7	35				
Shee A	2	-	4	2	4	2	-	3	3				
Share 5	3	6	7	4	7	1	-		6				
such a	6	0	3	17	9	4	-	6	3				
BH 14/01 5 02 4													
Bri-10 (91.5 - 92.4)			6	-									
KOD (N)	AI	As	<u>a</u>	<u>a</u>	Re	Mn	Mo	Pb	Zn				
566p 1	-	-	1	-	-	-	-	-	-				
Step 2	-	-	2	1	-	2	4	-	5				
Step 3	2	-	1	3	1	3	-	2	2				
Step 4	10	14	14	8	3	11	11	18	15				
Step S	5	6	13	8	6	5	8	12	6				
BH-35 (1.5 - 3.0)													
RSD (%)	AI	Az	G	<u>a</u>	Fe	Mn	Mo	Pb	Zn				
Step 1	-	-	1	•	-	-	-	•	-				
Step 2	-	-	2	•	-	3	-	•	19				
Step 3	1	-	4	3	3	1		1	7				
Step 4	16	23	15	15	17	17	17	32	24				
Step 5	10	-	14	18	16	11	-	11	7				
PH 2. (45.0 46.5)													
BH-35 (15.0 - 16.5)													
RSD (%)	AI	As	G	a	Fe	Mn	Mo	Pb	Zn				
Step 1	-	-	0	-	-	-	-	•					
Step 2	-	-	1	2	-	2	-	-	11				
amp a	3	-	4	3	4	3	-	10	69				
Step 4	3	6	16	3	3	6	3	3	5				
Step S	6	-	4	19	3	11	-	7	12				
BH-3d (24.0 - 25.5)													
RSD (N)	AI	As	0	a	Fe	Mn	Mo	Pb	Zn				
Step 1	-	-	1	-	-	-	-	-	-				
Step 2	-	-	0	2	-	2	1	0	16				
Step 3	1	2	7	1	0	1	-	1	1				
Step 4	4	4	11	9	3	5	4	17	8				
Step 5	2	15	- 4	10	4	4	-	10	17				
BH-3d (37.5 - 39.0)	-												
RSD (N)	AI	As	0	<u>a</u>	Fe	Mn	Mo	Pb	Zn				
Step 1	-	-	0	-	-	-	-	-	-				
Step 2	-	-	10	-	-	2	-	-	8				
Step 3	4	-	5	5	4	4	-	4	13				
Step 4	30	9	12	17	10	14	3	12	16				
Step 5	6	-	2	5	7	7	-	13	11				
Notes:													

- indicates samples with below detection limit concetrations (<0.2ppm) for all triplicate samples

Indicates RSD <10%

Indicates 10%<RSD <30% Indicates RSD >30%

## Table B.3 Percent recovery (total elemental concentration vs. cumulative leached)

	Al	As	Ca	Cu	Fe	Mn	Мо	Pb	Zn		Al	As	Ca	Cu	Fe	Mn	Mo	Pb	Zn
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	%recovery	%	%	%	%	%	%	%	%	%
Cummulative Method 1	5849.145	29.40005	383592.8	734.6647	5257.954	244.4205	14.00136	215.2124	1205.087	Method 1	106%	64%	256%	63%	83%	95%	57%	156%	93%
Cummulative Method 2	6251.744	45.33075	332155.3	677.8239	5522.783	271.7778	24.09525	223.5705	990.7009	Method 2	114%	99%	221%	58%	88%	105%	98%	162%	76%
BH-1s (10.5 - 12.0)	5500	46	>150000	1170	6300	258	24.5	138	1300										
Cummulative Method 1	25132.69	40.00991	72198.11	6610.484	90223.77	865.1267	36.79716	783.3079	6618.783	Method 1	131%	89%	189%	104%	134%	116%	73%	267%	144%
Cummulative Method 2	26099.02	46.14248	63710.69	6675.823	91732.82	889.6849	41.49972	676.6827	6470.909	Method 2	136%	103%	166%	105%	136%	120%	83%	231%	141%
BH-1s (19.5 - 21.0)	19200	45	38300	6360	67400	744	50.2	293	4600										
Cummulative Method 1	12919.6	40.50697	349859.8	710.9772	10535.64	495.8599	32.01614	1054.311	1293.143	Method 1	137%	62%	233%	70%	98%	98%	76%	185%	99%
Cummulative Method 2	12630.85	50.85265	305358.4	720.1278	11125.48	553.3211	33.06944	1072.579	1323.441	Method 2	134%	78%	204%	71%	104%	110%	79%	188%	102%
BH-1d (64.5 - 66.0)	9400	65	>150000	1020	10700	505	42.1	570	1300										
Cummulative Method 1	18955.24	85.23529	161689	4424.11	91714.87	1125.416	91.2796	1650.278	11127.71	Method 1	327%	91%	160%	110%	149%	103%	85%	189%	152%
Cummulative Method 2	19322.33	131.2723	168495.7	4596.769	117983.2	1177.997	129.0266	1707.352	10201.88	Method 2	333%	140%	167%	114%	192%	108%	121%	195%	140%
BH-1d (91.5 - 92.4)	5800	94	101000	4030	61500	1090	107	874	7310										
Cummulative Method 1	41781.12	50.10563	104623.7	802.7186	17767.24	477.4498	145.7708	459.4543	1172.295	Method 1	84%	51%	102%	64%	87%	84%	68%	125%	74%
Cummulative Method 2	41933.51	73.04047	122439.2	980.3522	21694.4	625.2274	187.5032	496.5238	1301.558	Method 2	85%	75%	119%	78%	106%	110%	88%	135%	82%
BH-3s (1.5 - 3.0)	49500	98	103000	1250	20500	569	213	367	1590										
Cummulative Method 1	29204.25	61.56246	100455.9	14938.3	85651.1	650.578	93.78637	61.65474	952.0413	Method 1	94%	72%	113%	80%	110%	107%	76%	123%	87%
Cummulative Method 2	29869.8	99.53734	112139.3	17454.36	91933.79	750.6287	111.5939	106.644	1122.745	Method 2	96%	116%	126%	94%	118%	123%	90%	213%	103%
BH-3s (15.0 - 16.5)	31100	86	89000	18600	77800	610	124	50.1	1090										
Cummulative Method 1	29819.59	154.4257	256187.9	5701.961	54815.54	1930.201	311.9222	1157.007	6897.801	Method 1	97%	80%	105%	90%	112%	104%	94%	165%	83%
Cummulative Method 2	31585.86	214.5543	262095.9	6961.461	59670.54	2083.118	324.9682	1217.201	9152.685	Method 2	103%	111%	107%	110%	122%	113%	98%	174%	110%
BH-3d (24.0 - 25.5)	30600	193	244000	6320	48800	1850	331	700	8290										
Cummulative Method 1	30326.14	31.20714	47943.76	2933.972	166736.7	287.3294	108.8965	136.0508	350.6762	Method 1	94%	57%	83%	78%	71%	80%	71%	116%	74%
Cummulative Method 2	31760.79	42.52382	34603.55	3024.954	185737.2	322.5714	110.3972	151.9514	400.0459	Method 2	98%	77%	60%	80%	79%	90%	72%	130%	85%
BH-3d (37.5 - 39.0)	32300	55	57600	3760	234000	360	154	117	473										
Notes:																			
For the % recovery calculation of Ca, the maximum detection value was used when greater the detection limit was encountered																			
57%	green high	nlights indi	icate cumu	lative valu	ies that are	70% <x>13</x>	0% of total	value											

