Geochemical Characterization of Coexisting Precipitates and Waters from High-Sulfidation Epithermal Gold Deposits

By

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Abstract

Water management and treatment at closed mine sites have become primary concerns for mining companies due to their costly nature, potential commitment of decades of water treatment, and impact on the environment. The long-term objective of this research investigates methods of extracting metals from acid mine waste in order to minimize the environmental impact of the drainage and decrease the financial burden on mining companies. However, understanding the mechanism of element mobility in mine waste requires a comprehensive assessment of the composition of the water and co-existing minerals at studied mines El Indio, Lagunas Norte and Pierina, which is the primary goal of this thesis. No study has previously provided a detailed analysis of the secondary precipitates at these mines or their role in storing trace elements.

Water samples were analyzed by inductively coupled mass spectrometry and inductively coupled optical emission spectrometry. Coexisting mineral samples were characterized using an environmental scanning electron microscope, X-ray diffraction and synchrotron-based microanalysis. The pH of waters is acidic with values of 2.24 to 4.5. Major elements in waters include Ca, Al, Fe and SO_4 ; minor elements include Cu, Mg, Mn, Zn, K, Na and trace elements consisted of As, Co, Ni, Sr, Pb and Cd. This study has identified previously unreported phases that may be placed into 3 broad groups: 1) hydrous Na-, Mg-, Ca, Cu- and other metal-sulfates such as blodite group minerals, hexahydrite and gypsum 2) Fe-oxides, oxyhydroxides and oxyhydroxysulfates such as ferrihydrite, goethite, scorodite and jarosite 3) other metal-rich, poorly crystalline Al phases. Synchrotron microanalysis has shown that these minerals sequester Cu, Mn, Zn, Cd, As, Ni and other trace elements.

This research has improved the understanding of the mobility of elements by identifying the trace elements associated with minerals and by characterizing the relationship between chemistry of precipitates and solution. The occurrence of secondary precipitates stands as evidence purporting that sulfide oxidation at these mine sites is ongoing. Barrick Gold Corporation can consider capturing the sulfate-rich secondary precipitates by mechanically enhanced pond-evaporation and precipitation of efflorescent salts, methods which may allow to efficiently capture elements of interest.

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List of abbreviations

ARD	Acid rock drainage
EMPA	Electron microprobe
ESEM	Environmental scanning electron microscope
HS	High-sulfidation
HDS	High density sludge
ICP-OES	Inductively coupled plasma optical emission spectrometry
ICP-MS	Inductively coupled mass spectrometry
LS	Low-sulfidation
MicroPIXE	Proton induced X-ray emission
MSP	Mounted secondary precipitates
MV	Metal value
NMR	Nuclear magnetic resonance imaging
ORP	Oxidation-reduction potential
QA/QC	Quality assurance and quality control
RC	Recovery cost
RO	Reverse osmosis
SI	Saturation index
TDS	Total dissolved solids
XRD	X-ray diffraction
μ XRD	Micro X-ray diffraction
XRF	X-ray fluorescence
XAFS	X-ray absorption fine structure
WTC	Water treatment cost

Chapter 1

Introduction

Acid rock drainage (ARD) is an important source of pollution in active and abandoned sulfide-rich mining areas (Carbone et al., 2013). The Rio Tinto in Spain, the Norwegian Raubekken, Iron Creek in Colorado and Iron Mountain in California are known cases of historical ARD. In a modern day setting, mining activities are known to accelerate the ARD process and are financially liable for the remediation of closed mine sites, and must meet regulations governing the quality of the effluent leaving their properties. One approach to limiting the financial burden and environmental impact of water treatment is to extract or isolate elements found in ARD that can be recovered to offset costs (Plumlee, 1999; MEND Treatment Committee, 2013; Lorax Environmental, 2003). Examples of elements of potential economic significance include Cu, Fe, Ag, Ni, Zn, Mn, Co, Mo, Te, Pb and environmentally harmful elements include Ag, As, Ce, Pb, Hg, Te, Sn amongst others (Krieger et al., 2000; Smith and Huyck, 2000). This thesis aims to understand the geochemistry of waters and secondary precipitates at three gold mines: El Indio in Chile, and Lagunas Norte and Pierina in Peru, thereby providing the necessary groundwork for the improvement of water treatment methods.

These high-sulfidation epithermal Au-mines are ideal sites to study as they produce ARD resulting from sulfide oxidation leading to the high concentration of elements in solution, as well as the formation of abundant secondary minerals that host various trace elements (Evans et al., 2012; Cerpa et al., 2013; Robert et al., 2007; Rainbow et al., 2005; Montgomery, 2012; Kohn Crippen Berger, 2012b, 2012a). The first descriptions of epithermal precious and base-metal deposits are dated to the early 20th century when Ransome (1907) documented and described the occurrence and association of gold with alunite at Goldfield, Nevada (Rainbow et al., 2005 after Ransome, 1907). Subsequently, Lindgren (1922) defined epithermal deposits as mineralization that forms within the first kilometer of the continental crust at

temperatures below 350°C (Rainbow, 2009). Plumlee et al. (1999) summarize many key geologic characteristics of mineral deposits that control their environmental signatures prior to and post mining.

Understanding the mechanisms of element mobility in mine waste requires a comprehensive assessment of the composition of the water and co-existing minerals, both primary ore and accessory minerals (source) and secondary precipitates (sink). Furthermore, understanding of trace elements and the secondary minerals that host them allows for the prediction of trace element behavior and mobility throughout a mine site (Lottermoser, 2010c, 2010b).

1.1 Objectives

The long-term objective of this research project is to investigate methods of extracting metals from acid mine waste in order to minimize the environmental impact of the drainage and to offset remediation costs. The primary goal of this thesis is to gain a more detailed understanding of the geochemistry of waters and secondary precipitates at El Indio, Lagunas Norte and Pierina HS gold mines and controls on metal mobility.

The objectives of this research were achieved by:

- 1- Characterizing the major and trace element composition of waters.
- 2- Characterizing secondary minerals co-existing with sampled waters.
- 3- Identifying the trace element content of the secondary sulfate minerals.
- 4- Relating the precipitates and waters by characterizing their relationship using geochemical modeling software.
- 5- Evaluating the importance of various techniques used to characterize secondary minerals and dissolved elements.
- 6- Evaluating the possibility of extracting valuable elements from effluent in order to offset water treatment costs.

1.2 Organization of the thesis

This thesis is organized into six chapters. Chapter 1 introduces El Indio, Lagunas Norte and Pierina mines and the objectives of this project followed by detailed explanations of mining history, local and regional geology, geography, and a description of HS epithermal deposits. Chapter 2 presents a literature review of ARD and secondary minerals associated with these systems, metal sulfates, their solubility and stability relationship, and viable water treatment methods for sulfate waters. This section also summarizes previous geochemical work conducted at El Indio, Lagunas Norte and Pierina mines, and a list of hypotheses. Chapter 3 describes the analytical methods used for the geochemical characterization of the solids and waters. Chapter 4 reports the mineralogical and geochemical results of water and secondary precipitate analyses. This descriptive section is followed by an interpretation of results and a discussion section in chapter 5. Finally, conclusions and recommendations for future work are included in the last chapter.

1.3 Background

1.3.1 High-sulfidation (HS) epithermal deposits, mineralogy and associated elements

HS epithermal deposits form when precious metals and gangue minerals are deposited from hydrothermal fluids at shallow crustal levels (<1km) and low temperatures (<300°) (Hedenquist et al., 2000). The metal-bearing hydrothermal fluids are magmatic and/or meteoric waters. Gold-silver epithermal deposits occur in volcano-plutonic arcs, island arcs and continental margins associated with subduction zones and convergent-plate settings (Taylor, 2007). The magmatic intrusions into volcanic arcs provide heat, which creates and drives convection of the hydrothermal fluids (Figure 1-2) (Corbett et al., 1998). At around 300°C, H₂SO₄ and HCl dissociate, where these molecules are split into smaller molecules or ions and release H⁺ into solution. The gradually formed hot acidic fluids then mix with meteoric waters and react with the country rock to form the deposit (Corbett et al., 1998). The host rock is extensively

leached creating a porous silica residue that eventually hosts the ore minerals to varying degrees (Corbett and Leach, 1998; Arribas, 1995).

Global distribution of epithermal gold deposits demonstrates that they are associated with the Circum-Pacific Belt as a result of their genetic relation to magmatic centers (Hedenquist et al., 2000). Numerous epithermal deposits are associated with dome complexes and summit domes, followed by central-vent volcano setting and calderas (Hedenquist et al., 2000). The ore bodies are situated close to volcanic vents and have numerous structural conduits. In fact, hot-springs, geysers and fumaroles represent modern-day epithermal systems (Corbett and Leach, 1998; Rowland and Simmons, 2012). Epithermal precious metal deposits are significant due to their global abundance, as well as their potential of high grade and tonnage.

Boiling followed by rapid cooling lead to the formation of steam-heated waters that are responsible for advanced argillic alteration in both high- and low-sulfidation systems (Figure 1-1) (Hedenquist et al., 2000). As the hypogene acid fluids from the volcanic-hydrothermal system leach the rocks upon their ascent, a core of vuggy silica is formed (Figure 1-1). This silicic core of leached, residual silica is the main host of HS ore and is the central part of the advanced argillic halo that is formed of hypogene quartz-alunite and kaolin minerals (Figure 1-1) (Hedenquist et al., 2000). Hydrothermal alterations present in HS epithermal deposits are advanced argillic, argillic, silicic, and propylitic (Figure 1-1)(Arribas, 1995). Kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), dickite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), pyrophyllite ($\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$), alunite ($\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$) and diaspore ($\text{AlO}(\text{OH})$) are minerals that are stable in acidic conditions and make up the alteration assemblages of HS epithermal type deposits (Arribas, 1995). Steam-heated overprinting from hypogene fluids may also occur and will vary vertically (Arribas, 1995).

Figure 1-1 Hydrothermal alterations present in typical epithermal deposits are advanced argillic, argillic, silicic, and propylitic (Hedenquist et al., 2000). Steam-heated acidic waters leach the country rock upon their ascent creating a core of vuggy silica. This silicic core of leached, residual silica is the main host of high-sulfidation ore and is the central part of the advanced argillic halo that is formed of hypogene quartz-alunite and kaolin minerals (Hedenquist et al., 2000). Mineral assemblages and zonation of alteration demonstrate evidence of neutralization of hydrothermal fluids by host-rock reaction further from the source.

1.3.2 HS and LS epithermal deposits

The two end members of epithermal deposits are of the high-sulfidation (HS) and low-sulfidation (LS) types. Although HS epithermal deposits show a clear relationship to subduction related magmatism, LS deposits do not demonstrate this (Taylor, 2007). The term “high-sulfidation” is used to specify the occurrence of high sulfidation state minerals such as enargite and tennantite (Corbett et al., 1998) and not the abundance of sulfur. HS epithermal deposits are dominated by acidic, hot and saline magmatic fluids, whereas LS epithermal deposits are formed by cool, near neutral pH and dilute meteoric waters (Corbett et al., 1998). All deposits studied in this thesis are of the HS type.

As previously mentioned, HS deposits form when highly acidic fluids are channeled from magma and directed along a fault. These acidic fluids dissolve the rock creating vuggy silica. Then, metal-rich brines from the magma precipitate metals in the vuggy silica zone (Arribas, 1995). Fluids forming LS veins interact with the rock for a longer period of time, become neutralized and dissolve silica (Arribas, 1995). Boiling of the fluids produces high-grade gold and silver deposits (Hedenquist and Lowenstern, 1994).

Boiling is a process that allows for bisulfide-complexed metal such as gold to precipitate (Hedenquist and Lowenstern, 1994). Experimental studies have demonstrated that metals and ligands could be completely mobilized by associated magmas (Hedenquist and Lowenstern, 1994). Magmas obtain metals from mass transfer from subducting oceanic lithosphere, mantle melting, which are subsequently concentrated beneath volcanic arcs (Hedenquist and Lowenstern, 1994).

Common host rocks of gold mineralization in epithermal deposits are volcanic or volcanoclastic rocks of calc-alkaline series or basement rocks (Hedenquist et al., 2000). These felsic volcanic rocks have a low buffering capacity. The effects of volatiles and metals are not as clear for LS deposits as it is for HS deposits. Furthermore, the origin of the heat source may vary for low-sulfidation deposits (Kerrick et al., 2005). Typically, the highest content of sulfides is associated with the silicified and leached zones in HS epithermal deposits.

Figure 1-2 Schematic cross-section of sub-volcanic intrusions and the environments deduced for the formation of porphyry Cu and HS epithermal deposits (modified from Hedenquist and Lowenstern, 1994). Boiling followed by rapid cooling lead to the formation of magmatic-sourced, steam-heated and acidic vapor that leaches the country rock (pink). Active volcanic-hydrothermal system extend from degassing magma to fumaroles and acidic springs (Hedenquist and Lowenstern, 1994). The different coloured magma chambers represent multiple intrusions.

Table 1-1 describes the main differences between high-sulfidation and low-sulfidation epithermal deposits:

Table 1-1 Key characteristics of HS and LS deposits (Hedenquist et al., 1994; White et al., 1995; Bowell et al., 2000).

	Low Sulfidation	High Sulfidation
	160-270°C depth of ≤1.0 km	
Ore minerals	pyrite, sphalerite, marcasite, galena, electrum, gold (arsenopyrite, argentite, chalcopyrite, tetrahedrite)	pyrite, enargite-luzonite, chalcopyrite, covellite, tetrahedrite-tennantite, gold (sphalerite, galena, tellurides)
Gangue minerals	quartz, chalcedony, calcite, rhodocrosite, adularia, barite, illite	quartz, kaolinite, alunite, barite
Dominant metals	Au, Cu, As, Hg	Au, Ag, Cu, As, Fe, Mn
Minor metals	Zn, Pb, Sb, Se	Pb, Hg, Sb, Te, Sn, Mo
Metals enriched in rocks	Cu, Zn, As, Se, Ag, Cd, Te, Au, Hg	Fe, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Sn, Sb, Te, Au, Hg, Tl, Pb, Bi
Alteration	(Neutral alteration) Sericitic/illitic clays → propylitic veins dominated by quartz, carbonate adularia	(Zoned pervasive acidic alteration): residual quartz → alunite → kaolinite → illite → propylitic
%Sulfide	<0.1-6.3	3.4-31
Final pH	2.82-6.54	0.78-4.56
Conditions	Reduced, alkaline	Oxidized, acidic

HS deposits are enriched in Fe, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sn, Sb, Hg, Pb, and Bi, whereas LS deposits are enriched in As, Se, Cd, and Pb (Bowell et al., 2000). Typically, up to 50% of the ore zone of HS deposits can be composed of sulfides (Bowell et al., 2000). HS deposits also contain ore minerals such as pyrite (FeS_2), enargite-luzonite (Cu_3AsS_4), chalcopyrite (CuFeS_2), covellite (CuS), tetrahedrite-tennantite ($(\text{Cu,Fe})_{12}\text{Sb}_4\text{S}_{13}$), sphalerite ($(\text{Zn,Fe})\text{S}$), galena (PbS) and tellurides (Bowell et al., 2000).

1.3.3 Deposit geology and mineralogy

1.3.3.1 El Indio

The El Indio Belt is a district of epithermal deposits containing four significant economic deposits: El Indio, Veladero, Tambo and Pascua-Lama. The El Indio belt is part of the Main Cordillera that was formed as a result of plate convergence and intermittent periods of regional extension (Chouinard et al.,

2005). The El Indio belt extends from Pascua-Lama-Veladero in the north to Coipita in the south (Charchaflié et al., 2007) and between latitudes 29°20' and 30°30' (Figure 1-3) (Bissig et al., 2003). The Nazca Plate was subjected to subduction beneath South America during the Miocene. A change in subduction angle from 35° to nearly horizontal has been observed (Pilger, 1984) and this flattening is assumed to be caused by the consumption of Juan Fernandez Ridge beneath the South American Plate (Bissig et al., 2003). Volcanic activity leading to the major economically viable deposits occurred prior to flattening of Nazca plate. The Au-rich deposits in the belt are directly associated with Miocene magmatic rocks between the Baños del Toro fault in the west and Colangul fault in the east (Chouinard et al., 2005), both reverse faults with opposite dips. As a direct result of periods of crustal shortening and subsequent relaxation, northerly trending high-angle reverse and normal faults and folds were formed in the El Indio belt (Kay et al., 1999). This deposit can be described in terms of the magmatic and plate tectonic evolution of the Nazca plate and South America margin from the Oligocene and Miocene (Oyarzun et al., 2007). The El Indio belt presently lies in an amagmatic sequence of the Chilean Andes (Chouinard et al., 2005).