## Table B.4 Mass loss experiment

Sample	Initial mass (g)	Loss (g)	Loss (%)
ЗНа	1.0039	0.0324	3.23%
16Ha	1.0012	0.0209	2.09%
17Ha	1.0027	0.0099	0.99%
20На	1.0003	0.0152	1.52%
23На	1.0026	0.0121	1.21%
24Ha	1.0021	0.04188	4.18%
3Dc	1.0002	0.0243	2.43%
16Dc	1.0029	0.0221	2.20%
17Da	1.0018	0.0008	0.08%
20Da	1.0034	0	0.00%
23Da	1.0014	0.0004	0.04%
24Da	1.0022	0.0033	0.33%

	BH-1s (10.5 - 12.0)	BH-1s (19.5 - 21.0)	BH-1d (64.5 - 66.0)	BH-1d (91.5 - 92.4)	BH-3s (1.5 - 3.0)	BH-3s (15.0 - 16.5)	BH-3d (24.0 - 25.5)	BH-3d (37.5 - 39.0)
pH initial	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
Method 2								
pH final	n/a	4.6	n/a	4.68	4.69	4.67	4.73	4.6
Method 2								
pH initial	5	5	5	5	5	5	5	5
Method 1								
pH final	5.59	5.06	5.42	5.22	5.3	5.24	5.46	5.1
Method 1								

# Appendix C Comparison of Sequential Extraction Procedures Method 1 and Method 2 and Differential X-ray Diffraction (DXRD) diffractograms


## C.1 SEP Results for Method 1 and Method 2

Figure C.1 Sequential extraction results Al (%) and Ca (%)





Figure C.2 Sequential extraction results Mn (%) and Mg (%)





Figure C.3 Sequential extraction results Fe (%) and As (%)





Figure C.4 Sequential extraction results Cu (%) and Mo (%)





Figure C.5 Sequential extraction results Pb (%) and Zn (%)

## C.2 XRD Results for Un-reacted Samples and Sample Residues After Application of





Figure C.6 BH1-1 XRD results from Method 1



Figure C.7 BH1-2 XRD results from Method 1



Figure C.8 BH1-3 XRD results from Method 1



Figure C.9 BH1-4 XRD results from Method 1



Figure C.10 BH3-1 XRD results from Method 1



Figure C.11 BH3-3 XRD results from Method 1



Figure C.12 BH3-2 XRD results from Method 1



Figure C.13 BH3-4 XRD results from Method 1



Figure C.14 BH1-1 XRD results from Method 2



Figure C.15 BH1-2 XRD results from Method 2



Figure C.16 BH1-3 XRD results from Method 2



Figure C.17 BH1-4 XRD results from Method 2



Figure C.18 BH3-1 XRD results from Method 2



Figure C.19 BH3-2 XRD results from Method 2



Figure C.20 BH3-3 XRD results from Method 2



Figure C.21 BH3-4 XRD results from Method 2

# Appendix D Geochemical Modelling of Oxalate Species and Saturation Indices for Metal

### Oxalates

	1	1	1	1	1			
sim	si_CaOxalate	si_CuOxalate	si_MgOxalate	si_MnOxalate	si_PbOxalate	si_ZnOxalate		
1	6.427	6.2691	3.0977	0.9617	3.752	6.6417		
	0	0	-3.1274	-4.6947	-0.8176	0		
2	6.5989	6.2782	3.1722	0.9085	3.6911	6.7162		
	0	-0.1097	-3.2188	-4.9295	-1.0193	0		
3	6.7544	6.2864	3.2481	0.8562	3.6311	6.792		
	0	-0.2547	-3.2982	-5.1499	-1.2151	0		
4	6.8989	6.2939	3.3252	0.8046	3.5719	6.8691		
	0	-0.3888	-3.3654	-5.3563	-1.4031	0		
5	7.0356	6.3008	3.4035	0.7539	3.5136	6.9475		
	0	-0.5151	-3.4237	-5.5523	-1.5853	0		
6	-999.999	6.2221	2.8133	1.1839	4.0035	6.3573		
	-999.999	0	-2.7842	-3.763	-0.1423	0		

#### Table D.1 Tabulated results of SI and precipitation scenarios

### D.1 PhreeqC Input File

```
SELECTED OUTPUT
   -file
                      SIs T UM.xls
   -reset
                      false
   -simulation
                      true
   -step
                       true
   -ph
                       true
   -pe
                       true
   -molalities Oxalate-2 H(Oxalate) - H2(Oxalate)
   -saturation indices CaOxalate CuOxalate MgOxalate MnOxalate
                      PbOxalate ZnOxalate
SOLUTION_MASTER_SPECIES
              Oxalate-2 2 88.06
                                                  88.06
   Oxalate
SOLUTION SPECIES
Oxalate-2 = Oxalate-2
   log k 0
H+ + Oxalate-2 = H(Oxalate)-1
    log k 4.2798
H+ + H(Oxalate) - 1 = H2(Oxalate)
     log k 1.27
PHASES
CaOxalate
   CaOxalate:H2O = Ca+2 + H2O + Oxalate-2
   log k -8.6345
CuOxalate
   CuOxalate = Cu+2 + Oxalate-2
   log k -9.3536
MgOxalate
   MgOxalate: 2H2O = 2H2O + Mg+2 + Oxalate-2
   log k
          -5.3161
MnOxalate
   MnOxalate: 2H2O = 2H2O + Mn+2 + Oxalate-2
   log k -6.7696
PbOxalate
   PbOxalate = Oxalate-2 + Pb+2
   log k -8.0706
ZnOxalate
   ZnOxalate: 2H2O = 2H2O + Oxalate-2 + Zn+2
   log k -8.8601
SOLUTION 1
   temp 25
   рН
           3
           3
   ре
   redox pe
units mol/l
   density 1
   Oxalate 0.2
   Ca 0.2
           0.2
   Cu
   Mg
           0.2
```

	Mn Pb Zn -water	0.2 0.2 0.2 1 # kg
EQUI	LIBRIUM_PF CaOxalate CuOxalate MgOxalate MnOxalate PbOxalate ZnOxalate	HASES 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0
END		
SOLU	JTION 2 temp pH pe redox units density Oxalate Ca Cu Mg Mn Pb Zn -water	25 3 pe mol/l 1 0.2 0.25 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2
EQU] END	LIBRIUM_PH CaOxalate CuOxalate MgOxalate MnOxalate PbOxalate ZnOxalate	HASES 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0
SOLU	JTION 3 temp pH pe redox units density Oxalate Ca Cu Mg Mn Pb Zn -water	25 3 pe mol/l 1 0.2 0.3 0.2 0.2 0.2 0.2 0.2 0.2 0.2 1 # kg