The alteration zones at El Indio are advanced argillic alteration mineral assemblages with kaolinite, alunite, and silica jaspers (Oyarzun et al., 2007), as well as sericitic and solfataric alterations (Jannas et al., 1990). The host rocks of El Indio are largely composed of felsic volcanic units (Bissig et al., 2003). The Au-Cu-Ag mineralization is hosted by ignimbrites and volcanic tuffs (Jannas et al., 1990). The hydrothermal fluids of the El Indio deposit were rich in sulfur and metal as a result of change in magmatism, leading to Cu-Au-As-S ore. The main ore minerals are enargite (Cu_3AsS_4), tennantite ($\text{Cu}_{12}\text{As}_4\text{S}_{13}$) and native gold. Other minerals present include alunite ($\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$), chalcocite (Cu_2S), chalcopyrite (CuFeS_2), galena (PbS), jarosite ($\text{KFe}^{3+}_3(\text{OH})_6(\text{SO}_4)_2$), pyrite (FeS_2), sphalerite ($(\text{Zn},\text{Fe})\text{S}$) and tellurium, hubernite (MnWO_4), bornite (Cu_5FeS_4), digenite (Cu_9S_5), emplectite (CuBiS_2), marcasite (FeS_2), and barite (BaSO_4) (Jannas et al., 1990; Arribas, 1995).

Figure 1-3 Geographic location of the El Indio deposit (Modified from Jannas et al., 1990).

Figure 1-4 Generalized geologic setting of north-central Chile and the location of the El Indio deposit (Modified from Jannas et al., 1990).

1.3.3.2 Lagunas Norte

The Lagunas Norte ore deposit is a Miocene HS epithermal Au-Ag deposit with a resource of ~ 14 M oz Au. The local geology is defined by folded and thrustured Upper Jurassic – Lower Cretaceous marine sedimentary strata that are unconformably overlain by lower Oligocene to Middle Miocene subaerial Calipuy Supergroup volcanic rocks (Montgomery, 2012). Mineralization is hosted in the highly-deformed

Valanginian Chimú Formation quartz arenite and in weakly-deformed, Lower Miocene dacitic volcanoclastic rocks (Montgomery, 2012).

There are six stages of mineralization at Lagunas Norte. Stage I represents quartzose replacement of sedimentary units with minor gold mineralization association (Montgomery, 2012). Stage II shows quartz arenite units associated with minor pyrite (FeS_2), enargite (Cu_3AsS_4) and gold. Stage III, the main mineralization event, is representative of the formation of vuggy silica (Montgomery, 2012). High-grade gold mineralization is associated with pyrite-enargite assemblages where pyrite is the main host for Au and is representative of Stage IV. Native sulfur and barite (BaSO_4) fill the remaining vugs in Stage V. Finally, Stage VI is the oxidation and release of Au from pyrite into goethite ($\text{FeO}(\text{OH})$).

Figure 1-5 Geographic location of Pierina and Lagunas Norte deposits.

Figure 1-6 Regional geological map of the Lagunas Norte Domain and the Quturvilca Domain (Modified from Montgomery, 2012).

1.3.3.3 Pierina

The Pierina ore deposit is an Au-Ag HS epithermal type deposit located 5 km north of the intermediate-sulfidation Santo Toribio Ag-base-metal epithermal deposit in the Cordillera Negra at elevations of 3800-4200 meters (McNulty and Farber, 1998). Pierina has a pre-mining resource of ~ 8M oz Au-(Ag). The regional geology is primarily Jurassic and Cretaceous marl, shale, limestone and clastics overlain by Eocene to Miocene volcanics (Rainbow et al., 2005). This deposit is typical of HS epithermal deposits and the alteration types include vuggy silica, silicic, quartz alunite, and argillic alterations (Rainbow et al., 2005). Paragenetic minerals that are of importance for ARD include alunite ($KAl_3(SO_4)_2(OH)_6$), pyrite (FeS_2), sphalerite ($(Zn,Fe)S$), bismuthinite-stibnite (Bi_2S_3 , Sb_2S_3), enargite (Cu_3AsS_4), galena (PbS), tennantite ($Cu_6[Cu_4(Fe,Zn)_2]As_4S_{13}$), covellite (CuS), native sulfur (S), schwertmannite ($Fe_8O_8(OH)_6(SO_4) \cdot nH_2O$), lepidocrocite ($FeOOH$), goethite ($FeOOH$), barite ($BaSO_4$), and acanthite (Ag_2S) (Rainbow et al., 2005).

The following is sourced from Klohn Crippen Berger (2012) unless stated otherwise. Mineralization at Pierina is confined in a zone of 450m by 1200m and controlled by a north, northeast and northwest trending fault system. The local geology of Pierina is composed primarily of units belonging to the Huaraz Group (29.3-14.8 Ma). These rocks include pyroclastics that overlay a dacitic flow-dome complex, as well as andesitic lavas. Tertiary rocks belong to the Calipuy Supergroup (Rainbow et al., 2005). Basement rocks include moderately folded Cretaceous Carhuaz and Santa formation hornfelsic sedimentary rocks. The deposit found at Pierina is representative of the last volcanic stage during the evolution of the Huaraz Group (Rainbow et al., 2005).

Figure 1-7 Regional geological map of Pierina mine with the outline of the Pierina pit highlighted (Modified from Rainbow et al., 2005).

1.3.4 Site location and operational history

Lagunas Norte and Pierina are located in Peru, and El Indio is located in Chile. Specifically, the Lagunas Norte open pit mine ($7^{\circ} 56'30''\text{S}$; $7^{\circ} 56'30''\text{S}$) is located 140 km east of the city of Trujillo and 175 km north of the Pierina open pit operation ($9^{\circ}26.5' \text{ S}$; $77^{\circ}35' \text{ W}$) in the Peruvian Andes at an elevation of 4,000-4,260 meters above sea level (Lacroix, 2012). Pierina is in the Ancash Department in close proximity to the city of Huaraz in north-central Peru, at an altitude of 4,100 meters. The El Indio underground mine, in Chile, is found 480 km north of Santiago, 160 km east of La Serena in the High Andes of north-central Chile and at an elevation of approximately 3,960 meters.

At Lagunas Norte and Pierina, the annual temperatures range from greater than 25°C to less than -10°C (Lacroix, 2012). Periods of extreme precipitation are not uncommon and the rainy season is from October to April. Temperatures at El Indio are similar, ranging from a high of 25°C in January to -10°C in August (Belanger, 2003). The wet season at these sites is from October to April and dry season from May to September. The average annual rainfall at Pierina is 1.16 meters (George et al., 2009). The month of March experiences the greatest amount of precipitation, whereas the month of August experiences the greatest amount of evaporation (George et al., 2009).

The Lagunas Norte deposit was discovered in the year 2002 and operations by Barrick Gold Corporation began in 2005 (Barradas, 2014; Thomaz, 2006). The Lagunas Norte mine is an open pit operation with major on site processes such as a two-stage crushers and a cyanide heap leach (Barradas, 2014; Thomaz, 2006).

The El Indio mine operations began in 1981 under owners such as St. Joe Minerals, Fluor Minerals, Bond Gold and Lac Minerals before Barrick Gold Corporation acquired it in 1994 (Jannas et al., 1990; Belanger, 2003). El Indio was an open pit and mineral processes included flotation, concentration, roasting and cyanide in pulp leaching (BGC personal communication, 2015). Depletion of reserves occurred in the year 2002 and a closure plan with the goal of minimizing the environmental impact of the mine was inaugurated (Pouiller, 2011). During its years of production, El Indio produced 5.5 million ounces of Au, 24 million ounces of Ag and 500 thousand tonnes of Cu (Pouiller, 2011).

Pierina is an open-pit mine, heap leach operation where ore is crushed and transported to the leach pad area (Craze, 2001). Closure activities were initiated at Pierina in August, 2013 (BGC, 2015). Nineteen Mt of mine materials are scheduled for extraction from 2012 to 2019. Barrick Gold Corporation acquired Pierina in 1996 when it was at the advances exploration stage, and operations began in 1998 (Craze, 2001).

1.3.5 Mine components and water management

The sampling locations of interest include pit walls, sedimentation ponds, dewatering stations, seepage collection ponds, water monitoring stations and water treatment plants. The water quality of the three mine sites, each with different water treatment methods, will be compared. There is no active water treatment at El Indio, whereas pH adjustment via lime addition and sedimentation are practiced at Pierina and high density sludge (HDS) and reverse osmosis (RO) plants currently being built (Thomaz, 2006; BGC, 2014b). Active treatment via lime neutralization and HDS generation is done at Lagunas Norte (Thomaz, 2006; BGC, 2014b). In addition, water treatment facilities at Lagunas Norte include cyanide destruction for barren process solutions, various solution storage ponds and associated water management infrastructure (Thomaz, 2006). Secondary water treatment plants are designed for ferric sulfate precipitation, which removes metals, and reverse osmosis to remove ammonia (Evans et al., 2012). At El Indio, there is only passive water treatment via the Pastos Largos sedimentation pond (BGC, 2014b).

El Indio is closed with mitigation measures near completion composed of waste rock dump covers, permeable underground portal plug, open pit backfilling, water diversions and monitoring. Pierina is at the late stages of operations and into the stage of progressive closure, and Lagunas Norte is in mid-life operations (BGC, 2014b, 2014a). Contact water is collected, monitored and mitigated by various strategies at all sites (BGC, 2014b, 2014a).

Table 1-2 Summary table of all deposits comparing information about the mine types, mineral reserves, average gold recovery, stage of mines, host rocks, tectonic setting, system emplacement, sulfidation state, associated economic metals, mineralogy, climate, precipitation, and present water treatment.

	El Indio	Lagunas Norte	Pierina
Mine type	Underground	Open pit	Open pit
Mineral reserves	10 Moz Au	~13.1Moz Au	~8Moz
Recovery Au (average)	-	~75%	~85%
Stage of mine	Closure	Operating	Operating, near closure
Host rocks	Miocene andesite, dacite, rhyolite tuffs. Volcaniclastic rocks of Tilito Member of Dona Ana Formation	Valaginian quartz arenite and Lower Miocene dacitic volcanics	Middle Miocene hypabyssal-to-extrusive pumice tuff and older dacitic flow-dome complex
Tectonic setting	Convergent margin		
Hydrothermal system emplacement	6.2-9.5 Ma	16.7-17.1 Ma	~14.4 Ma
Sulfidation	High and intermediate	High	High
Associated economic metals	Au-Cu-As	Au-Ag	Au-Ag
Mineralogy	Enargite-pyrite ± chalcopyrite, quartz-gold ± calaverite-enargite	Pyrite-enargite, goethite-hematite	Pyrite, bismuthinite-stibnite, enargite and barite, galena and sphalerite, hematite-goethite
Climate at site	From greater than 25°C to less than -10 °C		
Precipitation	1m (average/year)	-	1.16m (average/year)
Present water treatment	Passive treatment (current:sedimentation) (future:neutralisation, HDS, RO)	Lime addition and sedimentation, HDS (future:RO)	Cyanide destruction plant, ARD pond, sedimentation and secondary treatment plant
References	(Jannas et al., 1990), (Oyarzun et al., 2007)	(Cerpa et al., 2013), (Evans et al., 2012), (Montgomery, 2012)	(George et al., 2009), (Rainbow et al., 2005)

Chapter 2

Literature review

2.1 Factors influencing the formation of ARD

The formation of ARD has been extensively studied and described previously (Nicholson, 1994; Lottermoser, 2010b; Jönsson et al., 2006; Romero et al., 2011; Buckby et al., 2003; Jambor et al., 2000). The mineralogy and chemical nature of HS epithermal Au-Ag-Cu deposits enable the production of ARD and the release of elevated metal concentrations. Commonly occurring sulfides such as pyrite and pyrrhotite that are present at these types of deposits oxidize and produce H^+ ions, lowering the pH of the solution. The weathering of minerals can be classified as acid producing (generating H^+), acid buffering (consuming H^+), or neither. The weathering reaction of pyrite is acid producing, whereas the weathering of calcite is acid buffering (Lottermoser, 2010c). However, carbonate minerals are nonexistent at the studied mines, therefore acid buffering does not influence the chemistry of the waters. Furthermore, the sulfide mineral grains tend to be quite small, with high surface area, thereby increasing reactivity (Bowell et al., 2000).

Pyrite is the most abundant sulfide mineral, it commonly occurs with ore deposits and is only stable under strongly reducing conditions (Lottermoser, 2010c; Frau, 2000; Romero et al., 2006; Carbone et al., 2013; Jambor et al., 2000; Nordstrom et al., 1999). Pyrite oxidation mechanisms occur by: 1) oxidation by oxygen, 2) oxidation by oxygen in the presence of microorganisms, 3) oxidation by oxygen and iron, 4) oxidation by oxygen and iron in the presence of microorganisms (Lottermoser, 2010c). The indirect oxidation of pyrite, an exothermic process, occurs in 3 steps (Equations 2.1, 2.2, 2.3) and involves the oxidation of pyrite by both oxygen and ferric iron. Stoichiometric chemical reactions are used to describe the four oxidation mechanisms described. In abiotic and biotic direct oxidation processes, oxygen directly oxidizes pyrite (Equation 2.1).

Oxidation of pyrite by oxygen:

Oxidation of ferrous iron to ferric iron:

Oxidation of pyrite by ferric iron:

The three steps demonstrate how oxidized pyrite produces dissolved ferrous iron, sulfate and hydrogen ions. Subsequently, the dissolved iron sulfate ions increase the total dissolved solids of water and the release of hydrogen produces acid (Lottermoser, 2010c). The oxidation of ferrous iron to ferric iron by oxidation occurs during the second step at low pH conditions. The third step demonstrates ferrous iron as the oxidizing agent. Some aerobic bacteria and Archea may speed up the chemical oxidation rate of ferrous iron and sulfur when oxygen is present (Lottermoser, 2010a). Other sulfides (i.e. galena, pyrrhotite) demonstrate different stabilities, acid production potentials and reaction rates (Alpers et al, 1992; Nordstrom et al., 1992; Jambor et al., 2000; Lottermoser, 2010c).

2.2 Formation of secondary minerals in ARD

A consequence of ARD is the precipitation of secondary minerals. Secondary minerals form as a result of weathering of sulfides before, during or after mining activities which releases sulfate, metals and metalloids into coexisting solution thereby increasing the ionic content of the water (Lottermoser, 2010c). Ions may be absorbed by minerals such as chlorite, talc and illite or Fe or Mn oxyhydroxides (Lottermoser, 2010c). The remainder of the ions in the weathering solution eventually reach saturation levels and precipitate as secondary minerals. Evaporation is a mechanism conducive to forming these secondary precipitates (Lottermoser, 2010c). Surficial secondary minerals are known as efflorescences and may be

found in waste piles, stream beds, seepage areas and pit walls (Lottermoser, 2010c). These can also form by capillary migration of water to the surface of tailings or waste-rock piles (Romero et al., 2006).

The characteristics of the secondary precipitates formed in these environments are dependent on variations in conditions such as pH, Eh and T (Carbone et al., 2013). Efflorescence minerals are highly soluble, and may disappear with the arrival of the first rains and precipitate during dry periods (Romero et al., 2006; Keith et al., 2001). Oxidation, dehydration and neutralization reactions control the precipitation of efflorescent sulfates (Romero et al., 2006; Jambor et al., 2000). As such, changes in redox potential, humidity and temperature will cause changes in mineralogy (Romero et al., 2011; Frau, 2000; Jamieson et al., 2005).

Mechanisms of adsorption or coprecipitation significantly decrease the mobility of the elements in acid mine waters thereby temporarily naturally attenuating aqueous concentrations in mine effluent (Lottermoser, 2010c). Simple hydrous metal sulfates are generally soluble and easily release stored metals into mine waters when dissolved (Lottermoser, 2010c).

Various studies have analyzed and described the types of secondary precipitates formed at ARD settings (Nordstrom and Alpers, 1999; Lottermoser, 2010d; Buckby et al., 2003; Frau, 2000; Jönsson et al., 2006; Buurman, 1975). Lottermoser (2010a) describes the general mechanisms of the formation of secondary minerals in ARD environments. Carbone et al. (2013) describe minerals that can form in ARD settings and classify them into three broad groups:

1. Fe-oxides, -oxyhydroxides, and –oxyhydroxysulfates, and other low crystallinity Fe phases including ferrihydrites, goethite, hematite, schwertmannite, and jarosite
2. Hydrous Ca- Fe, Al- and other metal-sulfates including gypsum, melanterite, copiapite, halotrichite, chalcantite, epsomite
3. Other metal-rich phases

These minerals all have specific Eh and pH stability fields that occur in ARD environments (Carbone et al., 2013). Fe-sulfate-rich evaporative minerals from a specific deposit in Spain were analyzed by Buckby et al. (2003). Melanterite ($\text{Fe}(\text{SO}_4) \cdot 7(\text{H}_2\text{O})$), rozenite ($\text{Fe}(\text{SO}_4) \cdot 4(\text{H}_2\text{O})$), rhomboclase ($\text{HFe}(\text{SO}_4)_2 \cdot 4(\text{H}_2\text{O})$), szomolnokite ($\text{FeSO}_4 \cdot (\text{H}_2\text{O})$), copiapite ($\text{Fe}^{2+}\text{Fe}^{3+}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20(\text{H}_2\text{O})$), coquimbite ($\text{Fe}^{3+}_2(\text{SO}_4)_3 \cdot 9(\text{H}_2\text{O})$), hexahydrite ($\text{Mg}(\text{SO}_4) \cdot 6(\text{H}_2\text{O})$), halotrichite ($\text{FeAl}_2(\text{SO}_4)_4 \cdot 22(\text{H}_2\text{O})$) and gypsum ($\text{Ca}(\text{SO}_4) \cdot 2(\text{H}_2\text{O})$) were identified on the banks of the Rio Tinto for the first time in the study by Buckby et al. (2003). The formation-dissolution and precipitation cycle of melanterite from the Genna Lucas mine in Italy was analyzed by Frau (2000). The paragenetic sequence of ARD minerals formed in laboratory experiments by evaporating acid mine waters is also observed, alongside field observations (Frau, 2000; Buurman, 1975).