EQUILIBRIUM PHASES 1 CaOxalate 0 0 CuOxalate 0 0 MgOxalate 0 0 MnOxalate 0 0 PbOxalate 0 0 ZnOxalate 0 0 END SOLUTION 4 temp 25 рΗ 3 pe 3 redox pe units mol/l density 1 Oxalate 0.2 Ca 0.35 0.2 Cu 0.2 Mg 0.2 Mn 0.2 Pb Zn 0.2 -water 1 # kg EQUILIBRIUM PHASES 1 CaOxalate 0 0 CuOxalate 0 0 MgOxalate 0 0 MnOxalate 0 0 PbOxalate 0 0 ZnOxalate 0 0 END SOLUTION 5 25 temp рН 3 3 pe redox pe units mol/l density 1 0.2 Oxalate 0.4 Ca 0.2 Cu 0.2 Mg Mn 0.2 Pb 0.2 0.2 Zn 1 # kg -water EQUILIBRIUM PHASES 1 CaOxalate 0 0 CuOxalate 0 0 MgOxalate 0 0

	MnOxalate	0	0
	PbOxalate	0	0
	ZnOxalate	0	0
END			
	_		
SOLU	JTION 5		
	temp	25	)
	рН	3	
	pe	3	
	redox	ре	9
	units	mc	1/1
	density	1	
	Oxalate	0.	2
	Ca	0.	0
	Cu	0.	2
	Mg	0.	2
	Mn	Ο.	2
	Pb	Ο.	2
	Zn	Ο.	2
	-water	1	# kg
EQUI	LIBRIUM PH	IAS	SES 1
	CaOxalate	0	0
	CuOxalate	0	0
	MqOxalate	0	0
	MnOxalate	0	0
	PbOxalate	0	0
	ZnOxalate	0	0
END			

Appendix E Summary of XRD Results (Tabulated) and X-ray Diffractograms for East

**Dump Waste Rock Samples** 

# E.1 Tabulated XRD Mineralogy

Sample ID	Quartz	Orthoclas Albite	Biotite/Phlogopite	Muscovite	Calcite	Diopside	Hibschite	Grossular Garnet	Andradite	Vesuvianite	Wollastor	Actinolite	Tremolite	Magnetite	Pyrite	Molybden	Chalcopyr	phalerite	Chlorite	Gypsum	Smithsonite	Wulfenite	Hemimorphite	AI2O3
Mineral Formula	SiO <sub>2</sub>	KAISi <sub>3</sub> O <sub>8</sub> NaAlSi <sub>3</sub> O <sub>8</sub>	K(Mg,Fe) <sub>3</sub> (AlSi <sub>3</sub> O <sub>10</sub> )(F,OH) <sub>2</sub>	KAI <sub>2</sub> (AISi <sub>3</sub> O <sub>10</sub> )(F,OH) <sub>2</sub>	CaCO <sub>3</sub>	CaMg(Si <sub>2</sub> C	Ca <sub>3</sub> Al <sub>2</sub> (SiO <sub>4</sub> ) <sub>2</sub> (OH) <sub>4</sub>	Ca <sub>3</sub> Al <sub>2</sub> (SiO <sub>4</sub> ) <sub>3</sub>	Ca <sub>3</sub> Fe <sub>2</sub> (SiO	Ca10Mg2Al4(Si2O7)2(SiO4)5(OH)4	CaSiO <sub>3</sub>	Ca2(Mg,Fe)5Si8O22(OH)2.	Ca2Mg5Si8O22(OH)2	Fe <sup>3+</sup> <sub>2</sub> Fe <sup>2+</sup> C	FeS <sub>2</sub>	MoS <sub>2</sub>	CuFeS <sub>2</sub> (	Zn,Fe)S		CaSO <sub>4</sub>	ZnCO <sub>3</sub>	PbMoO <sub>4</sub>	Zn <sub>4</sub> Si <sub>2</sub> O <sub>7</sub> (OH) <sub>2</sub> •(H <sub>2</sub> O)	
BH-1s (1.5 - 3.0)	х	x x	x		х	х	x	х		x		x			х	х			х	x				
BH-1s (10.5 - 12.0)	х	x	x		х						х	x												
BH-1s (19.5 - 21.0)	х	x x	x		х		x			x		x			х					х				
BH-1d (1.5 - 3.0)	х	x x	x		х	х				x			x		х				х			x		
BH-1d (19.5 - 21.0)	х	x x	x		х	х		x		x		x			x		к			x		х		
BH-1d (25.5 - 27.0)	x	x x	x		x		x	x		x		x	x		x		ĸ		х	×				
BH-1d (39.0 - 40.5)	х	х х	x	х	х		x	х		x		×			х	х			х	x		x		х
BH-1d (42.0 - 43.5)	х	x x	x	x	х	х	x			x	х		x		х		)	(		x				
BH-1d (49.5 - 51.0)	х	x x	x	x	х		x					x	x		х	x	ĸ			x	x			
BH-1d (54.0 - 55.5)	х	x x	x		х		x					x			х	x			х					
BH-1d (64.5 - 66.0)	х	x x	x		х						х								х					
BH-1d (70.5 - 72.0)	х	x x	x		х		x				х	x			х	x	ĸ		х	x				
BH-1d (76.5 - 78.0)	х	x x	x		х		x			x		x		х	х		ĸ		х	x				
BH-1d (81.0 - 82.5)	х	x x	x		х							x			х		ĸ		х	x				
BH-1d (90.0 - 91.5)	х	x x	x		х	х	x		x	x					x		ĸ		х	x			х	
BH-1d (91.5 - 92.4)	х	x x	x		х		x		x	x			x		x		ĸ		х	x	x		х	
BH-3s (1.5 - 3.0)	х	x x	x		x										x	x	ĸ							
BH-3s (9.0 - 10.5)	x	x x	x		х							x			x	x			х	×	x			
BH-3s (10.5 - 12.0)	х	x x	x		х							x			х		ĸ		х	x				
BH-3s (15.0 - 16.5)	х	x x	x		х	х			х			x		x	х	х	ĸ		х	x		х		
BH-3s (21.0 - 22.5)	х	x	x		х		x	x	х	x							)	[	х	x				
BH-3d (10.5 - 12.0)	х	x x	x		х						х	x			х					x				
BH-3d (24.0 - 25.5)	х	x x	x		х		x			x	х	x	x		х	х	κ )	[		х		х		
BH-3d (37.5 - 39.0)	х	x x	x	х	х							x			x	x			х	х		x		
BH-3d (39.0 - 40.5)	х	x x	x	х	х							x			x	x			х	х				
BH-3d (48.0 - 49.5)	х	х х	x		x										х	x	ĸ			х				
BH-3d (72.0 - 73.5)	х	x x	x	x	х		x					x			x	x	ĸ		х	x		х		
BH-3d (88.5 - 90.0)	x	x x	x	x	x		x					x			x	x	ĸ		x	x	x			
BH-3d (91.5 - 93.0)	x	x x	×	x	x		x			x		x			x	x	ĸ		x	×				
BH-3d (94.5 - 96.0)	х	x x	×	x	x		x				х	x			x	x	ĸ		x	x		x		
BH-3d (112.5 - 114.0)	х	x x	x		х		x								х	x	к		х					
BH-3d (121.5 - 123.0)	х	x x	x		х							x			х				х					

### E.2 XRD Patterns for Individual Samples



Figure E.1 BH-1s (1.5 - 3.0)



Figure E.2 BH-1s (10.5 -12.0)



Figure E.3 BH-1s (19.5 - 21.0)



Figure E.4 BH-1d (1.5 - 3.0)



Figure E.5 Rietveld analysis of BH-1d (19.5 - 21.0)



Figure E.6 BH-1d (25.5 - 27.0)



Figure E.7 BH-1d (39.0 - 40.5)



Figure E.8 BH-1d (42.0 - 43.5)



Figure E.9 BH-1d (49.5 - 51.0)



Figure E.10 BH-1d (54.0 - 55.5)



Figure E.11 BH-1d (64.5 - 66.0)



Figure E.12 BH-1d (70.5 - 72.0)



Figure E.13 BH-1d (76.5 - 78.0)



Figure E.14 BH-1d (81.0 - 82.5)



Figure E.15 BH-1d (90.0 - 91.5)



Figure E.16 BH-1d (91.5 - 92.4)



Figure E.17 BH-3s (1.5 - 3.0)



Figure E.18 BH-3s (9.0 - 10.5)







Figure E.20 Rietveld analysis of BH-3s (15.0 – 16.5)



Figure E.21 BH-3s (21.0 – 22.5)



Figure E.22 BH-3d (10.5 - 12.0)



Figure E.23 BH-3d (24.0 - 25.5)



Figure E.24 BH-3d (37.5 - 39.0)



Figure E.25 BH-3d (39.0 - 40.5)



Figure E.26 BH-3d (48.0 - 49.5)



Figure E.27 BH-3d (72.0 - 73.5)



Figure E.28 BH-3d (88.5 - 90.5)



Figure E.29 BH-3d (91.5 - 93.0)



Figure E.30 BH-3d (94.5 - 96.0)



Figure E.31 BH-3d (112.5 - 114.0)



Figure E.32 BH-3d (121.5 - 123.0)
Appendix F Total Elemental Concentrations From 4-acid Digestions