2.3 The sulfate system: Compositions of hydrated metal sulfate salts

Sulfate is formed by the oxidation of sulfide minerals. Sulfate concentrations in mine drainage are generally higher than concentrations of Fe and other metals since few natural processes remove dissolved sulfate from ground and surficial waters (Jambor et al., 2000). Sulfate minerals in tailings and around mine sites are typically dominated by Fe since oxidation of Fe-sulfide releases both Fe and SO_4 . Magnesium-dominant sulfates form where gangue minerals contain dolomite or other relatively soluble Mg-bearing minerals (Jambor et al., 2000). Hydrated sulfate minerals with divalent cations, trivalent cations and those salts that contain both divalent and trivalent cations have been studied by Jambor et al. (2000). Gypsum most likely formed from the reactions between sulfuric acid and Ca-rich minerals (Deer et al., 1992).

Simple hydrated salts with divalent cations have the chemical formula $\text{Me}^{2+}(\text{SO}_4) \cdot n(\text{H}_2\text{O})$. Experiments show that “ n ” decreases with relative humidity and water activity, and increases with temperature and acidity of the solution (Jambor et al., 2000). Hydrated metal sulfate salt groups with divalent cations include: Melanterite group, epsomite group, hexahydrite group, chalcantite group,

rozenite group, kieserite group (Jambor et al., 2000). As noted by Nordstrom and Alpers(1999), at metal concentrations of 10^{-6} molar, metal hydroxides are likely to precipitate in the following sequence with increasing pH: Fe^{3+} , Pb, Al, Cu, Zn, Fe^{2+} , and Cd. Hydrated metal sulfate salts with trivalent cations include minerals such as: Lausenite ($\text{Fe}^{3+}_2(\text{SO}_4)_3 \cdot 6(\text{H}_2\text{O})$), kornelite ($\text{Fe}^{3+}_2(\text{SO}_4)_3 \cdot 7(\text{H}_2\text{O})$), coquimbite ($\text{Fe}^{3+}_2(\text{SO}_4)_3 \cdot 9(\text{H}_2\text{O})$), paracoquimbite ($\text{Fe}^{3+}_2(\text{SO}_4)_3 \cdot 9(\text{H}_2\text{O})$), quenstedtite ($\text{Fe}^{3+}_2(\text{SO}_4)_3 \cdot 11(\text{H}_2\text{O})$), alunogen($\text{Al}_2(\text{SO}_4)_3 \cdot 17(\text{H}_2\text{O})$) and meta-alunogen ($\text{Al}_4(\text{SO}_4)_6 \cdot 27(\text{H}_2\text{O})$) (Jambor et al., 2000). Hydrated metal sulfate salt groups with divalent and trivalent cations include: Halotrichite group, and copiapite group (Jambor et al., 2000).

Secondary precipitates such as chalcantite ($\text{Cu}(\text{SO}_4) \cdot 5(\text{H}_2\text{O})$), jarosite ($\text{KFe}^{3+}_3(\text{OH})_6(\text{SO}_4)_2$), scorodite ($\text{Fe}(\text{AsO}_4) \cdot 2(\text{H}_2\text{O})$), and Fe-sulfate salts have been observed at other HS epithermal deposits (Bowell et al., 2000). Halotrichite, melanterite and szomolnokite have also been documented at this type of deposits (Bowell et al., 2000). A wide array of secondary precipitates have been identified at tailing impoundments in arid climates including several Fe and Mg salts of the $\text{Me}^{2+}\text{SO}_4 \cdot n\text{H}_2\text{O}$. Some rare minerals such as blodite ($\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4(\text{H}_2\text{O})$) and hydrobasaluminite ($\text{Al}_4(\text{SO}_4)(\text{OH})_{10} \cdot 15(\text{H}_2\text{O})$) have been identified in Australia (Jambor et al., 2000).

The incorporation of trace elements in sulfate salts has been presented in various studies (Buckby et al., 2003; Romero et al., 2006, 2011; Jamieson et al., 2005). Buckby et al. (2003) have studied secondary minerals along the margins of the acidic Rio Tinto during 3 field seasons. Minerals were identified using XRD, SEM and ICP-AES, and melanterite displays high Cu (1.6 wt%) and Zn (1.0 wt%) concentrations. Frau (2000) Jambor et al. (2000), Hammarstrom et al. (2005), Peterson (2003) and Peterson et al. (2006) have discussed the ability of melanterite to sequester Cu and Zn. Melanterite has a structure that comprises a flexible array of metal-containing octahedra that are held together by hydrogen bonds and can incorporate divalent transition metals (Peterson, 2003).The results of chemical analyses conducted by

Peterson (2003) including electron microprobe (EMPA) work and ICP-MS on natural and synthetic samples, demonstrate that the composition of melanterite ranges from Fe end-member to some samples with equal amounts of Fe, Cu, Zn. Jamieson et al. (1999) identified maximum Zn concentrations of 22 wt% in melanterite, 17.4 wt% in szomolnokite, 7.6 wt% in voltaite and 1.0 wt% in romerite from samples collected at Iron Mountain and analyzed with the EMPA and microPIXE. In general terms, the substitutions of elements into the hexahydrate lattice are comparable to melanterite because of the similarity in crystal structures; however little is known about the limits of solid solution in hexahydrate (Buckby et al., 2003; Jambor et al., 2000). Romero et al. (2006) studied mineralogy and geochemistry of efflorescent sulfates that had precipitated along the acidic streams draining from the abandoned Pena del Hierro mine in Southwestern Spain. Samples were analyzed by XRD, SEM and XRF (X-ray fluorescence), and their results demonstrate that there is a replacement of Mg by Fe (0.68-1.74 wt%) and Mn (up to 0.62 wt%) in hexahydrate.

Studies by Manceau et al. (2000), have analyzed the crystal chemistry of trace elements in natural and synthetic goethite with the use of X-ray absorption fine structure spectroscopy (EXAFS) at the European Synchrotron Radiation Facility. These researchers have found Cr (0.73 wt%), Mn (0.88 wt%), Co (0.166 wt%), Ni (0.898 wt%), Cu (0.263 wt%) and Zn (0.026 wt%) in goethite. Jamieson et al. (2005) studied major and trace element compositions of copiapite-group minerals from Richmond mine in Iron Mountain, California using analytical techniques such as SEM, EMPA, microPIXE, and XRD. Copiapite-group minerals, which generally occur in the oxidation zone of sulfidic iron ore and massive sulfide deposits, may store Zn (0.142 wt%), Cu (0.027 wt%) and As (0.0064 wt%) (Jamieson et al., 2005). Arsenic has been assumed to substitute for SO_4^{2-} as AsO_4^{3-} in copiapite, but has also been suggested for jarosite (Dutrizac et al., 1987; Savage et al., 2005). Hydronium and Na substitution for K (15-25 mol%) in jarosite has also been noted by (Alpers and Brimhall, 1989; Dutrizac and Jambor, 2000; Robinson, 2000; Stoffregen et al.,

2000) with the use of NMR techniques. Furthermore, Cu, Zn and Pb can substitute for Fe^{3+} in the jarosite structure (Dutrizac et al., 1987). Solid solution in the alunite group exists between Fe^{3+} and Al^{3+} (Dutrizac et al., 1987). Stoffregen et al. (2000) have determined that the most significant substitution in alunite is that of Na^+ for K^+ . These authors also state that alunite from Goldfield samples contain up to 0.2 wt% BaO and 0.05 wt% P_2O_5 . It is not specified whether alunite in question is of primary or secondary nature.

Experimental neutralization of waters by Munk et al. (2006) shows that Pb, Cu, Zn, Ni are sorbed onto Al-hydroxysulfate minerals with increasing pH. They added a saturated solution of NaOH obtaining final pH values of 4.2, 4.8, 5.7, 6.0, 6.4 and 6.7. These solutions were stirred and measured daily until pH had stabilized. The increase in pH caused precipitates to form, and their experiments demonstrate that the sorption sequence is as follows, with a steady increase in pH: Pb, Cu, Zn, Ni. Finally, studies by Sracek et al. (2010) have previously identified small amounts of Co (2.28 wt%) and Mn in blodite based on energy-dispersive spectra.

Table 2-1 A list of a few secondary precipitates and their potential trace element compositions. The methods used to identify the compositions as well as references are included. Where there are no concentrations, the presence of the trace elements have been identified but the concentrations have not.

Secondary minerals precipitated from ARD	Measured trace element compositions	Methods	Reference
Melanterite	Cu (1.6 wt%), Zn (1.0 wt%), Ni, Mg (7.45wt%),	XRD, SEM, XRD and ICP-AES	Buckby et al., 2003; Peterson, 2003
Hexahydrite	Ni, Fe (0.68-1.74wt%), Mn (<0.62wt%)	XRD, SEM, XRF	Janijic et al., 1980
Copiapite	Zn (0.142wt%), Cu(0.027wt%), As (0.064wt%)	SEM, electron microprobe, micro-PIXE, XRD	Jamieson et al., 2005; Jamieson et al., 1999
Goethite	Cr (0.73wt%), Mn (0.88wt%), Co (0.166wt%), Ni (0.898wt%), Cu(0.263wt%) and Zn (0.026wt%)	XAFS	Manceau et al., 2000
Jarosite	AsO_4^{3-} , H_3O^+ , Cu (2wt%), Zn (2.1wt%), Pb (6.3wt%)	NMR	Dutrizac et al., 1987; Savage et al., 2005
Coquimbite	Al (0.56wt%-0.74wt%)	XRD, SEM, XRD	Romero et al., 2006; Jambor et al., 2000
Al-hydroxysulfates	Pb, Cu, Zn, Ni	ICP-MS, ICP-OES	Munk et al. 2006

The thermodynamic conditions of minerals allow the researcher to know if the minerals are likely to occur at the given sample site, they are also necessary to evaluate the role of the given minerals in

acidic waters and to model reaction pathways. Although Majzlan et al. (2006) have studied the thermodynamic properties and crystal structures of ferricopiapite, coquimbite and rhomboclase, significant gaps persist in literature with regards to our understanding of the thermodynamic description of sulfate mineral assemblages in ARD environments. Furthermore, very little thermodynamic data exists for Fe^{3+} and mixed Fe^{2+} - Fe^{3+} sulfates, as well as Na-Mg oxyhydroxide sulfates.

2.4 Sulfate and ARD water treatment

Regulations concerning the maximum allowable sulfate in drinking water varies worldwide (92 countries) from 250 to 500 mg/L (Philippe and Kirk, 2015). It is well-known that drinking water containing sulfate concentrations greater than 600 mg/L result in laxative effects, especially in infants. The World Health Organization recommends concentrations of sulfate to be less than 500 mg/L in drinking water (Philippe and Kirk, 2015). The Canadian standards for drinking water are at 500 mg/L (Health Canada, 2011). The Peruvian standards for irrigation and drinking water standards are 300 mg/L and 500 mg/L respectively (DIGE-SA, 1998). These are values that Barrick Gold Corporation must meet in its waste water effluent. Presently, ARD from mine waste is not strictly regulated for sulfate in Chile and these values are highly dependent on environmental authorities.

Rigorous regulatory standards for sulfate in mine effluent waters in South America amplify the necessity of sulfate treatment at the Barrick Gold Corporation mines in this study. The current treatment processes that are used to reduce sulfate in mine effluent waters include: (1) chemical treatment with mineral precipitation (i.e. lime or limestone addition, barium salt addition, (2) membrane exclusion technology (i.e. reverse osmosis, electrical dialysis reversal), (3) ion exchange, and (4) biological sulfate removal (i.e. bioreactors, wetlands, alkalinity producing systems (Dupon and Figueroa, 2015)). In many cases, a combination of these processes is applied for maximal results. These processes are selected for discussion based on their applicability for sulfate removal, and availability of data from pilot plants or larger field-trials.

Ion exchange (IX) is a process that uses the adsorption of ions of a specific charge in a solution onto the surface of a solid material, the ion exchange resin (MEND, 2014). The resin used is insoluble in water but it is hydrated and may be a salt, acid or even a base (MEND, 2014). Resins are typically designed to selectively remove one or few parameters and are selected based on their affinity for certain metals. As such, numerous ion exchange steps and different types of resins are necessary to achieve the removal of a large number of parameters.

Neutralization using hydrated lime (Ca(OH)_2) is the most common technology used for acid neutralization and removal of metals from effluent as a result of its low cost. Lime neutralization produces sludge that contains metal contaminants as metal hydroxides and can precipitate many species (MEND Treatment Committee, 2013). In the HDS process, hydroxide minerals are formed with the metals as large and dense particles that can readily settle (Aube, 2004). In a conventional treatment plant, the slurry is sent to a clarifier for physical solid and liquid separation (Aube, 2004).

Membrane exclusion technology such as nanofiltration removes dissolved parameters (i.e. Al, As, Fe, Pb, Mn, Ni, Zn, SO_4 , etc.) from solutions with a pressurized application of the effluent to a charged and selectively permeable membrane. Nanofiltration has been described to remove 95% of targeted ions or molecules in effluent. Efficiency of membrane exclusion technologies depend on effluent quality and the concentration and types of parameters found in the feed.

2.5 Solubility of secondary minerals and stability relationships

The type of secondary minerals formed at mine sites is controlled by the composition of the waste, creating a range in solubilities between minerals formed where some are susceptible to dissolution more readily than others (Lottermoser, 2010c; Frau, 2000). HS epithermal deposits are most likely to contain Fe, Al and metal-rich sulfate salts. Research by Lottermoser (2010) states that simple hydrous metal sulfates are soluble in water; however, Fe and Al hydroxysulfates are relatively insoluble. Poor solubility

minerals are sinks and their precipitation may be effective control on the amount of SO_4 , Ba, Sr and Pb in acidic solutions (Lottermoser, 2010c).

The most common secondary minerals are water soluble hydrous metal sulfates with divalent cations ($\text{Me}^{2+}\text{SO}_4 \cdot n\text{H}_2\text{O}$), where Me can be Ca, Mg, Fe, Mn, Co, Ni, Cu or Zn and $n=1$ to 7. Furthermore, these hydrous sulfates may dehydrate to less hydrous compositions which tend to be more stable with an increased resistance to dissolution (Lottermoser, 2010). A common example observed in the field is melanterite precipitating ($\text{Fe}(\text{SO}_4) \cdot 7(\text{H}_2\text{O})$) to be subsequently dehydrated to rozenite ($\text{Fe}(\text{SO}_4) \cdot 4(\text{H}_2\text{O})$) or szomolnokite ($\text{Fe}(\text{SO}_4) \cdot (\text{H}_2\text{O})$) (Lottermoser, 2010). Furthermore, Fe^{2+} sulfates will oxidize to Fe^{2+} - Fe^{3+} sulfate salts and then Fe^{3+} sulfate salts (Lottermoser, 2010c; Jambor et al., 2000).

Elements that form oxy-anions in water such as As, Se, Sb, Mo, V, W, are relatively mobile under neutral pH conditions (Lottermoser, 2010b). This implies that lime addition may not be enough to control the mobility of certain elements. Minerals whose solubilities are likely to control metal concentrations in mine waters are listed in Table 2-2. The list is created from Nordstrom and Alpers (1999) out of modeling experience and is meant as a guide.

Table 2-2 Minerals whose solubilities are likely to control metal concentrations in mine waters (Nordstrom and Alpers, 1999).

Solubility equilibrium likely	Solubility equilibrium possible
alunogen	alunite
anglesite	ankerite
basaluminite	antlerite
calcite	atacamite, paratacamite
cerussite	azurite
chalcantite	bronchantite
epsomite	chrysocolla
ferrihydrite	goethite
gibbsite	hemimorphite
goslarite	hematite
gypsum	hydrozincite
halotrichite	jarosite
manganese oxides	kaolinite
melanterite	kutnohorite
otavite	malachite
rhodochrosite	natroalunite
schwertmannite	natrojarosite
scorodite	plumbojarosite
siderite	
silica	
smithsonite	
witherite	

2.6 Effects of climate on sulfates

The presence of soluble secondary minerals is directly influenced by climate (Jambor et al., 2000). For example, in humid conditions, soluble sulfate minerals may not accumulate. Dissolution of formed sulfates increases significantly during storm runoff, thereby increasing the concentrations of dissolved metals and sulfate (Jambor et al., 2000). The dissolutions of sulfates give a rapid geochemical response following the first storm of the wet season (Jambor et al., 2000; Keith et al., 1998; Keith et al., 1999). Moreover, (Dagenhart, 1980) and (Alpers et al., 1992) attribute changes in metal and sulfate concentrations, as well as Zn/Cu ratios through seasonal wet and dry cycles to the dissolution and reprecipitation of metal-sulfate salts. Nordstrom (2009) has studied the influence of climate change on

ARD based on data collected from mines in the United States and internationally. In his research, the dynamic changes in concentrations are highlighted and are related to the dissolution of soluble salts and flushing out of waters that were previously concentrated by evaporation. A large increase in concentrations is during the first flush, the discharge following dry spells. An increased amount of droughts are associated with climate change, Hence, flushing of mine sites will cause larger sudden increase in concentrations that can deem deadly for the surrounding biosphere.

2.7 Microbiological activity

Although this project does not directly deal with microbial characterization, biogeochemical processes are of equal importance to ARD waters as they directly or indirectly impact the chemistry of ARD waters. Such processes can occur in surface and underground waters (Lottermoser, 2010). ARD waters cannot support normal aquatic biota and the diversity of plants is limited; however, these waters display ubiquitous microorganisms (Archaea, Bacteria, Eukarya).

Specifically, extremophiles thrive in these acidic conditions. A case study by Ariza (1998) identifies over 1300 microorganisms in the acidic waters of the Rio Tinto in Spain. These microorganisms are able to survive and thrive because they can tolerate high concentrations of dissolved metals and metalloids, and they use the energy from chemical oxidation reactions for growth (Lottermoser, 2010). These microbes can remove metals and metalloids through adsorption and precipitation processes. The bacterium *Acidithiobacillus ferrooxidans* oxidizes Fe^{2+} , which allows the precipitation of iron as iron oxides and hydroxides (Lottermoser, 2010; Ferris et al., 1989).

2.8 Environmental geology of HS epithermal deposits

Hs epithermal deposits are acid generating and contains a high potential for the release of potentially toxic elements. Pathfinder elements associated with this type of deposit include As, Sb, Bi, Hg, Te, Sn, Pb, Mo and Se, which are all considered potentially hazardous as dissolved elements in mine

drainage (Hedenquist et al., 1994). The geological, mineralogical and geochemical characteristics described in the previous chapter influence the environmental behavior of elements and altered rocks. Secondary precipitates such as chalcantite, jarosite, scorodite, Fe-sulfate salts, halotrichite, melanterite and szomolnokite have also been documented at this type of deposits (Bowell et al., 2000).

The high acid generating capacity of this type of deposit is a reflection of its high sulfide content and low amount of carbonates. The minimal amount of neutralizing potential is only observed in the peripheral zones of the deposit, where propylitic alteration, or where post-deposit carbonate overprint has been created (Bowell et al., 2000).

2.9 Previous geochemical characterization at mines

2.9.1 Pierina

Previous geochemical characterization work at this mine site was conducted by Klohn Crippen Berger in 2012. It has been noted that contact waters pre-treatment are described as a Ca-Fe-Al-H-SO₄ system and most parameters are above Peruvian water quality guidelines. Studies of temporal variations demonstrate that acidity at monitoring stations are increased during the wet season as a result of dissolution and flushing of secondary acidic minerals. Secondary minerals identified in this study include alunite (KAl₃(SO₄)₂(OH)₆), calcite (CaCO₃), gypsum (Ca(SO₄)), chalcantite (Cu(SO₄)·5(H₂O)), paracoquimbite (Fe³⁺₂(SO₄)₃·9(H₂O)), coquimbite (Fe³⁺₂(SO₄)₃·9(H₂O)), zincocopiapite (ZnFe₄(SO₄)₆(OH)₂·18(H₂O)), brochantite (Cu₄(SO₄)(OH)₆), antlerite (Cu₃(SO₄)(OH)₄) and posnjakite (Cu₄(SO₄)(OH)₆·(H₂O)). With the identification of these minerals, assuming ideal mineral lattice, it was shown that K, Al, SO₄, Ca, C, Cu, Fe and Zn are attenuated by secondary mineral precipitation. Authors claim that Cu, Co, Mn, S, Al, Si, Na, Pb and Mn can also become attenuated as a result of substitution or sorption.

2.9.2 Lagunas Norte

Roscoe Postle Associates Inc. has conducted extensive geological research on the Lagunas Norte Mine (Evans et al., 2012). The main goal of the report was to support public disclosure of the mineral resource and mineral estimates at the Lagunas Norte project. This document also touches on the environmental considerations taken at the mine site, stating that “the environmental and social practices at Lagunas Norte appear to be very effective”(Evans et al., 2012). Water monitoring is conducted at 31 points throughout the mine. Although geochemical characterization of primary minerals has been conducted (Cerpa et al., 2013; Lacroix, 2012; Montgomery, 2012), no previous research is piloted on the geochemical characterization of waters or the secondary precipitates observed on site. Montgomery (2012) does state that approximately 85% of this deposit has been oxidized, and that the Au is hosted in goethite, hematite, and jarosite.

2.9.3 El Indio

The geology, genesis and tectonic settings of the El Indio belt and deposit have been extensively studied (Back and Walford, 1996; Oyarzun et al., 2007, 2004; Jannas et al., 1990; Bissig et al., 2003; Heberlein, 2008; Kerrich et al., 2005; Martin et al., 1999); however, there is a lack of research with regards to the secondary minerals that have formed and water chemistry. Szomolnokite, gypsum, anglesite ($\text{Pb}(\text{SO}_4)$), and barite ($\text{Ba}(\text{SO}_4)$) have been previously identified as post-ore minerals and possibly secondary mineral at localities along the El Indio mineralization belt (Chouinard et al., 2005).

2.10 Synchrotron micro-analysis

No samples collected from Lagunas Norte, Pierina or El Indio have previously been analyzed with synchrotron techniques. As described by Jamieson et al. (2011), synchrotron microanalysis is a powerful diagnostic tool that can be used to characterize metal-bearing particles in mine tailings, soils, and even lake sediments. Specifically, combined experiments of X-ray fluorescence and diffraction, as well as

absorption that use a microfocused beam lead to a detailed understanding of elemental concentration, crystal structure, and oxidation state of particles (Jamieson et al., 2011). Synchrotron microanalysis is not a readily available technique, therefore, not much research focusing on secondary sulfates use this tool. The crystal chemistry of goethite from a saprolite formation has been measured and analyzed by fluorescence-yielding extended X-ray absorption fine structure (EXAFS) spectroscopy with use of the European Synchrotron Radiation Facility (ESRF) (Manceau et al., 2000). Synchrotron XRD patterns of ferric sulfates were collected by Majzlan et al. (2006) for their study on the thermodynamic properties and crystal structure refinement of minerals ferricopiapite, coquimbite, rhomboclase and $\text{Fe}_2(\text{SO}_4)_3 \cdot 5(\text{H}_2\text{O})$. This research used synthetic material for all the compounds with the exception of coquimbite, which was a natural specimen.

2.11 Hypotheses

The hypotheses of this research are based on the literature review:

- 1- Minerals common in ARD such as Fe and Al oxides and oxyhydroxides, and metal sulfates will be prevalent at these sites because they are influenced by the chemical compositions of the effluent from HS epithermal deposits which tend to be enriched in sulfate and metals.
- 2- Trace elements will be partly attenuated by minerals where they form a major constituent and in association with Fe and Al oxides.
- 3- The expected complexity of these samples may influence the ability to associate the trace elements to the secondary minerals.
- 4- Because the minerals and waters are not always in direct contact with one another, a relationship with regards to specific chemistry is not expected. Field observations will be used to evaluate whether the water and minerals sampled are likely to be in equilibrium and this will be tested using speciation modelling.

- 5- Using various analytical techniques is expected to be important because previous studies have suggested that characterization of secondary precipitates requires techniques that provide information at various scales will be used to reconfirm the occurrences of specific minerals at various scales.
- 6- If Barrick Gold Corporation recovers a substantial amount of metals from the effluent, then they will be able to offset water treatment costs. Elemental concentrations, flow rates, as well as recovery and treatment costs will be considered to test this hypothesis.

Chapter 3

Sampling and analytical methods

3.1 Waters

3.1.1 Sampling methods

Figure 3-1: Sampling and water analysis at Lagunas Norte

Sample locations were chosen based on the availability of coexisting drainage waters, secondary precipitates and biofilm, and ease of field accessibility. With one exception, the sites were upstream of treatment points. Prior to field work and sample collection, the YSI 556 MPS Multi-Probe Field Meter was calibrated for all the field variables measured. Surface waters were collected into 1 liter bottles that were rinsed with the sample 3 times prior to collection to avoid contaminants. Temperature, pH, Eh, dissolved oxygen (DO) and conductivity were measured immediately after collection with the YSI 556 MPS Multi-Probe Field Meter. Calculated

pe used in modeling was determined from measured ORP recorded in the field. These waters were filtered with 0.45 μm syringe filters in the field and then divided into aliquots for cations, anions, Fe speciation, sulfate content, and alkalinity. Additional unfiltered and acidified aliquots were collected at Pierina and Lagunas Norte to determine the amount of suspended material in the samples. Finally, two blanks were created at each mine site. The first, an acid blank, where HNO_3 was added to deionized water. The second was a sample blank, where the deionized water was filtered prior to 1% HNO_3 acidification. The samples collected for the purpose of metal analyses were acidified to 1% with 8N HNO_3 . Fe speciation and sulfate content were determined by spectrometry with a HACH DR/2400, within 12 hours of collecting the samples. Table 3-1 lists the types of water samples that were collected from all mine sites, where UA is

unfiltered and acidified, FA is filtered to 0.45 µm and acidified, FU is filtered and unacidified and FFA is ultrafiltered to 0.01 µm.

3.1.1.1 El Indio

The initial sampling strategy was to target sites with low pH and high concentrations of dissolved metals and sites that are representative of mine drainage. Target sampling locations were primarily chosen based on field accessibility, flow of water, and anticipated orders of magnitude of exceedances of elements of concern, based on previous data. These sites were analyzed from the furthest upstream location (IN-23) to the furthest downstream location (IN-13), so as to identify change in water conditions and quality (pH, TDS, ORP) (Figure 3-3, Figure 3-4).

3.1.1.2 Lagunas Norte

Seven sites were visited for sampling and included LN-DAR-1, LN-SP-3 (twice), LN-DW-B-11, ARD water treatment plant, LN-PW-1, LN-BP, LN-PW-2 and LN-VWD. These sites were chosen because the waters are representative of mine drainage (Figure 3-5, Figure 3-6). Some of these locations have long data sets collected by Barrick Gold Corporation for comparison and most are in contact with secondary precipitates.

3.1.1.3 Pierina

The sites visited include P-WRD and P-ARD-17, the pit dewatering station (P-PD) and pit runoff in the Emilio Cocha pond (P-EC). YSI measurements were taken at various streams that provide input to these ponds with the goal of observing different properties of the waters and effects on the geochemistry of the pond. These sampling points were chosen based on being representative of mine drainage and pre-existing data sets collected from Barrick Gold Corporation, required water flow and field accessibility. A description of the samples taken at the 3 mines is provided in Table 3-1, the sampling locations are specified in Appendix A.

Table 3-1: Water sampling locations, description and elevation (m).

	Sample no.	Description	Elevation (m)
El Indio	IN-23	Natural ARD upstream of mine tailings/stream	4100
	IN-28	San Pablo closed tunnel downstream from tailing	3650
	IN-RMATR	Upstream from settling pond	3550
	IN-2	Downstream from settling pond	3250
	IN-13	Downstream from settling pond	2080
Lagunas Norte	LN-DAR-1	Confluence of surface and understrain acid rocks	4200
	LN-DW-B-11	Pit dewatering station	3903
	LN-SP3-W1	Settling pond	4007
	LN-SP3-W2	Settling pond second sample.	4007
	LN-PW-1	Pit wall (no ARD)	3683
	LN-BP	Blessed pond, bottom of the open pit	3957
	LN-PW2	Pit wall (almost pH neutral)	3926
Pierina	LN-VWD	Waste rock leachate before collection pond (Vizchaz pond 1) for treatment	3951
	P-WRD	Waste rock drainage	4104
	P-ARD-17	closed portal of old mine	3867
	P-PD	Pit dewatering station	3842
	P-PW1	Pit wall 1	3847
	P-PW2	Pit wall 2	3851
	P-EC	Bacrock stream draining wetland going into mine pit (Emilio Cocha)	3813

3.1.2 Ultrafiltration

Ultrafiltration to 0.01 μm was conducted on all 7 samples from Lagunas Norte and all 4 samples from Pierina to determine how much colloidal material was present in the samples. The ultrafiltration technique was used to collect colloidal particles present in solution. Initially, tweezers and the ultrafiltration cell were cleaned with dilute HCl (1 N) to get rid of any trace metals. These were then rinsed with deionized water and the filter was added, shiny side up, ensuring that no creases were created on the surface. Finally, the “O” ring was placed holding the polycarbonate filter to the apparatus (Figure 3-2). The top-most, tube-like piece was then screwed on by applying pressure. Once the setup was complete, deionized water was filtered through the unit. N_2 gas at 30 psi was used to increase pressure and allow

the solution to readily pass through the filter. With all the deionized water passed through, a separate receptacle was placed to capture the filtrate. Finally, filtrates from Lagunas Norte and Pierina mines were forced through a polycarbonate membrane with pore sizes of $0.01\ \mu\text{m}$, separating colloids from dissolved elements and solution. Ultrafiltration was not conducted at El Indio due to unavailability of N_2 gas. It is assumed that $0.01\ \mu\text{m}$ filtrate is dissolved since these are the smallest available membranes. The full procedure can take anywhere between 1-3 hours per sample.

Figure 3-2 A schematic representation of the ultrafiltration method. A $0.01\ \mu\text{m}$ filter paper was placed in the filtration cell and was stabilized with an “O” ring placed on top.

3.1.3 Laboratory analyses

Water analysis for dissolved metals and anions was conducted at the Analytical Services Unit of Queen’s University. Metals were measured by inductively coupled plasma- mass spectrophotometry (ICP-MS) for 60 elements (Al, Ag, As, B, Ba, Be, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Ho, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, P, Pb, Pd, Pr, Pt, Rb, Rh, Re, Ru, S, Sb, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, U, V, W, Y, Yb, Zn, Zr) and by inductively coupled plasma optical emission spectroscopy (Varian,

AX-Vista Pro CCD Simultaneous ICP-OES) for 30 elements (Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Ce, Sn, Sr, Ti, Tl, U, V, Zn). Determination of anions (SO_4^{2-} , Cl^- , F^- , NO_3^- , NO_2^-) was conducted by ion chromatography.

3.1.4 PHREEQC

Saturation indices for minerals were calculated for these waters using PHREEQC 3 software (Parkhurst & Appelo, 2013). This geochemical modeling program designed and distributed by the US Geological Survey calculates saturation indices using the formula: $\text{SI} = \log_{10} (\text{IAP}/K_T)$ where IAP represents the activity product of the ions that are produced by the dissolution of the mineral and K_T is the equilibrium constant (Went et al., 1999). The ICP-MS analyses for both 0.45 μm and 0.01 μm filtrates were entered into PHREEQC to determine the phases that are most likely supersaturated and speciation of elements. PHREEQC input included 25 elements (O, F, Cl, N(+3), N(+5), S(6), Al, As, Ba, B, Cd, Ca, Cu, Fe, Pb, Li, Mn, Ni, K, Rb, Na, Sr, U, Zn), as well as temperature, pe and pH. Hence, 38 elements that were analyzed by ICP-MS and ion chromatography were not included in the WATEQ4F database, and therefore not considered in SI and speciation analyses. Elements exceeding a SI of 0 have likely precipitated out of solution and should be found in XRD analysis of bulk samples. Because these calculations are approximations, minerals or species >0 SI can be considered as potentially saturated. These values were entered in mg/L into the program.

Evaporation simulations were also conducted to understand the paragenetic sequence of secondary minerals and were accomplished by removing water from the chemical system in PHREEQC. In order to do so, water was specified as an irreversible reactant with a negative reaction coefficient in the “reaction” keyword input (Parkhurst & Appelo, 2013). Specifically, this method was used to simulate the concentration of solutions by 20-fold by removing 95% of the water. After the composition of the collected

sample is defined, the amount of water, in moles, to be removed from the aqueous phase is specified. In order to concentrate the solution 20-fold, 52.73 moles of water are removed.

3.2 Secondary precipitates

3.2.1 Sampling methods

Samples of secondary precipitates were carefully collected with a clean hand trowel and spatulas, wrapped in plastic film and placed in multiple self-sealed plastic bags with a low volume of air. This storage method was designed to create a micro-environment around the sample that would limit dehydration or deliquescence (Chou et al., 2013). Mineralogy at sites were spatially heterogeneous, as such, samples were collected based on obvious visual differences such as color and texture. Samples were kept chilled and were later sub-sampled and prepared for geochemical and mineralogical characterization. Figure 3-3, Figure 3-4, Figure 3-5, Figure 3-6, Figure 3-7 show sampled locations and images of secondary precipitates at El Indio, Lagunas Norte and Pierina.

IN28

IN-RMATR

Figure 3-3 Images of secondary precipitates sampled at El Indio and map (IN-28, IN-RMATR, IN-2). IN28 is a sampling location from San Pablo, a closed tunnel downstream from tailings. IN-RMATR is found upstream from the settling pond and IN-2 is downstream from settling pond. Red boxes indicate samples that were made into thin sections.