## Table F.1 Tabulated elemental concentrations from 4-acid digestions

Date	: Sept 26	2013																																														
Sample ID	Aq	AI	Ba	Ca	Cr	Cu	Fe	к	Li	Ma	Mn	Na	Ni	Р	s	Sr	TI	r 2	n Z	r Ad	В	e E	Bi Cd	0	e Co	c	s Ga	Hf	In	La	Lu	Mo	Nb	Pb	Rb	Sb	Sc	Se	Sn	Ta	Tb	Te	Th	п	U	w	Y	Yb
	nnm	*	nom	*	nom	nom	%	~	nom	~	nom	*6	nom	nom	~	nom	% n		m na	m nn			nm nng		m nom	00	m nom	nom	nom	0000	nom	0000	nom	nom	nom	nnm	nom	nom	nom	nom	nom	nnm	nom	nom	nnm	nom	nom	nom
Mathod Code	IC ACM	IC404	10404	10404	IC40A	10404	IC404	10404	IC404	10404	10404	10404	IC404	10404	10404	1C404	C40A IC	0.0	04 104		M ICA	OM ICA	40M IC40	M ICA	OM IC40M	1 104	IOM IC40M	IC40M	IC40M	IC40M	IC40M	IC40M	IC40M	IC40M	IC40M	CAOM I	IC40M	CAOM	IC40M	IC40M	IC40M	IC40M	IC40M	IC 40M	IC40M	IC40M	IC40M	IC40M
LOD	0.02	0.01	1	0.01	1	0.5	0.01	0.01	1	0.01	2	0.01	0.5	50	0.01	0.5	0.01			5 1		1 0	04 0.07	2 00	05 0.1		5 0.1	0.02	0.02	0.1	0.01	0.05	0.1	0.5	0.2	0.05	0.1	2	0.2	0.05	0.05	0.05	0.2	0.02	0.05	0.1	0.1	0.1
BU 4= (40 E 42)	4.07	0.01	40	0.01	40	4470	0.01	0.43	10	0.01	250	0.01	4.3	400	0.01	3750	0.01		· ·	4 4	0.	2 8	22 2.2		0.1		e 40	0.04	0.42	0.1	0.01	0.00	0.1	430	48.3	0.05	0.1	2	0.0	0.00	0.00	0.00	0.2	0.02	0.00	22.2	4.0	0.1
BH+15 (10.5 +12)	1.6/	0.00	42	310	10	1170	0.65	0.43	10	0.55	200	0.11	4.3	100	0.45	2/00	0.03	1 12	00 1.	1 40	0.	2 0.	.23 3.3	. 0.0	53 3.6		0 1.9	0.04	0.42	3.2	0.02	24.0	2.2	130	10.3	2.04	0.5	3	0.9	0.23	0.06	0.11	0.2	0.22	0.00	23.3	1.2	0.1
BH-15 (19.5 -21)	0.69	1.92	43	3.83	58	6360	6.74	0.95	10	0.56	744	0.11	7.9	350	25	48.1	0.09 4	1 46	00 11	./ 40	0.	8 12	2.9 10.4	2/	.5 11.6	<	15 15.3	0.62	6.84	17.6	0.15	40.4	5.8	293	35.9	16.2	3	1/	42.9	0.4	0.3	1.2/	2.1	0.74	4.6/	30.2	8.9	0.9
BH-10 (64.5 -66)	3.57	0.54	40	310	21	1020	1.07	0.00	12	0.54	500	0.09	5	3/0	0.55	114	0.00	9 12	10 7.	3 60	0.	· · · ·	0.0 3.76		0 3.4		.5 4	0.25	0.32	9.5	0.07	42.1	3.3	070	20.1	10.7	1.1	0	1.7	0.35	0.19	0.34	0.9	0.31	1.00	10.4	4.0	0.5
BH-10 (91.5 -92.4)	>10	0.58	34	10.1	53	4030	6.15	0.46	1/	0.71	1090	0.05	1.2	720	1.52	165	0.09 4	1 /2	10 1	2 94	0.	.9 84	4.3 21.6	23	12.3	<	5 15.4	0.48	10.9	16.5	0.09	107	5.3	8/4	32.2	13.1	1	30	52.3	0.51	0.23	1.2/	0.6	0.5	4.44	1//	4.5	0.6
Date	: JUIY 15,	2013																		- · ·									- · ·	1												<u> </u>	-		<u> </u>			- 10
Sample ID	Ag	A	ва	Ca	ur	Cu	Pe	n.	u	Mg	Mn	Na	NI	۲	5	sr		4	n 2	A	в	с <u>г</u>	BI CO		e		is Ga	HT	in	La	Lu	MO	ND	PD	KD	50	50	se	Sn	18	ID	1e	in i			w		TD
-	ppm	%	ppm	%	ppm	ppm	%	%	ppm	%	ppm	%	ppm	ppm	%	ppm	% pi	m pg	im pp	m pp	n pp	im pp	pm ppn	n pp	im ppm	PP	om ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Method Code	IC40A	IC40A	IC40A	IC40A	IC40A	IC40A	IC40A	IC40A	IC40A	IC40A	IC40A	IC40A	IC40A	IC40A	IC40A	IC40A	C40A IC4	OA IC4	OA IC4	0A IC40	M IC4	OM IC4	40M IC40	M IC4	OM IC40M	1 IC4	IC40M	IC40M	IC40M	IC40M	IC40M	IC40M	IC40M	IC40M	IC40M	C40M I	IC40M I	C40M	IC40M	IC40M	IC40M	IC40M	IC40M	IC40M	IC40M	IC40M	IC40M	IC40M
LOD	0.02	0.01	1	0.01	1	0.5	0.01	0.01	1	0.01	2	0.01	0.5	50	0.01	0.5	0.01		0	5 1	0.	.1 0.	.04 0.03	2 0.0	05 0.1	1	5 0.1	0.02	0.02	0.1	0.01	0.05	0.1	0.5	0.2	0.05	0.1	2	0.3	0.05	0.05	0.05	0.2	0.02	0.05	0.1	0.1	0.1
BH-3s ( 1.5-3.0 )	4.26	4.95	410	10.3	69	1250	2.05	3.04	36	0.7	569	0.52	4.4	620	0.83	511	0.11 3	7 15	90 9.	3 96	1.	.2 23	3.2 3.5	1 28	.9 6.9	e	6 14.4	0.25	0.42	15.9	0.09	213	5.2	367	114	7.03	4.1	3	3.1	0.15	0.29	0.5	6.3	1.6	1.47	18.9	7.8	0.6
BH-3s (15.0 - 16.5)	11	3.11	259	8.9	71	18600	7.78	2.24	24	0.66	610	0.53	4.2	570	4.07	326	0.09 7	1 10	90 7.	4 86	0.	.9 4.	.46 2.12	2 27	.8 22	<	:5 17	0.2	1.65	14.7	0.07	124	2.6	50.1	73.9	15.3	2.8	4	22.2	0.1	0.24	0.2	4.3	2.99	2.28	8.1	5.2	0.5
BH-3d (24.0 - 25.5)	21.3	3.06	37	24.4	83	6320	4.88	0.43	16	1.27	1850	0.06	3.4	680	1.06	353	0.13 4	5 82	90 4	4 19	3 1.	.3 14	45 18.8	3 33	16.3	e	6 12.1	1.18	3.23	20.9	0.15	331	5.2	700	25.1	29.6	4.2	6	13.7	0.05	0.35	0.75	5.6	0.37	3.8	48.5	10.9	1
BH-3d (37.5 - 39.0)	4.04	3.23	84	5.76	71	3760	23.4	1.24	16	0.64	360	0.09	4.9	450	26.8	89.9	0.1 E	1 4	3 14	.1 55	1.	.2 1	75 0.8	5 29	43.5		5 11.5	0.39	0.64	18.3	0.09	154	5.3	117	54.5	5.96	3.8	22	12.8	0.31	0.27	1.08	4.8	0.45	2.4	162	7.2	0.6
Date	: January	22, 2014																																														
Sample ID	Ag	AI	Ba	Ca	Cr	Cu	Fe	к	Li	Mg	Mn	Na	Ni	Р	S	Sr	TI 1	1 2	n Z	r As	В	e E	Bi Cd	c	e Co	c	s Ga	Hf	In	La	Lu	Mo	Nb	Pb	Rb	Sb	Sc	Se	Sn	Та	Tb	Te	Th	т	U	w	Y	Yb
	ppm	%	ppm	%	ppm	ppm	%	%	ppm	%	ppm	%	ppm	%	%	ppm	% p	m pg	im pp	m pp	n pp	im pp	pm ppn	n pp	im ppm	PP	om ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Method Code	ICM40B	ICM40B	ICM40B	ICM40B	ICM40B	ICM40B	ICM40B	ICM40B	ICM40B	ICM40B	ICM40B	ICM40B	ICM40B	ICM40B	ICM40B	ICM40B	M40B ICN	40B ICN	40B ICM	40B ICM4	OB ICM	40B ICM	140B ICM4	DB ICM	40B ICM408	B ICM	140B ICM40B	ICM40E	B ICM40B	ICM40B	3 ICM40B	ICM40B	ICM40B	ICM40B	CM40B II	CM40B K	CM40B K	M40B	ICM40B	ICM40B	ICM40B	ICM40B	ICM40B	ICM40B	ICM40B	ICM40B	ICM40B	ICM40B
LOD	0.02	0.01	1	0.01	1	0.5	0.01	0.01	1	0.01	2	0.01	0.5	0.005	0.01	0.5	0.01		0.	5 1	0.	.1 0.	.04 0.02	2 0.0	0.1	1	1 0.1	0.02	0.02	0.1	0.01	0.05	0.1	0.5	0.2	0.05	0.5	2	0.3	0.05	0.05	0.05	0.2	0.02	0.05	0.1	0.1	0.1
BH-1s (1.5-3.0)	5.37	4.87	144	>15	75	1340	4.21	1.82	17	1.37	1520	0.32	9.9	0.074	0.73	371	0.21 E	6 6	4 48	.4 10	1 2.	2 3	34 2.1	45	5 7.7	9	9 13.4	1.59	1.03	25.8	0.22	468	11.1	2080	79.6	14.1	6.4	7	9.7	1.15	0.5	1.36	8.1	0.61	3.2	53	14.2	1.3
BH-1d (1.5-3.0)	4.08	2.3	92	>15	35	1030	2.35	1.12	12	1	590	0.14	8.5	0.055	1.36	809	0.1 5	1 15	50 17	.9 15	1 1	1 20	0.4 5.02	2 2	2 6	e	6 5.6	0.39	0.62	11.7	0.12	27.2	4.7	800	58.6	8.18	3.6	4	4	0.32	0.26	0.78	3.6	1.01	1.88	29.5	8.2	0.7