IN2

IN13

Figure 3-4 Images of secondary precipitates sampled at El Indio and map (IN-13, IN-2). Samples from IN-2 and IN-13 are collected downstream from the settling pond. Sample site IN-13 is located the furthest downstream. Red boxes indicate samples that were made into thin sections.

LN-DAR-1

LN-SP-3

LN-PW1

LN-PW2

LN-VWD

Figure 3-5 Images of secondary precipitates sampled at Lagunas Norte and map (LN-DAR-1, LN-SP-3, LN-PW1, LN-PW2, LN-VWD-P1, LN-VWD-P2). Sample site LN-DAR-1 is representative of the confluence of surface and underdrain ARD. LN-SP3 is a sampling site found at the settling pond, LN-PW1 and LN-PW2 are collected from the pit wall. LN-VWD is a sample from the waste rock leachate before the collection pond. The red box indicates samples that were made into thin sections.

Figure 3-6 Aerial image of Lagunas Norte (left) and solid and water sampling sites (right). LN-DAR-1 is representative of the confluence of surface and underdrain ARD. LN-SP3 is a sampling site found at the settling pond, LN-PW1 and LN-PW2 are collected from the pit wall. LN-VWD is a sample from the waste rock leachate before the collection pond.

Figure 3-7 Images of secondary precipitates sampled at Pierina and map (P-WRD, P-EC, P-PW1, P-PW2). Secondary precipitates were only collected from sample site P-PW1, which is located along the pit wall. Sample site P-WRD is representative of waste rock drainage, P-EC is a sampling site along the Emilo Cocha pond, P-PD is a pit dewatering station and P-ARD-17 is located at the closed portal of the old mine.

3.2.2 Laboratory analyses

Analysis of secondary precipitates for cations was conducted at the Analytical Services Unit of Queen's University. Samples were manually crushed, using a clean mortar and pestle. A total of 1.5 g or more of each sample was sent to Analytical Services, where 0.5g were used per run, and 0.5g for replicate. Metals were measured by inductively coupled plasma- mass spectrophotometry (ICP-MS) for 60 elements (Al, Ag, As, B, Ba, Be, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Ho, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, P, Pb, Pd, Pr, Pt, Rb, Rh, Re, Ru, S, Sb, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, U, V, W, Y, Yb, Zn, Zr) and by inductively coupled plasma optical emission spectroscopy (Varian, AX-Vista Pro CCD Simultaneous ICP-OES) for 31 elements (Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Ce, Si, Sn, Sr, Ti, Tl, U, V, Zn). QA/QC of the analyzed samples is discussed in Appendix E: QAQC & chemistry of .

3.2.3 Thin section preparation

A thin film of Vaseline was applied to the bottom of a 10 dr vial. Secondary precipitates were then placed at the bottom of the vial with clean tweezers and were covered in Sealtronic epoxy made by System Three. These vials were covered and left to dry for 2 days. Vials with dried epoxy and sample were sent to Vancouver Petrographics to be made into thin sections. Thin sections were carefully separated from the glass slide using a razor blade.

3.2.4 Statistical analyses

Statistical analyses were performed using Spearman correlation matrices for bulk geochemistry results from ICP-OES analyses. Spearman rank correlation provides a distribution free measure of correlation between two variables (Bonett and Wright, 2000). This method is preferred over the Pearson correlation because it looks at the correlation between ranked values and not absolute values, and is therefore less influenced by outliers and non-normally distributed populations (Lehman, 2005). Elements

that demonstrated a high percentage of values that are below their detection limit were not included in the correlation matrices since unknown values could not be correlated. These functions were conducted using Excel and ioGasTM (REFLEX®).

3.2.5 Environmental scanning electron microscopy (ESEM)

Two types of samples were analyzed by ESEM: a) ultrafiltration filters b) mounted secondary precipitates (MSP). Ultrafiltration filters were mounted on carbon stubs and examined for colloids using the environmental scanning electron microscope FEI-MLA Quanta 650 FEG-ESEM at Queen's University. These stubs were carbon coated to enhance imaging quality and were examined under high vacuum conditions at 10KeV to image potential organic and inorganic colloids present and to prevent sample damage. Secondary precipitates were stuck on stubs using a modeling epoxy. These samples were carbon coated and examined under both high vacuum or low vacuum conditions depending on the amount of sample charging. The energy used on the secondary precipitates was 15 KV and 10KV.

3.2.6 Bulk X-ray diffraction (XRD)

The major crystalline phases present in collected samples were identified by using X-ray diffraction methods (XRD) with the Philips X-Pert diffractometer at Queen's University. Samples were crushed using a clean mortar and pestle as sample preparation. Secondary precipitates from the El Indio, Lagunas Norte, and Pierina mine sites were analyzed and the mineralogical phases were identified using PANalytical X-Pert Highscore Mineral Identification software.

3.2.7 Synchrotron micro-analysis

Micro-scale characterization of lifted thin sections of secondary precipitates mounted on Kapton[®] taped slide holders was conducted at synchrotron beamline 13-IDE at the Advanced Photon Source (APS), Argonne National Laboratory in Argonne, IL. This specific beamline is an undulator-based, hard X-ray microprobe instrument that emphasizes the application of X-ray microbeam analytical techniques for

research in geochemistry and environmental sciences (GSECARS, 2013). At the Sector 13-IDE beamline, analyses were conducted under micro-focused beam for μ XRD, and XRF mapping in August of 2014. This beamline has a spectral range from 2.4 to 28 KeV. The source of this beam is a 3.6 cm period undulator that is optimized to provide the abovementioned energy range. An X-ray energy of 17480 eV was used, with an intensity and flux of 1572×10^{11} Hz and 0.0104 μ A. The beam resolution can be smaller than $1 \mu\text{m}$. This X-ray energy allows for the excitement of elements K- and L- edge emissions are below that of Yttrium. Beam spot size was approximately 1 by $2 \mu\text{m}$, with μ XRF maps having a step (pixel) size of 3 to 25 μm and a dwell time of 20 milliseconds/pixel. Thin sections used were detached from the glass slide using a razor blade, and were mounted on Kapton™.

Micro-X-ray fluorescence mapping was performed to understand the general chemistry of the samples and hosts of metals. This mapping can analyze a large area of a sample for potential μ XRD samples. The 250 μ XRD diffraction patterns were all calibrated with Al_2O_3 and lanthanum hexaboride standards, their backgrounds were corrected, and finally converted to 2-D spectra using Fit2D (Hammersley, 2004). Finally, macro-crystallinity bright spots were masked and the 1-D diffraction pattern was integrated in order to allow accurate identification of phases.

Chapter 4

Results

4.1 Chemical characterization of waters

4.1.1 Bulk chemical analysis of waters

Waters analyzed at El Indio, Lagunas Norte and Pierina are typical acid sulfate waters normally seen in acid mine drainage. Waters draining from HS deposits are highly acidic and can contain very high concentrations of a variety of elements that have been leached from alteration zones, wallrock and ore minerals (Plumlee et al., 1999). Major elements are defined in this study as ≥ 100 ppm, minor elements are 100ppm-10ppm and trace elements < 10 ppm. Major elements in waters sampled from El Indio include

Ca and SO₄, minor elements include Na>Mg>Al>Mn>Cu>Fe>K, and trace elements are Zn>Sr>Pb>Co>As>Ni>Cd. Differences in elemental concentrations are observed at Lagunas Norte where major elements consist of SO₄>Ca>Fe>Al, minor elements comprise Mg>Cu>Zn>Na>Mn, and trace elements are Sr>K>As>Co>Ni>Pb>Cd. Finally, SO₄>Fe are the most concentrated elements at Pierina, with Mn>Mg>Zn>Cu as minor elements and K>As>Sr>Co>Pb>Cd>Ni as trace elements. The concentrations of all elements are listed in Appendix F: QAQC water and site specific chemistry will be discussed in section 4.1.2.

Table 4-1 Chemical analysis of filtered and acidified samples from El Indio demonstrating concentrations of major and minor elements in mg/L.

Sample	pH	Ca	SO ₄	Al	Cu	Mg	Mn	K	Fe	Na
Units		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
IN23-W	6.7	80	870	<0.0050	<0.0050	12	0.0015	1.1	<0.05	18
IN28-W	4.4	160	67	15	28	32	3.1	12	23	69
IN-RMATR-W	3.5	180	86	31	20	41	41	12	23	66
IN2-W	3.4	200	1050	46	16	51	7.5	10	13	65
IN13-W	4.3	250	995	24	8.5	62	5.2	15	3.6	180

Table 4-2 Chemical analysis of filtered and acidified samples from El Indio demonstrating concentrations of trace elements in µg/L.

Sample	pH	As	Co	Ni	Sr	Pb	Cd	Zn
Units		µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
IN23-W	6.7	2.87	<0.050	<1.0	807	<2.0	<0.030	<10
IN28-W	4.4	110	56	40	1000	450	9.1	1967
IN-RMATR-W	3.5	6.9	87	59	890	0.91	17	3800
IN2-W	3.4	2.4	110	77	843	1.0	19	4100
IN13-W	4.3	62	75	50	1100	0.33	11	2400

Table 4-3 Chemical analysis of filtered and acidified samples from Lagunas Norte demonstrating concentrations of major and minor elements in mg/L.

Sample	pH	Ca	SO ₄	Al	Cu	Mg	Mn	Fe	Na
Units		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
LN-SP3-W	2.9	120	690	47	9.5	17	5.8	48	12
LN-DW-B-11-W	2.8	78	845	28	110	3.9	2.2	170	15
LN-DAR-1-W	2.6	400	5400	380	17	130	40	640	27
LN-BP-W	3	31	190	6.25	3.8	2.8	0.965	13	16
LN-PW2-W	6.2	150	310	0.059	0.0075	3.8	0.0060	0.050	27
LN-VWD-W	2.6	500	3600	200	22	74	32.5	495	49.5

Table 4-4 Chemical analysis of filtered and acidified samples from Lagunas Norte demonstrating concentrations of trace elements in µg/L.

Sample	pH	As	Co	Ni	Sr	Pb	Cd	Zn	K
Units		µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
LN-SP3-W	2.9	10	150	140	610	30	34	2100	2400
LN-DW-B-11-W	2.8	1300	210	150	350	290	170	5100	1100
LN-DAR-1-W	2.6	920	933	870	2050	3.5	180	14000	1300
LN-BP-W	3	3.1	86	42	100	46	6.7	107	1700
LN-PW2-W	6.2	9.1	0.52	1.0	1000	0.23	0.16	10	377
LN-VWD-W	2.6	335	910	975	2950	6.8	130	7000	955

Table 4-5 Chemical analysis of filtered and acidified samples from Pierina demonstrating concentrations of major and minor elements in mg/L.

Sample	pH	Ca	SO ₄	Al	Cu	Mg	Mn	Zn	Fe	Na
Units		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
P-ARD-17-W	3.1	2.5	54	2.4	0.61	0.72	1.6	1.8	5.1	1.1
P-WRD-W	2.6	385	2750	120	37	47	140	37	470	12
P-PD-W	2.7	34	880	44	0.022	5.3	16	39	230	3.3
P-EC-W	2.8	0.36	1200	40	5.4	16	34	23	35	13

Table 4-6 Chemical analysis of filtered and acidified samples from Pierina demonstrating concentrations of trace elements in µg/L.

Sample	pH	As	Co	Ni	Sr	Pb	Cd	K
Units		µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
P-ARD-17-W	3.1	33	3.4	2.4	655	5.0	2.1	1300
P-WRD-W	2.6	890	760	200	1300	16	310	1300
P-PD-W	2.7	1800	530	170	37	730	5.8	1300
P-EC-W	2.8	4.9	360	100	900	120	5.0	4800

All surface waters collected were analyzed for 5 anions, F⁻, Cl⁻, NO₂⁻, NO₃⁻, SO₄²⁻ in the <0.45µm samples (results are shown in Appendix F: QAQC water). At El Indio, NO₂⁻ and NO₃⁻ were found to be below the instrumental detection limit of 2.0 mg/L. At Lagunas Norte, F⁻, Cl⁻ and NO₂⁻ are consistently found below their instrumental detection limits of 2.0 mg/L. At Pierina all anions, except for SO₄²⁻, are below their respective instrumental detection limits. Sulfate is consistently in greatest concentrations (followed by F, Cl, NO₃⁻ and NO₂⁻ respectively) and sulfate has concentrations greater than 100 times relative to the other anions (870 mg/L to 1,100 mg/L at El Indio, 5,400 mg/L to 190 mg/L at Lagunas Norte and 3,600 mg/L to 53 mg/L at Pierina). Pristine alpine waters are known to contain 10-20 mg/L of sulfate; however,

the concentration in HS mine-drainage waters can be more than several thousand mg/L (Ficklin and Mosier, 2000). Anion analysis also reveals highest Cl^- and F^- concentrations at El Indio and highest SO_4^{2-} and nitrate concentrations at Lagunas Norte. Low pH values present at all mine sites are indicative of open-system weathering of sulfide minerals and have an important effect on elemental mobility. Specifically, under these conditions, most trace elements will be mobilized rapidly.

Box and whisker diagrams were used to depict the analytical results (Figure 4-1, Figure 4-2, Figure 4-3, Figure 4-4, Figure 4-5, Figure 4-6). Water analysis diagrams demonstrate a variance in the chemical compositions of the different types of elements.

Figure 4-1 Major and minor element concentrations from all filtered and acidified sample sites at El Indio. The central box is the middle 50% of data with a highlighted median line. Circles represent outliers further than $1.5 \times (Q3 - Q1)$ from the box. A triangle represents outliers that are further than $3.0 \times (Q3 - Q1)$. The whiskers represent the extreme values that are not outliers.

El Indio Water Analysis Results

Figure 4-2 Minor and trace element concentrations from all filtered and acidified sample sites at El Indio. Circles represent outliers further than $1.5 \times (Q3 - Q1)$ from the box. A triangle represents outliers that are further than $3.0 \times (Q3 - Q1)$. The whiskers represent the extreme values that are not outliers.

Lagunas Norte Water Analysis Results

Figure 4-3 Major and minor element concentrations from all filtered and acidified sample sites at Lagunas Norte. Circles represent outliers further than $1.5 \times (Q3 - Q1)$ from the box. A triangle represents outliers that are further than $3.0 \times (Q3 - Q1)$. The whiskers represent the extreme values that are not outliers

Lagunas Norte Water Analysis Results

Figure 4-4 Minor and trace element concentrations from all filtered and acidified sample sites at Lagunas Norte. Circles represent outliers further than $1.5 \times (Q3 - Q1)$ from the box. A triangle represents outliers that are further than $3.0 \times (Q3 - Q1)$. The whiskers represent the extreme values that are not outliers.

Pierina Water Analysis Results

Figure 4-5 Minor and trace element concentrations from all filtered and acidified sample sites at Pierina. Circles represent outliers further than $1.5 \times (Q3 - Q1)$ from the box. A triangle represents outliers that are further than $3.0 \times (Q3 - Q1)$. The whiskers represent the extreme values that are not outliers.

Figure 4-6 Major and minor element concentrations from all filtered and acidified sample sites at Pierina. Circles represent outliers further than $1.5 \times (Q3 - Q1)$ from the box. A triangle represents outliers that are further than $3.0 \times (Q3 - Q1)$. The whiskers represent the extreme values that are not outliers.

Field parameters for surface waters collected at the 3 mines are listed in Table 4-7, Table 4-8, Table 4-9. The pH values ranged from 2.45 to 7.31, with a majority below 4. The highest pe value of 13.1 came from the waste rock leachate before the collection pond at Lagunas Norte. Dissolved oxygen was not measured at El Indio; however, results from Lagunas Norte and Pierina are fairly similar, with the highest value being 7.21 mg/l at Lagunas Norte and lowest value 2.07 mg/L at Pierina. Specific conductance demonstrated a wide range of values in each mine site. For example, a variation of 251 $\mu\text{S}/\text{cm}$ to 4000 $\mu\text{S}/\text{cm}$ was observed at Pierina, values ranging from 3200 $\mu\text{S}/\text{cm}$ to 433 $\mu\text{S}/\text{cm}$ were observed for Lagunas Norte whereas a minimum value of 458 $\mu\text{S}/\text{cm}$ and a maximum value of 1798 $\mu\text{S}/\text{cm}$ was measured at El Indio.

Table 4-7 Field variables measured at El Indio with YSI meter measured in May 2014. Where there is an “x”, the given variable was not measured.

Site	pH	TDS	Conductivity	ORP	Temperature	DO	pe
		g/l	$\mu\text{S}/\text{cm}$	mV	C	mg/L	
IN-23	7.31	0.30	458	256	10.3	x	8.1
IN-28	4.51	0.68	1128	440	11.2-11.4	x	11.3
IN-RMATR	3.49-3.69	0.77-0.88	1180	300	9.96-9.09	x	8.9
IN-2	2.65 -3.38	0.99	1530	460	3.46	x	11.7
IN-13	4.68-4.53	1.2	1798	259.2	14.8	8.2	8.1

Table 4-8 Field variables measured at Lagunas Norte with YSI meter measured in May 2014.