BH-1d (19.5-21.0)	6.74	3.72	251	7.65	81	5740	8.55	2.66	21	0.88	518	0.37	2.6	0.086	>5	260	0.13 5	4 45	00 15	.9 49	1.	.4 23	3.2 14.9	3 24	.6 8.4	5	5 16.7	0.5	5.83	13.2	0.12	104	4.8	195	90.4	7.21	4.5	12	37.3	0.38	0.28	1.25	5.2	0.94	3.17	26	8.1	0.7
BH-1d (25.5-27.0)	9.48	1.95	34	8.06	97	7070	>15	0.78	13	0.73	653	0.07	9.5	0.056	>5	103	0.09 5	1 76	60 18	.8 68	1.	2 43	26 23.9	3 21	.6 27.6	1	18 10.7	0.56	5.39	12	0.12	71.5	5	646	28.9	10.7	3.3	27	27	0.36	0.27	3.18	3.6	0.55	2.6	586	7.9	0.7
BH-1d (39.0-40.5)	5.01	3.73	147	13	80	2410	8.42	1.92	15	0.82	563	0.18	5.4	0.055	>5	382	0.12 5	9 24	60 20	.8 92	1.	4 6	59 8.12	2 27	.9 28.8	2	9 10.8	0.57	1.31	15	0.12	169	5	563	64.7	8.51	4.1	9	12.8	0.38	0.3	1.12	5	1.28	2.01	113	8.2	0.7
BH-1d (42.0-43.5)	14.3	3.22	61	>15	87	1390	6.79	0.98	13	1.11	1620	0.1	19.1	0.071	2.21	403	0.16 7	1 65	50 42	.4 48	1.	.2 11	82 17.6	5 25	.5 9.1	4	4 10.4	1.14	2.35	13.7	0.18	62.7	7.6	540	39.3	8.04	4.9	10	10.4	0.51	0.36	2.79	4.8	0.39	2.22	104	11.8	1
BH-1d (49.5-51.0)	5.8	4.11	285	12.3	106	1720	5.59	3.13	22	0.8	774	0.44	23.7	0.065	3.58	435	0.15 5	4 35	90 20	.2 68	1.	.4 5	92 11.4	27	.1 12.2	1	12 12.7	0.63	1.67	13.6	0.12	103	5.5	462	93.9	15	4.4	7	9.3	0.4	0.31	1.57	5.1	0.9	1.71	82.3	8.9	0.7
BH-1d (54.0-55.5)	2.26	5.67	482	9.02	76	1440	2.7	4.1	25	0.77	432	1.06	5.4	0.069	1.46	525	0.18 5	9 0	58 13	.3 28	2.	.1 20	0.3 1.9	1 32	6 7.6	٤	8 16.1	0.42	0.44	15.8	0.13	103	5.9	108	131	4.34	5.6	2	5.3	0.48	0.37	0.32	6.3	0.79	1.53	39.4	9.7	0.8
BH-1d (70.5-72.0)	8.96	3.3	274	12.5	98	>10000	5.61	2.59	19	0.63	1260	0.55	4.4	0.039	2.11	474	0.1 3	9 9	91 14	.8 58	1.	.3 27	7.6 2.56	5 2	6 12.7	5	5 12.5	0.46	2.52	11.6	0.09	285	3.3	160	83.2	13.3	2.7	5	24.1	0.24	0.25	0.48	4	1.46	2.84	9.7	6.1	0.5
BH-1d (76.5-78.0)	8.81	2.51	105	>15	66	6650	5.96	1.14	14	1.03	1200	0.19	9.3	0.067	2.98	549	0.11 8	1 41	90 22	.8 63	1	50	0.5 12.5	5 23	15.6	4	4 10.7	0.58	1.95	12.8	0.13	80.2	4.4	970	47.6	15.7	4.1	8	9	0.29	0.3	1.21	3.8	1.12	2.22	24.8	9.2	0.8
BH-1d (81.0-82.5)	2.82	4.11	384	10.4	85	3880	2.28	3.39	27	0.6	517	0.63	5.8	0.057	1.09	483	0.09 3	9 8	57 6.	2 11	1 1.	2 7.	.99 2.1	22	4 6.8		5 12.1	0.17	0.62	10.8	0.07	215	2.3	295	106	13	3.4	3	4.4	0.18	0.23	0.23	4.6	1.52	1.3	6.4	6	0.4
BH-1d (90.0-91.5)	22.9	2.18	26	>15	70	5530	15	0.43	11	0.71	1360	0.06	2.1	0.068	1.86	166	0.1 4	4 >10	000 3	3 11	3 1.	.6 68	8.8 25.1	2	3 22.5	2	3 16	0.86	12.5	15.7	0.16	73.3	4.8	593	27.6	12.4	3.4	27	55.4	0.3	0.28	1.24	3.1	0.48	5.38	176	10.3	0.9
BH-3s (9.0-10.5)	8.96	3.04	215	>15	61	3540	3.37	2.29	20	0.93	820	0.28	16.5	0.055	1.89	950	0.12 4	7 37	50 21	1 79	1.	.1 41	1.8 11	24	9 8.8		5 9.9	0.45	1.26	13.1	0.11	94.4	5.5	1800	79	11.4	3.7	5	6.3	0.38	0.28	1.73	4.7	1.09	1.93	29.2	8.3	0.7
BH-3s (10.5-12.0)	2.73	4.21	298	11.6	89	4400	3.85	2.95	24	0.9	721	0.4	10.1	0.059	1.92	458	014 /	6 9	1 17	1 90	1	4 5	86 3.30	3 29	7 10.5		7 12.6	0.34	0.76	14.8	0.13	84.7	6.2	412	103	6.57	49	2	7.1	0.4	0.35	0.33	5.5	1.32	1.38	29.6	97	0.8
BH-3s (21.0-22.5)	8.5	2.45	49	>15	67	4750	4.52	0.54	11	1.12	1270	0.08	6.7	0.06	0.64	665	0.11 4	2 40	00 32	5 15	2 1.	1 6	65 9.85	5 22	6 10.7		5 9	0.87	2.85	12.5	0.13	77	4.7	631	27	21.4	3.5	4	13.7	0.29	0.27	0.73	3.7	0.37	2.62	47.2	9	0.8
BH-3d (10 5-12 0)	3.23	1 72	127	>15	59	5510	2.92	1.25	15	0.68	503	0.22	3.5	0.038	1 27	521	0.06 2	2 8	i0 5	5 65	0	8 5	68 2.3	14	1 89		6 69	0.17	0.5	6.8	0.06	41.8	2	168	46.6	12.4	22	2	5.4	0.12	0.16	0.14	24	0.85	1.77	3.6	4.5	0.4
BH-3d (39.0-40.5)	2.51	3.04	61	4 79	142	3180	>15	1.31	15	0.64	284	0.1	0.7	0.05	>5	123	0.09	7 3	19 17	4 43	1	3 1	07 0.8	25	1 39.4	1	6 96	0.34	0.61	14.7	0.09	150	43	74	51	4.47	3.8	20	12.5	0.3	0.26	1.11	47	0.42	2.02	148	72	0.6
RH-3d (48 0-49 5)	4.71	4.76	284	6.2	125	6120	2.60	3.74	28	0.59	830	0.66	6	0.059	1.04	207	0.12	4 6	10 1	4 75	2	2 1	14 1 2	25	9 12.9		9 14.1	0.46	0.66	20.8	0.1	200	4.2	259	136	10.9	4.2	2	7.4	0.36	0.2	0.46	67	1.44	1.00	14.2	7.7	0.6
BH-3d (72.0-73.5)	2.92	3.23	101	8.76	97	2650	14.7	1.59	16	0.69	407	0.19	13	0.049	>5	237	01	2 9	16	3 43	1	4 9	94 2.54	3 26	5 32.7		8 98	0.44	0.86	14.8	0.09	129	46	156	57.1	6.56	37	16	11.3	0.34	0.27	1.47	46	0.48	1.94	144	74	0.6
BH-24 (88 5-90 0)	16.1	5.16	225	10.1	444	5350	6.01	2.59	27	0.96	1150	0.59	0.2	0.064	3.62	245	0.16 6	5 45	70 2	7 10	. 2	3 3	69 12 1	2 2	4 12.9		7 16.9	0.94	3.00	17.6	0.12	210	5.0	208	120	52.2	4.9		15.0	0.46	0.25	2.07	6.9	0.91	2.60	622	0.2	0.8
DH 34 (04 E 03 0)	0.5	4.00	400	10.1	400	4500	44.0	0.00	21	0.90	018	0.08	4.0	0.004		470	0.10 0	e 193	20 2			0 2	00 12.		- 12.0		7 44.6	0.64	3.00	17.5	0.13	405	5.3	200	88.0	40.0	4.4		10.3	0.44	0.30	4.72		0.7	2.55	457	0.0	0.3
BH-34 (94 5-95.0)	6.04	4.05	189	3.09	109	4000	11.2	1.02	25	0.82	918	0.26	4.2	0.052	- 6<	221	0.13 0	0 3/ 4 1-14	20 2	2 15	1.	7 4	09 10.0	30	29.6	1 3	7 14.6 5 12.7	0.62	3.59	14.0	0.12	242	5.9	204	65.2	40.0	4.4	14	10.4	0.44	0.32	4.73	6.4	0.49	2.00	*0/	0.0	0.7
DU 24 (442 E 444 0)	0.04	5.01 E.04	442	8.04	400	2,300	1.2	2.04	-0	0.74	607	0.20	-2	0.055	-0	272	0.42		50 Z4	2 42		7 44	00 0.00	21			e 127	0.02	0.24	14.0	0.00	140	3.4	100	400	3.50	4.7		2.0	0.07	0.29	0.44		4.00	4.04	40.7	7.0	0.0
BH-3d (1215-114.0)	1.00	4.65	413	0.24	109	2050	2.99	3.61	35	1.24	087	0.61	15.7	0.081	0.71	3r3 600	0.12 4	4 15 6 40	10 11	a 12	1.	9 5	24 2.0	2/	0 0.2	2	0 13.5	1.02	0.31	22.6	0.09	140	3.4	200	95.5	3.99	9.5	-2	2.0	0.2/	0.62	0.44	0.2	0.79	2.1	12.7	19.6	1.6
porrou (121.0123.0)	1.30		. 135	<ul> <li>A10</li> </ul>	. 14	• 242			~	1 1.44	1			0.004	- w.//	~~~	We7 0		10 1 40			~ 4	NT 1 4.25		0.4			. 1.00	. 3.03	. 23.5	· v.20	10	11.0	A1004	March M	F - 1 M		2.4	7.1	~~~	w.96			· v./0 /			10.0	