Site	pH	DO	TDS	Conductivity	ORP	Temperature	pe
		mg/l	g/l	$\mu\text{S}/\text{cm}$	mV	C	
LN-DAR-1	2.45	5.94	2.1	3200	547.8	14.8	13.1
LN-DW-B-11	2.74	2.03	0.80	1242	-25.70	10.8	3.1
LN-SP3-W1	3.01	6.19	0.57	875	485.7	16.3	11.9
LN-SP3-W2	3.05	5.43	0.66	1020	488.8	15.2	12.0
LN-PW-1	5.47	5.20	0.75	1148	121.6	18.4	5.6
LN-BP	3.31	6.10	0.28	434	429.0	14.0	11.0
LN-PW2	6.4	6.40	0.28	433	-132.9	13.0	1.2
LN-VWD	2.63	7.21	1.9	2882	566.0	12.7	13.5

Table 4-9 Field variables measured at Pierina with YSI meter measured in May 2014.

Site	pH	DO	TDS	Conductivity	ORP	Temperature	pe
		mg/l	g/l	$\mu\text{S}/\text{cm}$	mV	C	
P-WRD	2.8	5.56	2.6	4000	479.4	17.3	11.8
P-ARD-17	3.0	5.56	0.163	251	468.4	14.0	11.7
P-PD	3.1	2.07	0.868	1336	372.3	17.0	9.94
P-EC	4.3	6.81	1.117	1719	387.0	17.3	10.2

4.1.2 Site-specific chemistry

Comparison of metals and anions shows a significant variation of concentrations between mines and from one site to another (Figure 4-10, Figure 4-24). Iron concentrations ranged from 22 mg/L (IN-RMATR) to 23 mg/L (IN28) at El Indio, 50 µg/L (LN-PW2) to 640 mg/L (LN-DAR-1) at Lagunas Norte, and 5.1 mg/L (P-ARD17) to 473 mg/L (P-WRD) at Pierina. The most concentrated parameter in waters, SO₄, demonstrates a range of concentration from 870 mg/L (IN23) to 1,100 mg/L (IN2) at El Indio, 190 mg/L (LN-VWD-W) to 5,400 mg/L (LN-DAR-1-W) at Lagunas Norte, and 53 mg/L (P-ARD17) to 2,900 mg/L (P-WRD) at Pierina. Calcium is also elevated in concentration at all mines. Specifically, the range of concentrations lie between 85 mg/L (IN23) to 250 mg/L (IN13) at El Indio, 31 mg/L (LN-BP) to 500 mg/L (LN-VWD) at Lagunas Norte, and 2.45 mg/L (P-ARD17) to 383 mg/L (P-WRD). Anion analysis reveals the highest concentration of F⁻ as 3.8 mg/L (IN-RMATR) at El Indio, and values below detection limits for Lagunas Norte and Pierina. The highest concentration of Cl⁻ is 140 mg/L at El Indio (IN13), 6.4 mg/L (LN-PW2) at Lagunas Norte, and 0.55 mg/L (P-ARD17) at Pierina.

Figure 4-7 Concentration of elements at IN23 on a scatterplot.

Figure 4-8 Concentration of elements at IN28 on a scatterplot.

Figure 4-9 Concentration of elements at IN-RMATR on a scatterplot.

Figure 4-10 Concentration of elements at IN2 on a scatterplot.

Figure 4-11 Concentration of elements at IN13 on a scatterplot.

Figure 4-12 Concentration of elements at LN-SP3 on a scatterplot.

Figure 4-13 Concentration of elements at LN-DW-B11 on a scatterplot.

Figure 4-14 Concentration of elements at LN-DAR-1 on a scatterplot.

Figure 4-15 Concentration of elements at LN-BP on a scatterplot.

Figure 4-16 Concentration of elements at LN-PW2 on a scatterplot.

Figure 4-17 Concentration of elements at LN-VWD on a scatterplot.

Figure 4-18 Concentration of elements at P-ARD17 on a scatterplot.

Figure 4-19 Concentration of elements at P-WRD on a scatterplot.

Figure 4-20 Concentration of elements at P-PD on a scatterplot.

Figure 4-21 Concentration of elements at P-EC on a scatterplot.

At El Indio, changes in water chemistry from upstream to downstream are noted (see Figure 3.3, Figure 3.4). IN23-W, the most upstream site which is unaffected by mining activities, has the lowest concentrations of all elements amongst the 5 sampling sites and the highest pH at 6.7. IN28-W has the highest concentration of As at 110 µg/L, Cu at 29000 µg/L and Fe at 24000 µg/L. IN-RMATR-W has the lowest pH but does not have the highest metal concentrations. IN2-W demonstrates the highest concentrations of sulfate, F, Al, Cd, Co, Mn, Ni, Zn. IN13-W has the highest concentration of Cl, Ca, Ce, Mg, K, Na, Sr. A general increase of SO₄ and metals is observed in the downstream direction with the highest concentrations at sites IN2 and IN13 (Figures 3.3, Figure 3.4) (Table 4-1).

The sampling sites were not distributed along simple drainage patterns at Lagunas Norte and Pierina as they were at El Indio (Figure 3.5 and Figure 3.6 respectively) (Table 4-3). At Lagunas Norte, sampling locations with the lowest pH is LN-DAR-1 (2.6 pH) and the location with the highest pH is LN-PW2 (6.2 pH). Fluoride, Cl, NO₂ and NO₃ are below detection limits at all sites, with the exception of Cl at LN-PW2 that is measured at 6.4 mg/L. Aluminum concentrations are highest at LN-DAR-1 (380 mg/L) followed by LN-VWD (200 mg/L) and LN-SP3 (50 mg/L). Similarly, SO₄, Al, Ca, Ni are highest at LN-DW-B11 followed by LN-VWD. Copper is also highest at DW-B-11 (110 mg/L), followed by LN-VWD (23 mg/L).

Arsenic and Fe are highest at LN-DW-B-11 with concentrations of 1.4mg/L and 650 mg/L. respectively. DW-B-11 has the highest concentrations of Pb and Zn at 0.29 mg/L and 14 mg/L respectively. LN-VWD shows evidence of sodium concentrations (50 mg/L) greater than other sampling locations. Magnesium concentrations are highest at DAR-1-W (150 mg/L), followed by LN-VWD (75 mg/L), whereas Mn is most concentrated at LN-DAR-1 (42 mg/L). LN-PW2 generally has low metal concentrations with the exception of Mo (0.037 mg/L) which is the highest from all the sampling locations. Out of the 6 sampling locations, the water chemistry at LN-DW-B-11 and LN-VWD is the most enriched in metals and elements that may be potentially toxic or economically valuable.

At Pierina, sample sites P-PD, P-ARD-17, P-WRD, and P-EC were distributed throughout the mine and demonstrate a wide range of concentrations (Figure 3.6) Table 4-5. Sulfate and Fe are the most heavily concentrated at P-WRD (2.75 mg/L & 480 mg/L respectively). Calcium, Ce, Cu, Mg, Y, Zn and Mn amounts are greatest P-WRD followed by P-EC. Cadmium has the highest concentrations at P-PD (2.3 mg/L) followed by P-EC (1.2 mg/L). Changes in Cu concentrations at these sites depict the variation in chemistry throughout the mine, from 0.022 mg/L at P-PD to 37 mg/L. Potassium and Na are found in their highest concentration at P-EC.

4.1.3 Ultrafiltration

Ultrafiltration was used to capture colloids from the water samples collected in the field at Pierina and Lagunas Norte. In this research, it is assumed that the difference between the concentrations in the 0.45 μm and the 0.01 μm ultrafiltered samples is equivalent to the concentration found in the colloidal phase:

$$[Me]_{colloidal} = [Me]_{0.45\mu\text{m}} - [Me]_{0.01\mu\text{m}} \quad \text{Equation 4.1}$$

The component of the initial concentration retained on the filter paper can be calculated by subtracting a value of 1 from the quotient of [Me] permeate and [Me] retentate.

$$RC = 1 - \frac{[Me]_{permeate}}{[Me]_{retentate}} \quad \text{Equation 4.2}$$

The results from calculations demonstrate that Al, Ca, Cu, Fe, Mg, Mn, K, S and Zn are present as colloids in Pierina and Al, Ca, Cu, Fe, Mg, Mn, Na, S, Sr and Zn at Lagunas Norte. The concentration of elements at Lagunas Norte and Pierina are listed in Table 4-11 and Table 4-13. The percentage of elements in colloids was also calculated and is tabulated in Table 4-10 and Table 4-12. This is done by dividing $[Me]_{\text{colloidal}}$ by the average concentration of the element in the FA sample. The negative values are assumed to be caused by sampling or analytical errors.

Table 4-10 Relative percent concentrations of Al, As, Ca, Cu, Fe, Mg, Mn, K, S, Zn as colloids from ultrafiltration results at Pierina.

	P-ARD-17-W	P-WRD-W	P-PD-W	P-EC-W
Temperature	13.95	17.25	16.98	17.27
Ionic strength	1.41E-03	6.54E-02	1.99E-02	2.83E-02
Elements				
Al	2%	14%	10%	4%
As	18%	5%	22%	-421%
Ca	2%	6%	7%	0%
Cu	7%	5%	-20%	5%
Fe	11%	5%	6%	5%
Mg	6%	6%	2%	0%
Mn	6%	25%	17%	21%
K	8%	-3%	2%	2%
Na	9%	8%	4%	8%
Sr	1%	21%	6%	4%
S	0%	12%	3%	18%
Zn	-6%	24%	12%	21%

Table 4-11 List of elements with average colloidal concentrations in ppb at sampling locations within Pierina.

	Units	P-ARD-17-W	P-WRD-W	P-PD-W	P-EC-W
Temperature	°C	13.95	17.25	16.98	17.27
Ionic strength		1.41E-03	6.54E-02	1.99E-02	2.83E-02
Elements					
Al	ppb	50	16,667	4,333	1,667
As	ppb	6	47	400	-20
Ca	ppb	50	23,333	2,333	0
Cu	ppb	40	2,000	-4	267
Fe	ppb	550	23,333	13,333	1,667
Mg	ppb	40	3,000	133	0
Mn	ppb	100	36,667	2,667	7,000
K	ppb	100	-33	33	100
Na	ppb	100	1,000	133	1,000
Sr	ppb	0	267	2	40
S	ppb	0	110,000	6,667	70,000
Zn	ppb	-100	8,667	4,667	4,667

Table 4-12 Relative percent concentrations of Al, As, Ca, Cu, Fe, Mg, Mn, K, S, Zn in colloid and dissolved from ultrafiltration at respective sampling sites within Lagunas Norte.

Elements	LN-SP3-W	LN-SP3-W2	LN-DW-B-11-W	LN-DAR-1-W	LN-BP	LN-PW2-W	LN-VWD-W
Al	5%	7%	7%	3%	7%	1%	5%
As	-79%	-14%	18%	-4%	-90%	-32%	4%
Ca	0%	8%	0%	5%	13%	9%	8%
Cu	6%	5%	9%	8%	5%	-97%	0%
Fe	3%	13%	0%	3%	10%	-44%	9%
Mg	6%	11%	-3%	5%	11%	8%	11%
Mn	4%	7%	10%	2%	6%	-41%	-2%
K	4%	-15%	-6%	0%	6%	7%	-3%
S	7%	4%	1%	6%	3%	19%	-3%
Zn	8%	5%	9%	0%	10%	0%	7%

Table 4-13 List of elements with average colloidal concentrations at sampling sites within Lagunas Norte.

	Units	LN-SP3-W	LN-SP3-W2	LN-DW-B-11-W	LN-DAR-1-W	LN-BP	LN-PW2-W	LN-VWD-W
Temperature	°C	16.33	15.15	10.82	14.83	14.04	12.99	12.68
Ionic Strength		9.19E-03	8.27E-02	1.70E-02	1.12E-01	4.14E-03	8.66E-03	8.00E-02
Elements								
Al	ppb	2,333	3,500	2,000	13,333	450	0.3	10,000
As	ppb	-8.0	-2	233.3	-40	-2.8	-2.9	15
Ca	ppb	0.0	10,000	0.0	20,000	4,000	13,333	40,000
Cu	ppb	600.0	450	10,000	1,333	200	-7.9	0
Fe	ppb	1,333	7,000	0.0	20,000	1500	-22.0	45,000
Mg	ppb	1,000	2,000	-100.0	6,667	300	300.0	8,000
Mn	ppb	233	400	233.3	667	55	-2.4	-500
K	ppb	100.0	-400	-66.7	0	100	26.7	-25
S	ppb	20,000	150,000	3,333	100,000	150,000	833,333	-150,000
Zn	ppb	166.7	100	433.3	0	11	0	500

Filters analyzed by the ESEM did not show any colloids. Only gypsum crystals were observed which had likely precipitated during the drying of the samples before carbon coating. The results are problematic and will be discussed in section 5.1.2.

4.1.4 PHREEQC modelling

Data collected from all water samples were modelled using PHREEQC-3, a geochemical speciation model distributed by the US Geological Survey (see section 4.1.4-PHREEQC modelling). Thermodynamic modelling of waters from El Indio, Lagunas Norte and Pierina indicates that various secondary minerals can precipitate, controlling the concentration of certain elements. Saturation indices (SI) of potential

secondary minerals were identified through PHREEQC-3. A positive SI value is indicative of supersaturation and increased likelihood of precipitation if there are no kinetic barriers. Minerals with positive SI values are listed in Appendix B. Minerals with a simple stoichiometry, reactive nature and stability at near surface conditions, are those most likely to precipitate.

Alunite, $\text{Ba}_3(\text{AsO}_4)_2$, basaluminite, boehmite, cupric and cuprous ferrite, diaspora, $\text{Fe}(\text{OH})_{2.7}\text{Cl}_3$, gibbsite, goethite, hematite, maghemite and magnetite were calculated to have $\text{SI} \geq 0$ from the samples collected from El Indio. Elemental As and Cu, basaluminite, boehmite, cupric and cuprous ferrite, cuprite, diaspora, $\text{Fe}(\text{OH})_{2.7}\text{Cl}_3$, goethite, hematite, magnetite, U_4O_9 , UO_2 (amorphous), and uraninite have $\text{SI} > 0$ in the samples collected from Lagunas Norte. Alunite, basaluminite, boehmite, cupric and cuprous ferrite, diaspora, $\text{Fe}(\text{OH})_{2.7}\text{Cl}_3$, gibbsite, goethite, hematite, maghemite and magnetite were calculated to have $\text{SI} > 0$ from the samples collected from Pierina. The results suggest that precipitates will include phases containing Fe, Al and Cu. The results from PHREEQC modelling combined with the results of positively identified secondary precipitates listed in the following section can be used to inform future water treatment plant designs and closure plans.

Analytical methods (i.e XRD, μXRD , μXRF , ESEM) were used to identify precipitates, which were mostly sulfates, whereas PHREEQC predicts the precipitation of Fe, Cu, or Al oxides and oxyhydroxides. Evaporation of these waters, and forward modelling by concentrating waters 20-fold using PHREEQC generally predict an increase in the number of Fe, Al and Mn oxyhydroxides, as well as Cu and Fe sulfates. An example of forward modeling is observed in Table 4-14 from water samples collected from LN-PW2-W. Specifically for waters collected from LN-PW2-W, 17 new minerals are predicted to be oversaturated in waters concentrated 20 times. These minerals include Fe, Al and Mn oxides and oxyhydroxides, as well as Al and Ba sulfates. Only waters collected from sample sites P-WRD and LN-VWD show no oversaturation of new minerals. The list of the oversaturated minerals ($\text{SI} \geq 0$ ConcX1 and ConcX20) are found in Appendix C.

Table 4-14 List of minerals with SI>0 from waters collected at LN-PW2-W (conc 1X) and minerals with SI>0 from 20-fold concentrated waters.

LN-PW2-W			
Conc.1X		Conc.20X	
Basaluminite	Al ₄ (OH) ₁₀ SO ₄	Al(OH) ₃ (a)	
Boehmite	AlOOH	Alunite	KAl ₃ (SO ₄) ₂ (OH) ₆
Cu		Barite	BaSO ₄
Cuprite	Cu ₂ O	Basaluminite	Al ₄ (OH) ₁₀ SO ₄
CuprousFerrite	CuFeO ₂	Boehmite	AlOOH
Diaspore	AlOOH	Birnessite	MnO ₂
Gibbsite	Al(OH) ₃	Bixbyite	Mn ₂ O ₃
UO ₂ (a)		CuprousFerrite	CuFeO ₂
Uraninite	UO ₂	CupricFerrite	CuFe ₂ O ₄
		Diaspore	AlOOH
		Fe(OH) ₂ ·7Cl ₂ ·3H ₂ O	
		Fe(OH) ₃ (a)	
		Gibbsite	Al(OH) ₃
		Goethite	FeOOH
		Hausmannite	Mn ₃ O ₄
		Hematite	Fe ₂ O ₃
		Maghemite	Fe ₂ O ₃
		Magnetite	Fe ₃ O ₄
		Manganite	MnOOH
		Nsutite	MnO ₂
		Pyrolusite	MnO ₂

4.2 Geochemical and mineralogical characterization of secondary precipitates

4.2.1 Bulk geochemistry

Solid-phase bulk geochemistry results for major, minor and trace elements of mineral precipitates are plotted in box and whisker diagrams using ioGAS™ (REFLEX®) to evaluate and observe variations through sample sites and mine sites (Figure 4-22, Figure 4-24, Figure 4-25). The elements in highest concentration for the secondary precipitates from the El Indio, Lagunas Norte and Pierina mines are in Al, Ca, Cu, Fe, Mg, K, P, Mn, Na, S, and Zn. In general, most secondary precipitates at El Indio showed higher average concentrations in Al (1.41 wt%), As (1,143 ppm), Fe (10.3 wt%), Mg (2.09 wt%), Mn (3,780 ppm), K (3,458 ppm), Na (4.15 wt%), S (10.8 wt%) and Zn (2,102 ppm) than at Lagunas Norte where concentrations may be of magnitude lower for these elements: Al (8,375 ppm), As (196 ppm), Fe (3.87 wt%), Mg (4,922 ppm), Mn (468 ppm), Na (242 ppm), S (4.72 wt%), Zn (110 ppm). Pierina demonstrates the second highest concentrations of As (790 ppm), Mn (594 ppm), K (3,202 ppm), Na (262 ppm), S (6.06

wt%) and Zn (163 ppm), the highest average concentration of Fe (15.1 wt%) and Pb (366 ppm) and the lowest in Ca (2,196 ppm), Cu (776 ppm) and Mg(1,256 ppm). For full analytical results, see Appendix E: QAQC solids.

Spearman correlations matrices of concentrations of trace and major metals were created. The major elements included in the matrices are Al, Ca, Cu, Fe, K, Mg, Na, P, Zn, Mn and S. The trace and minor metals used in the matrices include Ag, As, Cd, Pb, Sb. Elements that had a majority of concentrations below detection limit were not included due to the lack of absolute values. At El Indio, the trace metals generally demonstrate a moderate (0.40-0.59) to strong correlations (0.60-1.0) with one another. Notably, the strongest (anti)correlations are between Fe and As (0.96), Zn and Cd (0.92), Fe and Na (-0.9), as well as Na and Mg (0.98). Other elements show little correlation, such as Cd with Ag (-0.13) and As, or Cu with Ag (-0.076). Sb, Ca and Ag lack significant correlations. Strong (anti)correlations are observed between Mg and As (-0.84), Na and As (-0.84), Cu and Cd (0.81), Mn and Cd (0.87), Fe and Mg (-0.89), Pb and Mg (-0.81), Zn and Mn (0.89).

At Lagunas Norte, trace metals demonstrate weak (<0.39) to strong correlations (>0.60). The strongest elemental correlations at Lagunas Norte are between Zn and Cd (0.96), S and Ni (0.93), As with Sb (0.89), and Na with As (0.81). Trace elements at Pierina generally demonstrate moderate (0.40-0.59) to strong correlations (0.60-1.0). Various very strong correlations are observed between elements at Pierina notably between Al and Cu (-0.95), Al and Ag (0.95), Al and S (-0.95), Cd and Ca (1), Cd and Mg (1), Cd and Mn (1), Cd and Zn (1), Ca and Mg (1), Ca and Mn (1), Fe and S (1), Pb and Ni (1), Pb and P (0.95), Mn and Zn (1), Mg and Zn (1), Ni and Ag (-1), K and Na (-1), Ag and S. The standard errors are considered in the discussion section.

Table 4-15 Spearman correlation matrix of major, minor and trace elements of interest, from secondary precipitates digested by aqua regia and analysed by ICP-OES at El Indio. Coloured cells are indicative of correlation coefficients ≥ 0.80 (pink) or ≥ 0.9 (red).

	Al	Sb	As	Cd	Ca	Cu	Fe	Pb	Mg	Mn	Ni	P	K	Ag	Na	S	Zn
Al	1.0																
Sb	-0.36	1.0															
As	-0.018	0.48	1.0														
Cd	0.76	-0.64	-0.43	1.0													
Ca	0.32	-0.43	-0.27	0.38	1.0												
Cu	0.80	-0.55	-0.22	0.81	0.41	1.0											
Fe	-0.083	0.47	0.96	-0.48	-0.37	-0.34	1.0										
Pb	-0.042	0.26	0.80	-0.40	-0.062	-0.13	0.77	1.0									
Mg	0.22	-0.39	-0.84	0.62	0.37	0.40	-0.89	-0.81	1.0								
Mn	0.60	-0.62	-0.64	0.87	0.3	0.69	-0.68	-0.61	0.78	1.0							
Ni	0.61	-0.57	-0.5	0.8	0.53	0.76	-0.55	-0.48	0.73	0.79	1.0						
P	-0.27	0.58	0.8	-0.57	-0.59	-0.50	0.82	0.52	-0.69	-0.68	-0.65	1.0					
K	-0.17	-0.23	-0.68	0.21	0.40	0.14	-0.77	-0.50	0.76	0.31	0.45	-0.60	1.0				
Ag	0.040	0.56	0.45	-0.13	-0.14	-0.076	0.41	0.40	-0.23	-0.24	-0.24	0.46	-0.21	1.0			
Na	0.17	-0.38	-0.84	0.60	0.40	0.39	-0.9	-0.75	0.98	0.71	0.70	-0.70	0.79	-0.25	1.0		
S	0.60	-0.61	-0.46	0.72	0.64	0.77	-0.53	-0.26	0.43	0.66	0.63	-0.79	0.23	-0.39	0.44	1.0	
Zn	0.80	-0.61	-0.39	0.92	0.34	0.84	-0.43	-0.33	0.56	0.89	0.78	-0.52	0.081	-0.10	0.51	0.66	1.0

Table 4-16 Spearman correlation matrix of major, minor and trace elements of interest, from secondary precipitates digested by aqua regia and analysed by ICP-OES at Lagunas Norte. Coloured cells are indicative of correlation coefficients ≥ 0.80 (pink) or ≥ 0.9 (red).

	Al	Sb	As	Cd	Ca	Cu	Fe	Pb	Mg	Mn	Ni	P	K	Ag	Na	S	Zn
Al	1.0																
Sb	-0.13	1.0															
As	-0.018	0.89	1.0														
Cd	0.054	0.21	0.11	1.0													
Ca	0.18	-0.36	-0.36	0.36	1.0												
Cu	-0.59	0.43	0.18	0.71	0.01	1.0											
Fe	0.13	0.36	0.61	0.29	-0.11	0.071	1.0										
Pb	0.23	0.71	0.68	0.071	-0.39	0.071	0.64	1.0									
Mg	0.67	-0.61	-0.5	0.010	0.75	-0.57	-0.21	-0.39	1.0								
Mn	0.67	-0.32	-0.071	0.46	0.50	-0.25	0.32	-0.18	0.68	1.0							
Ni	-0.17	-0.31	-0.71	0.54	0.086	0.66	-0.6	-0.43	-0.086	-0.029	1.0						
P	-0.66	-0.49	-0.31	-0.14	0.37	-0.086	0.029	-0.66	0.086	0.086	-0.3	1.0					
K	0.67	0.071	0.39	-0.14	0.29	-0.64	0.46	0.25	0.54	0.61	-0.77	-0.029	1.0				
Ag	-0.31	0.70	0.30	0.70	0.80	0.70	0.10	0.50	-0.20	-0.30	0.40	-0.40	-0.10	1.0			
Na	-0.24	0.63	0.81	0.41	-0.036	0.41	0.77	0.41	-0.41	0.16	-0.64	0.20	0.31	0.21	1.0		
S	-0.56	-0.27	-0.45	0.59	0.40	0.74	-0.20	-0.49	-0.09	-0.018	0.93	0.43	-0.67	0.62	0.018	1.0	
Zn	0.13	0.43	0.32	0.96	0.32	0.68	0.36	0.25	-0.036	0.43	0.31	-0.31	2.40E-17	0.70	0.52	0.41	1.0

Table 4-17 Spearman correlation matrix of major, minor and trace elements of interest, from secondary precipitates digested by aqua regia and analysed by ICP-OES at Pierina. Coloured cells are indicative of correlation coefficients ≥ 0.80 (pink) or ≥ 0.9 (red).

	Al	Sb	As	Cd	Ca	Cu	Fe	Pb	Mg	Mn	Ni	P	K	Ag	Na	S	Zn
Al	1.0																
Sb	0.32	1.0															
As	-0.32	0.60	1.0														
Cd	0.63	-0.40	-0.40	1.0													
Ca	0.63	-0.40	-0.40	1.0	1.0												
Cu	-0.95	-0.20	0.20	-0.80	-0.80	1.0											
Fe	-0.63	0.00	0.80	-0.20	-0.20	0.40	1.0										
Pb	0.5	0.63	0.63	0.32	0.32	-0.63	0.32	1.0									
Mg	0.63	-0.40	-0.40	1.0	1.0	-0.80	-0.20	0.32	1.0								
Mn	0.63	-0.40	-0.40	1.0	1.0	-0.80	-0.20	0.32	1.0	1.0							
Ni	-0.63	-0.40	-0.40	-0.60	-0.60	0.80	-0.20	-0.95	-0.60	-0.60	1.0						
P	0.32	-0.20	0.20	0.80	0.80	-0.60	0.40	0.63	0.80	0.80	-0.80	1.0					
K	0.63	0.40	0.40	0.60	0.60	-0.80	0.20	0.95	0.60	0.60	-1.0	0.80	1.0				
Ag	0.95	0.20	-0.20	0.80	0.80	-1.0	-0.40	0.63	0.80	0.80	-0.80	0.60	0.80	1.0			
Na	0.32	-0.20	0.20	0.80	0.80	-0.60	0.40	0.63	0.80	0.80	-0.80	1.0	0.80	0.60	1.0		
S	-0.95	-0.20	0.20	-0.80	-0.80	1.0	0.40	-0.63	-0.80	-0.80	0.80	-0.60	-0.80	-1.0	-0.60	1.0	
Zn	0.63	-0.40	-0.40	1.0	1.0	-0.80	-0.20	0.32	1.0	1.0	-0.60	0.80	0.60	0.80	0.80	-0.80	1.0

Figure 4-22 Concentration of elements Ag, As, Cd, Cu, Mn, Pb, Zn, Al, Cu, Fe, K, Mg, Na, P, S, Ca, Te of all sampling sites at El Indio, in ppm and on a box and whisker diagram. The highest concentrations are S, Fe, Ca, Na and Al.

Figure 4-23 Concentration of elements Ag, As, Cd, Cu, Mn, Pb, Zn, Al, Cu, Fe, K, Mg, Na, P, S, Ca, Te of all sampling sites at Lagunas Norte, in ppm and on a box and whisker diagram. The highest concentrations are S, Fe, Ca, Cu and Al.

Figure 4-24 Concentration of elements Ag, As, Cd, Cu, Mn, Pb, Zn, Al, Cu, Fe, K, Mg, Na, P, S, Ca, Te of all sampling sites at Pierina, in ppm and on a box and whisker diagram. The highest concentrations are S, Fe, and Al.

4.2.2 Site-specific chemistry

4.2.2.1 El Indio

4.2.2.1.1 IN28

These secondary precipitates were collected close to the San Pablo tunnel, a closed tunnel downstream from the tailings (Figure 3-3, Figure 3-4). Since few secondary precipitates were visible at the tunnel's entrance, samples were collected on an adjacent hill, approximately 100 meters away. Seepage waters, assumed to be similar to those emerging from the tunnel, produced abundant precipitates in this area. Several different colours of precipitate were collected in plastic wrap including white, yellow, dark yellow, and black crust.

X-ray diffraction allowed for the occurrence of a member of the halortichite group, possibly dietrichite ($\text{ZnAl}_2(\text{SO}_4)_4 \cdot 22(\text{H}_2\text{O})$), based on the presence of Zn, and a copiapite group mineral, likely magnesiocopiapite ($\text{MgFe}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20(\text{H}_2\text{O})$) because of the high Mg content at IN28-P2, possible dietrichite ($\text{ZnAl}_2(\text{SO}_4)_4 \cdot 22(\text{H}_2\text{O})$), melanterite ($\text{FeSO}_4 \cdot 7(\text{H}_2\text{O})$) and magnesiocopiapite ($\text{MgFe}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20(\text{H}_2\text{O})$) at IN28-P3, finally, only quartz (SiO_2) at IN28-P4 (Table 4-20).

The occurrences of these minerals are based on the chemistry analyzed by Analytical Services Unit at Queen's University, physical properties of the sample such as colour and XRD analyses (Figure 4-25). IN28-P2 is a bright yellow colour and its highest concentrations are Al, Mg, Zn, and S. For this sample magnesiocopiapite was identified based on colour, elemental concentration and XRD peak matching. Magnesiocopiapite is a typical secondary mineral that forms by the oxidation of pyrite (Lottermoser, 2010c; Hammarstrom et al., 2005). Based on this information, both are likely to form in this setting. IN28-P3 is a lighter coloured sample and contains an additional mineral, melanterite, an Fe oxy-hydroxide. Because IN28-P4 is black, it likely contains Fe or Mn-oxides; however, these minerals may not show XRD patterns because of their amorphous nature. In fact, only quartz is identified and ICP-OES data does demonstrate elevated concentrations of Fe, as well as Cu, S, and As.

Thin sections from samples IN28-P2 and IN28-P4 were analyzed by μ XRD (Figure 4-27, Figure 4-26) and ESEM (Figure 4-28), and MSP of sample IN28-P2 were analyzed by ESEM. The minerals identified by μ XRD are compared to those identified from XRD in Table 4-18 and Table 4-19. Potassium-rich and Na-rich end members of the alunite group, jarosite and natrojarosite were potentially identified based on μ XRD and chemistry data. At least 5 distinct phases were identified from the MSP stubs, clearly demonstrating differing morphology and chemistry: (1) desiccated mass of Al sulfate (2) platy aggregates of interpreted magnesiocopiapite (3) granules of Na Mg sulfate (4) tabular Na Mg sulfate (5) anhedral Fe sulfate phase. Because ESEM analysis is semi-quantitative, only general chemical formulae of minerals are known with hydration states left unknown. As such, in Table 4-18, all probable occurrences of minerals are identified in the column labelled "ESEM". Magnesiocopiapite is the only common phase between the 4 analytical methods in sample IN28-P2 and quartz the only common phase between 3 analytical methods in sample IN28-P4. Dietrichite is only potentially identified with the XRD and the presence of Zn, and a Na Mg phase is identified on the MSP using the ESEM.

Figure 4-25 Concentrations in mg/kg of elements in samples IN28-P1, IN-28-P2, IN-28-P3 and IN28-P4 as measured by ICP-OES.

Figure 4-26 μ XRD 2D diffraction pattern (bottom left) of natrojarosite, quartz, alunite and magnesiocopiapite. The associated 1D diffraction pattern with matched mineral profiles is on the right.

Figure 4-27 μ XRD elemental maps collected on thin section IN28-P2.

Table 4-18 List of minerals identified at IN28-P2 with μ XRD methods at the synchrotron, bulk XRD and ESEM.

IN28-P2 Minerals	Formula	Identification Method		
		XRD	μ XRD	ESEM
Natrojarosite	$\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$		x	x
Jarosite	$\text{KFe}^{3+}_3(\text{OH})_6(\text{SO}_4)_2$		x	x
Natroalunite	$(\text{Na}_{0.75}\text{K}_{0.25})\text{Al}_3(\text{SO}_4)_2(\text{OH})_6$		x	
Magensicopiapite	$\text{MgFe}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20(\text{H}_2\text{O})$	x	x	x
Muscovite	$\text{KAl}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2$		x	
Hexahydrite	$\text{Mg}(\text{SO}_4) \cdot 6(\text{H}_2\text{O})$		x	
Goethite	$\text{FeO}(\text{OH})$		x	x
Alunogen	$\text{Al}_2(\text{SO}_4)_3 \cdot 17(\text{H}_2\text{O})$		x	x
Dietrichite (?)	$\text{ZnAl}_2(\text{SO}_4)_4 \cdot 22(\text{H}_2\text{O})$	x		
Na Mg sulfate				x

Figure 4-28 ESEM images of sample IN28-P2. (A) Desiccated mass of Al sulfate alongside platy aggregates of interpreted magnesiocopiapite and granules of Na Mg sulfate. (B) Anhedral to subhedral tabular Na Mg sulfate and darker anhedral Fe sulfate phase. (C) Amalgamation of platy probable magnesiocopiapite crystallites.

Figure 4-29 μ XRD elemental maps collected on thin section IN28-P4.

Table 4-19 List of minerals identified on thin section IN28-P4 through μ XRD bulk XRD and ESEM analyses.