Appendix G Sequential Extraction Procedure (SEP) Results for East Dump Waste Rock Samples



Figure G.1 SEP results for Al (ppm) inset graph shows total elemental from 4-acid digestions Al (ppm)



Figure G.2 SEP results for Al (%) inset graph shows total elemental from 4-acid digestions Al (ppm)



Figure G.3 SEP results for Ca (ppm) inset graph shows total elemental from 4-acid digestions Ca (ppm)



Figure G.4 SEP results for Ca (%) inset graph shows total elemental from 4-acid digestions Ca (ppm)



Figure G.5 SEP results for Fe (ppm) inset graph shows total elemental from 4-acid digestions Fe (ppm)



Figure G.6 SEP results for Fe (%) inset graph shows total elemental from 4-acid digestions Fe (ppm)



Figure G.7 SEP results for Mn (ppm) inset graph shows total elemental from 4-acid digestions Mn (ppm)



Figure G.8 SEP results for Mn (%) inset graph shows total elemental from 4-acid digestions Mn (ppm)



Figure G.9 SEP results for As (ppm) inset graph shows total elemental from 4-acid digestions As (ppm)



Figure G.10 SEP results for As (%) inset graph shows total elemental from 4-acid digestions As (ppm)



Figure G.11 SEP results for Cu (ppm) inset graph shows total elemental from 4-acid digestions Cu (ppm)



Figure G.12 SEP results for Cu (%) inset graph shows total elemental from 4-acid digestions Cu (ppm)



Figure G.13 SEP results for Mo (ppm) inset graph shows total elemental from 4-acid digestions Mo (ppm)



Figure G.14 SEP results for Mo (%) inset graph shows total elemental from 4-acid digestions Mo (ppm)



Figure G.15 SEP results for Pb (ppm) inset graph shows total elemental from 4-acid digestions Pb (ppm)



Figure G.16 SEP results for Pb (%) inset graph shows total elemental from 4-acid digestions Pb (ppm)



Figure G.17 SEP results for Zn (ppm) inset graph shows total elemental from 4-acid digestions Zn (ppm)



Figure G.18 SEP results for Zn (%) inset graph shows total elemental from 4-acid digestions Zn (ppm)

Appendix H SEM and EDS Investigation Images and Elemental Wt.%

		As	Mo	Cu	Ph	Zn	C	S	0	Fo	K	A1	Ca	Cd	Mn	Si	ті	Bi	Total
		0/	0/	0/	0/	2/11 0/	0/	0/	0/	0/	1X 0/	0/	0/	04	0/	0/	0/	D1 0/	10tai 0%
Figure	Sample ID	70	70	70	70	70	70	70	70	70	70	70	70	70	70	70	70	70	70
Figure H.1-1	BH-1d (19.5 – 21.0)			8.6	0	28.5	7.8	0.2	21.8	0.1		0.1	0.4	0.3	0.4	0.1			68.3
Figure H.1-2	BH-1d (19.5 – 21.0)			46.1	0	1.5	5.5	6	15.3	0.4		0.2	0.1			0.2			75.3
Figure H.2-1	BH-1d (90.0 – 91.5)					49.5	2.7		16.1							9			77.3
Figure H.2-2	BH-1d (90.0 – 91.5)			41.6	0	12.7	9.4		22.8										86.5
Figure H.3	BH-1d (90.0 – 91.5)			18.2	0	32.1	9.6		18.9							0.2			79
Figure H.4	BH-1d (90.0 – 91.5)			45.8	0	8.9	6.6		21	0.5						0.4			83.2
Figure H.5	BH-3s (15.0 – 16.5)			53.5	0	0	6.5	7.8	13.9	0.2		0.7	1.8			0.3			84.7
Figure H.6-1	BH-3s (15.0 – 16.5)			64.4	0	0	3.7	7.2	8			0.2				0.1			83.6
Figure H.6-2	BH-3s (15.0 – 16.5)			8.5				3.2	28.6	25.3	1.14	4.9	1.5			5.1			78.24
Figure H.7	BH-3s (15.0 – 16.5)			62.3	0	0.8	6.2	6.2	12.5	0.3		0.3	0.2		0.1	0.3			89.2
Figure H.8	BH-1s (1.5 – 3.0)				3		5.2	9.6	30.3	31.4	6.4						0.2		86.1
Figure H.9	BH-1d (19.5 – 21.0)			0.4			6.7	9.4	31	26.1	5.5						0.34		79.44
Figure H.10	BH-1s (1.5 – 3.0)			0.5	4.3	1	19.9		21.4	27.7			1.2			2.7			78.7
Figure H.11-1	BH-1s (1.5 – 3.0)			0.8	2.4	1.1	5.9		31.7	39.4		0.6	2.4			6.5			90.8
Figure H.11-2	BH-1s (1.5 – 3.0)			1.1	1.3	1	6.5		28.5	39.1		0.3	2.1			5.3			85.2
Figure H.12	BH-1d (90.0 – 91.5)			4.1	1.2	4.5		0.1	23	43		0.1	0.6			4			80.6
Figure H.13	BH-1d (90.0 – 91.5)		0.01	1.9	2	7.8			26	40.8		1.4	0.4			4.3			84.61
Figure H.14	BH-1d (90.0 - 91.5)			2.1	1.4	5.2			10.4	45.4		0.3	0.4			3.1			68.3
Figure H.15-1	BH-1d (90.0 – 91.5)			0.4	0.7	1.8	6.9		30.8	48.6			0.3			3			92.5
Figure H.15-2	BH-1d (90.0 – 91.5)			0.4	0.1	1.5	9.6		30.8	30		0.2	0.3			13.3			86.2
Figure H.16	BH-1d (19.5 – 21.0)			0.3		1.1	6	0.6	32.6	45.7		0.4	0.3			2.7			89.7
Figure H.17	BH-1d (90.0 – 91.5)			2.8		1	8	0.39	30.4	35.1		0.6	0.6			8.1			86.99
Figure H.18	BH-3d (24.0 – 25.5)	0.6		4.5		3.3	10.2		23.3	30.8		1	2.1		0.1	6			81.9
Figure H.19	BH-3d (24.0 – 25.5)	1.5	0.04	4.6	2.1	6	5		22.5	33			1.1		0.1	3.8		4.4	84.14

## H.1 EDS Un-normalized Wt.% of Elements from Semi-quantitative Analysis of EDS

Table H.1 EDS un-normalized wt.% of elements from semi-quantitative analysis of EDS

		As	Mo	Cu	Pb	Zn	С	S	0	Fe	K	Al	Ca	Cd	Mn	Si	Ti	Bi	Total
Figure	Sample ID	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
Figure H.20	BH-3d (24.0 – 25.5)	0.3	0.11	6.6	0.7	2.5	11.6		19.7	31.5			0.5			3.4		0.3	77.21
Figure H.21-1	BH-3d (48.0 – 49.5)	0.2		0.05	1.5	0.48			23.5	53		0.2	0.4			1.2			80.53
Figure H.21-2	BH-3d (48.0 – 49.5)	0.4	0.01	0.5	0.6	2.3			20.6	47		0.9	0.5			1.9			74.71
Figure H.22	BH-3d (48.0 -49.5)	0.2	0.5	13.3		0.7		0.9	22.3	30.4	0.2	0.7	2.3			5.9			77.4
Figure H.23	BH-3d (91.5 – 93.0)	0.3		1		0.4		2.1	23.7	42.1	0.6	3.8	2.6		0.2	3			79.8
Figure H.24	BH-3d (91.5 – 93.0)	0.2		2.05		4.15	7.02	1.4	29.1	38.7		0.7	1.17			2.7			87.19



Figure H.1 Images from BH-1d (19.5 – 21.0) A) Plane-polarized transmitted light photograph of silicate/calcite mineral with black and blue/green secondary mineral coating. B) SEM/BSE image



Figure H.2 Images from BH-1d (90.0 – 91.5) A) Plane-polarized transmitted light photograph of zinc silicate mineral (hemimorphite) with blue/green secondary mineral coating. B) SEM/BSE image



Figure H.3 Images from BH-1d (90.0 – 91.5) A) Plane-polarized transmitted light photograph of mineral B) SEM/BSE image



Figure H.4 Images from BH-1d (90.0 – 91.5) A) Plane-polarized transmitted light photograph of mineral B) SEM/BSE image



Figure H.5 Images from BH-3s (15.0 – 16.5) A) Plane-polarized transmitted light photograph of mineral B) SEM/BSE image



Figure H.6 Images from BH-3s (15.0 – 16.5) A) Plane-polarized transmitted light photograph of blue/green secondary mineral associated with oxidized chalcopyrite grain (Cpy) B) SEM/BSE image



Figure H.7 Images from BH-3s (15.0 – 16.5) A) Plane-polarized transmitted light photograph of mineral B) SEM/BSE image



Figure H.8 Images from BH-1s (1.5 – 3.0) A) Plane-polarized transmitted light photograph of mineral B) SEM/BSE image



Figure H.9 Images from BH-1d (19.5 – 21.0) A) Plane-polarized transmitted light photograph of mineral with coating B) SEM/BSE image



Figure H.10 Images from BH-1s (1.5 – 3.0) A) Plane-polarized transmitted light photograph of pyrite mineral (Py) with iron oxide coatings in a calcite grain B) SEM/BSE image



Figure H.11 Images from BH-1s (1.5 – 3.0) A) Plane-polarized transmitted light photograph of Chalcopyrite (Cpy) coated with iron oxide B) SEM/BSE image of same mineral showing zoning of iron oxide



Figure H.12 Images from BH-1d (90.0 – 91.5) A) Plane-polarized transmitted light photograph of iron oxide grain. B) SEM/BSE image



Figure H.13 Images from BH-1d (90.0 – 91.5) Plane-polarized transmitted light photograph of iron oxide coating hemimorphite (white mineral) B) SEM/BSE image



Figure H.14 Image from BH-1d (90.0 - 91.5) A) Plane-polarized transmitted light photograph of iron oxide coating hemimorphite (white mineral) B) SEM/BSE image (300 micron scale)



Figure H.15 Images from BH-1d (90.0 – 91.5) A) Plane-polarized transmitted light photograph of weathered opaque mineral with iron oxide coating B) SEM/BSE image



Figure H.16 Images from BH-1d (19.5 – 21.0) A) Plane-polarized transmitted light photograph of pyrite (with Zn) mineral with iron oxide coatings B) SEM/BSE image



Figure H.17 Images from BH-1d (90.0 – 91.5) A) Plane-polarized transmitted light photograph of pyrite (with 0.2 wt.% Zn) mineral with iron oxide coating B) SEM/BSE image



Figure H.18 Images from BH-3d (24.0 – 25.5) A) Plane-polarized transmitted light photograph of calcite mineral with iron oxide coatings B) SEM/BSE image



Figure H.19 Image from BH-3d (24.0 – 25.5) A) Plane-polarized transmitted light photograph of garnet (?) mineral with iron oxide coatings B) SEM/BSE image



Figure H.20 Images from BH-3d (24.0 – 25.5) A) Plane-polarized transmitted light photograph of garnet and other mineral (calcite?) with iron oxide coating B) SEM/BSE image magnified into iron oxide coating (50 micron scale)



Figure H.21 Images from BH-3d (48.0 – 49.5) A) Plane-polarized transmitted light photograph of pyrite (with 0.23 wt.% Zn) with iron oxide oxidation rim B) SEM/BSE image



Figure H.22 Image from BH-3d (48.0 -49.5) A) Plane-polarized transmitted light photograph of pyrite (Py) (with 0.22 wt.% Zn) and chalcopyrite (Cpy) with iron oxide coating B) reflected light microscope image C) SEM/BSE image



Figure H.23 Image from BH-3d (91.5 – 93.0) A) Plane-polarized transmitted light photograph of silicate minerals with iron oxide coatings. B) SEM/BSE image



Figure H.24 Image form BH-3d (91.5 – 93.0) A) Plane-polarized transmitted light photograph of pyrite (Py) (with Zn) with iron oxide coating B) SEM/BSE image
Appendix I Drainage Chemistry Geochemical Modelling

## I.1 Example PhreeqC Input File for Geochemical Modelling of East Dump Seepage Chemistry

SELECTED	OUTPUT																													
-file	CO_28	.xls																												
-reset	false																													
-simulation true																														
-solution true																														
-ph	true																													
-pe	true																													
-alkalini	ty tru	2																												
-charge	balance	true																												
-percent_error tr		true																												
-saturation_indices Calcite Gypsum Malachite Antlerite																														
Brochantite Fe(OH)3(a) Jarosite-K Goethite																														
Goslarite Rhodochrosite Cerrusite Rosasite Aurichal																														
Smithsonite Hydrozincite_Preis Wulfenite																														
Powellite																														
SOLUTION	SPREAD																													
-pe 1	2																													
-units I	ng/l																													
number	Alkalinity	рН	Temp	S(6)	CI	N(5)	Р	Ag	Al	As	Ва	В	Si	Ca	Cd	Cu	Fe	К	Li	Mg	Mn	Mo	Na	Ni	Pb	Se	Sr	Zn	F	pe
	as HCO3																													O2(g) -0.8
508	155.6	8		457	19	1.0	2 0.	3 0.01	0.18	0.001	0.037	0.03	8.6	248.1	0.003	0.045	0.001	3.48	0.02	15.26	0.081	0.01	3.02	0.01	0.015	0.0002	1.688	0.403	0.28	12