IN28-P4 Minerals	Formula	Identification Method		
		XRD	μ XRD	ESEM
Goethite	$\text{FeO}(\text{OH})$		x	x
Quartz	SiO_2	x	x	x
Alunite	$\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$		x	x
Muscovite	$\text{KAl}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2$		x	x
Anhydrite	$\text{Ca}(\text{SO}_4)$		x	x
Jarosite	$\text{KFe}^{3+}_3(\text{OH})_6(\text{SO}_4)_2$		x	x
Scorodite	$\text{Fe}(\text{AsO}_4) \cdot 2(\text{H}_2\text{O})$		x	x

4.2.2.1.2 IN-RMATR

Secondary precipitates were collected upstream of the settling pond (Figure 3-3). Mine waters enter the settling pond in order to remove turbidity from tunnel waters, specifically particles containing Fe, As and Cu. Samples collected include abundant and varied precipitates collected along the stream edge on both sides of the road including white (IN-RMATR-P1), yellow (IN-RMATR-P2), blackish (IN-RMATR-P3), pinkish (IN-RMATR-P4), greenish (IN-RMATR-P5) and water-saturated Fe oxides (IN-RMATR-FeOx1, IN-RMATR-FeOx2).

The occurrences of these minerals are based on the bulk chemistry, physical properties of the sample such as colour and XRD analyses. Potassium and Na endmembers of the alum group, alum-Na

($\text{NaAl}(\text{SO}_4)_2 \cdot 12(\text{H}_2\text{O})$), alum-K ($\text{K}(\text{Al}(\text{SO}_4)_2 \cdot 12(\text{H}_2\text{O}))$), as well as gypsum ($\text{Ca}(\text{SO}_4) \cdot 2(\text{H}_2\text{O})$), alunogen ($\text{Al}_2(\text{SO}_4)_3 \cdot 17(\text{H}_2\text{O})$) and scorodite ($\text{FeAsO}_4 \cdot 2(\text{H}_2\text{O})$) are the minerals likely present in IN-RMATR-P1 (Table 4-20). A mineral from the copiapite group, likely magnesiocopiapite ($\text{MgFe}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20(\text{H}_2\text{O})$), quartz (SiO_2), gypsum ($\text{CaSO}_4 \cdot 2(\text{H}_2\text{O})$), alunogen ($\text{Al}_2(\text{SO}_4)_3 \cdot 17(\text{H}_2\text{O})$) and scorodite ($\text{FeAsO}_4 \cdot 2(\text{H}_2\text{O})$) are identified in RMATR-P2. Only quartz and gypsum are observed in RMATR-P3 and RMATR-P4 respectively (Table 4-20).

The most concentrated elements in RMATR-P1 and RMATR-P2 include Al, As, Ca, Mg, Fe, S (Figure 4-30). Alum is a common mineral formed at HS epithermal deposits as a result of sulfide mineral oxidation (Szakáll et al., 1997). Alunogen forms by reaction of sulfates from decomposing sulfides with aluminous minerals in pyritic deposits (Schindler et al., 2006; Keith et al., 2001; Keith, D. C., Runnells, 1998; Buckby et al., 2003). Scorodite is a common secondary mineral formed by the oxidation of arsenopyrite or other arsenic-bearing minerals (Charykova et al., 2010; Cheng et al., 2009; Camus, 1990; Bowell et al., 2000; Jamieson, 2011). RMATR-P4 is beige, and thus may contain quartz and gypsum, as suggested from the bulk XRD results; however, amorphous minerals that could not be identified with XRD may also be present. RMATR-P3 and RMATR-P5 have high concentrations of Al, Ca, Cu, Fe, Mg, Mn, S, and Zn. These minerals

containing these elements have not been identified by XRD due to their amorphous nature.

Figure 4-30 Concentrations of samples RMATR-P1, RMATR-P2, RMATR-P3, RMATR-P4 and RMATR-P5 from El Indio through ICP-OES analysis.

4.2.2.1.3 IN2

These secondary precipitates were collected from mine drainage waters downstream of the settling pond. Precipitates were not quite as abundant as the previous two sites and include black and brownish samples. Bulk XRD results have identified quartz (SiO_2) and albite ($\text{Na(AlSi}_3\text{O}_8)$) in IN2-P1. Quartz, albite ($\text{Na(AlSi}_3\text{O}_8)$) and alunite ($\text{K(Al}_3\text{(SO}_4)_2\text{(OH)}_6)$) were the main minerals in IN2-P2, and jarosite ($\text{KFe}^{3+}_3\text{(OH)}_6\text{(SO}_4)_2$), alum-Na ($\text{NaAl(SO}_4)_2 \cdot 12\text{(H}_2\text{O)}$), epsomite ($\text{Mg(SO}_4) \cdot 7\text{(H}_2\text{O)}$) and gypsum ($\text{Ca(SO}_4) \cdot 2\text{(H}_2\text{O)}$) were positively identified in IN2-P3 (Table 4-20).

IN2-P1 shows highest concentrations in Al, As, Fe, S, K, Ti (Figure 4-31). IN2-P2 and IN2-P3 demonstrate highest concentrations in Al, As, Ca, Fe, Mg, K, S, Ti (Figure 4-31). Albite and quartz are common minerals found in HS epithermal deposits (Hedenquist et al., 2000). Alunite is a common alteration mineral in these types of deposits, and alum is a common mineral formed from sulfide mineral oxidation (Szakáll et al., 1997). Espomite is a secondary mineral that is often found growing on the walls of metal mines through sulfide oxidation (Jambor et al., 2000; Steiger et al., 2011; Sracek et al.,

2010; Matýsek et al., 2014; Buckby et al., 2003; Jamieson et al., 2015)

Figure 4-31 Concentration of elements in solid samples IN2-P1, IN2-P2, and IN2-P3 with ICP-OES analysis.

4.2.2.1.4 IN13

Secondary precipitates were collected from mine drainage waters furthest downstream from the settling pond. This site demonstrates the most variety of mineral precipitates in terms of colour. Pink/brick-red spheres/rosettes (IN13-P4), mint green smooth-surfaced crusts (IN13-P5 & IN13-P2), yellowish crusts that turn to powder when handled (IN13-P3), and the pure white crusts were found at this location IN13-P1. Two samples of the yellow material were taken as they looked slightly different.

IN13-P1 has elevated concentrations of Al, Ca, Cu, Fe, K, Mg, Na, P (Figure 4-32). IN13-P2 demonstrates high amounts of Al, Ca, Cu, K, Mg, Mn, Na, S, Zn. Al, B, Ca, Cu, Mn, Na, S and Zn have elevated concentrations in IN13-P3 (Figure 4-32). IN13-P4 and IN13-P5 have high concentrations of Al, Ca, Cu, Fe, K, Mg, Mn, Na, S, Zn (Figure 4-32). If the elements were not present in the identified minerals, it is presumed that they were adsorbed onto the structures or entered the crystal structure.

The occurrence of the following minerals are based on the bulk chemistry, physical properties of the sample such as colour and XRD analyses. Minerals identified in IN13-P1 include blodite

($\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4(\text{H}_2\text{O})$) based on the occurrence of a blodite group mineral and the predominance of Mg, alum-Na and gypsum ($\text{Ca}(\text{SO}_4) \cdot 2(\text{H}_2\text{O})$) (Table 4-20). In IN13-P2, gypsum ($\text{Ca}(\text{SO}_4) \cdot 2(\text{H}_2\text{O})$), boyleite ($(\text{Zn,Mg})(\text{SO}_4) \cdot 4(\text{H}_2\text{O})$), chrysocolla ($\text{Cu}_{2-x}\text{Al}_x(\text{H}_{2-x}\text{Si}_2\text{O}_5)(\text{OH})_4 \cdot n(\text{H}_2\text{O})$) and bonattite ($\text{Cu}(\text{SO}_4) \cdot 3(\text{H}_2\text{O})$). Minerals identified in IN13-P3 include halite (NaCl), gypsum ($\text{Ca}(\text{SO}_4) \cdot 2(\text{H}_2\text{O})$), hexahydrate ($\text{Mg}(\text{SO}_4) \cdot 6(\text{H}_2\text{O})$) and starkeyite ($\text{Mg}(\text{SO}_4) \cdot 4(\text{H}_2\text{O})$). Halite (NaCl), starkeyite ($\text{Mg}(\text{SO}_4) \cdot 4(\text{H}_2\text{O})$), hexahydrate ($\text{Mg}(\text{SO}_4) \cdot 6(\text{H}_2\text{O})$), quartz (SiO_2) and gypsum ($\text{Ca}(\text{SO}_4) \cdot 2(\text{H}_2\text{O})$) were identified in IN13-P4 (Table 4-20).

Hexahydrate is a monoclinic sulfate with water content and was observed as encrustations in the field and its occurrence is a result of sulfide mineral oxidation (Jambor et al., 2000). Starkeyite is a dehydrated version of hexahydrate. Quartz and halite are common minerals found in this setting, and gypsum formed on drying in the field or during sample preparation. Loweite and blodite may both occur in evaporitic environments and from sulfidic mine waste (Leduc, 2010; Stoilova and Wildner, 2004; Lottermoser, 2010c). Bonattite may form as a dehydration product of chalcantite (Sracek et al., 2010). Boyleite, of the rozenite group, and chrysocolla are minerals of secondary origin that form in the oxidation zones of copper ore bodies (Carbone et al., 2013).

Figure 4-32 Elemental concentrations in mg/kg in solid samples IN13-P1, IN13-P2, IN13-P3, IN13-P4 and IN13-P5 from ICP-OES measurements.

Table 4-20 Positively identified minerals by bulk XRD from secondary precipitate samples collected at El Indio.

Sample	Minerals	Chemical Formula	Sample	Minerals	Chemical Formula	Sample	Minerals	Chemical Formula	
IN13-P1	Blodite	Na ₂ Mg(SO ₄) ₂ ·4(H ₂ O)	IN2-P1	Quartz	SiO ₂	IN28-P4	Quartz	SiO ₂	
	Gypsum	Ca(SO ₄)·2(H ₂ O)		Albite	NaAlSi ₃ O ₈		RMATR-FeOx-P1	Quartz	SiO ₂
IN13-P2	Chrysocolla	Cu _{2-x} Al _x (H _{2-x} Si ₂ O ₅)(OH) ₄ ·x(H ₂ O)	IN2-P2	Quartz	SiO ₂	RMATR-FeOx-P2	Quartz	SiO ₂	
	Boyleite	(Zn,Mg)SO ₄ ·4(H ₂ O)		Albite	NaAlSi ₃ O ₈		RMATR-FeOx-P3	No bulk XRD	
IN13-P3	Gypsum	Ca(SO ₄)·2(H ₂ O)	IN2-P3	Alunite	K(Al ₃ (SO ₄) ₂ (OH) ₆)	RMATR-P1	Alum-Na	NaAl(SO ₄) ₂ ·12(H ₂ O)	
	Bonattite	Cu(SO ₄)·3(H ₂ O)		Alum-Na	NaAl(SO ₄) ₂ ·12(H ₂ O)		Alum-K	KAl(SO ₄) ₂ ·12(H ₂ O)	
	Halite	NaCl		Epsomite	Mg(SO ₄)·7(H ₂ O)		Gypsum	Ca(SO ₄)·2(H ₂ O)	
	Gypsum	Ca(SO ₄)·2(H ₂ O)		Gypsum	Ca(SO ₄)·2(H ₂ O)		Alunogen	Al ₂ (SO ₄) ₃ ·17H ₂ O	
	Hexahydrite	Mg(SO ₄)·6(H ₂ O)		Jarosite	KFe ₃ (OH) ₆ (SO ₄) ₂		Scorodite	FeAsO ₄ ·2(H ₂ O)	
	Starkeyite	Mg(SO ₄)·4(H ₂ O)		No bulk XRD			RMATR-P2	Magnesiocopiapite	MgFe ₄ (SO ₄) ₆ (OH) ₂ ·20(H ₂ O)
IN13-P4	Halite	NaCl	IN2-P5	No bulk XRD				Quartz	SiO ₂
	Starkeyite	Mg(SO ₄)·4(H ₂ O)	IN28-P1	Alum-Na	NaAl(SO ₄) ₂ ·12(H ₂ O)		Gypsum	Ca(SO ₄)·2(H ₂ O)	
	Hexahydrite	Mg(SO ₄)·6(H ₂ O)		Alum-K	KAl(SO ₄) ₂ ·12(H ₂ O)		Alunogen	Al ₂ (SO ₄) ₃ ·17(H ₂ O)	
	Quartz	SiO ₂		Magnesiocopiapite	MgFe ₄ (SO ₄) ₆ (OH) ₂ ·20(H ₂ O)		Scorodite	FeAsO ₄ ·2(H ₂ O)	
IN13-P5	Gypsum	Ca(SO ₄)·2(H ₂ O)		Loweite	Na ₁₂ Mg ₇ (SO ₄) ₁₃ ·15(H ₂ O)	RMATR-P3	Quartz	SiO ₂	
	Halite	NaCl	IN28-P2	Dietrichite	ZnAl ₂ (SO ₄) ₄ ·22(H ₂ O)	RMATR-P4	Gypsum	Ca(SO ₄)·2(H ₂ O)	
	Gypsum	Ca(SO ₄)·2(H ₂ O)		Magnesiocopiapite	MgFe ₄ (SO ₄) ₆ (OH) ₂ ·20(H ₂ O)				
	Hexahydrite	Mg(SO ₄)·6(H ₂ O)	IN28-P3	Dietrichite	ZnAl ₂ (SO ₄) ₄ ·22(H ₂ O)				
	Muscovite	KAl ₂ Si ₃ AlO ₁₀ (OH) ₂		Magnesiocopiapite	MgFe ₄ (SO ₄) ₆ (OH) ₂ ·20(H ₂ O)				
	Starkeyite	Mg(SO ₄)·4(H ₂ O)		Melanterite	FeSO ₄ ·7(H ₂ O)				

Synchrotron micro-analysis was conducted on thin sections made from samples IN13-P1, IN13-P2, IN13-P3, IN13-P4, IN13-P5 (Figure 4-33, Figure 4-35, Figure 4-36, Figure 4-37, Figure 4-39, Figure 4-41). Mounted secondary precipitates of IN13-P1, IN13-P3, IN13-P4 and IN13-P5 were analyzed by ESEM. The identified minerals from the bulk XRD were compared to those from the ESEM and μ XRD and show similar results; however, an increased amount of phases were identified by μ XRD analysis (Table 4-21, Table 4-22, Table 4-23, Table 4-24, Table 4-25). Approximately 7-15 spots were chosen for μ XRD and were based on observed elemental variation from XRF maps. Albite, loweite, alunite, hexahydrite were phases identified by μ XRD and not by XRD at IN13-P1. Out of 8 minerals identified through various methods at sample IN13-P2, only gypsum was identified through XRD analysis. Anorthite, halite and changoite, were not identified by bulk XRD within sample IN13-P3. Albite, magnetite and montmorillonite were not identified by bulk XRD analysis in sample IN13-P4. Within this same sample, probable kaolinite and atacamite minerals were identified by the ESEM of the mounted secondary precipitates. Albite, bassanite, gypsum, loweite, blodite were not identified by XRD analyses.

Morphological features and measured chemistry in samples were associated with the most likely phases already identified by XRD and μ XRD. At least 6 distinct phases were identified at IN13-P1 through ESEM analysis (Figure 4-34): (1) flat hexagonal crystallites of Ca sulfates with evidence of Cu (2) euhedral crystals of Na K sulfate phase interpreted as potentially thenardite (3) irregularly shaped halite masses (4) euhedral intergrowth of varying sizes of Na Mg sulfates interpreted to be blodite or loweite (5) fine groundmass of probable alunite (6) intergrown nodules of alunite and quartz. Not less than 7 distinct phases were identified at IN13-P3 through ESEM analysis (Figure 4-38): (1) cubic crystals of halite (2) fine grained Na, Mg sulfate (3) tabular to lamellar aggregates of Mg sulfate (probably starkeyite) (4) microcrystals of kaolinite (5) unknown phase of fine grained Mg, Al sulfate (likely pickeringite) (6) micronodules of Cu halite (7) Euhedral cubic Na Mg sulfate covered by crusts of halite and probably pickeringite. At the minimum 6 distinct phases were identified at IN13-P4 through ESEM analysis (Figure

4-40): (1) Globular masses of Cu halite mineral presumed to be atacamite (2) anhedral mass of mixed quartz, Mg Al sulfate and probable montmorillonite (3) microcrystalline alum-K and albite (4) minor phase of probable kaolinite (5) large halite cube (6) cubic crystals of Na Mg sulfates. At least 10 distinct phases were identified at IN13-P5 through ESEM analysis (Figure 4-42): (1) euhedral crystals of probable blodite (2) cubic halite (3) microcrystallites of unidentified Mg sulfate (4) cubic sylvite (KCl) (5) cubic Mg Na sulfate with flattened terminations (6) aggregates of tabular Ca sulfate (gypsum or anhydrite) (7) globules of subhedral to anhedral Al sulfates (8) crusts and nodules of Cu halide with traces of Mg (9) spherical aggregates of tabular Na Mg Cl sulfate (10) anhedral globules of unidentified Mg sulfate.

A few phases identified with the ESEM were not previously observed from XRD and μ XRD analyses. These include Mg-Al sulfate (likely pickeringite), Cu halides, sylvite and Na K sulfate (potentially aphtitalite). At IN13-P1, only blodite and quartz are identified with all 3 techniques, further demonstrating the importance of using various tools to understand the mineralogy of a sample (Table 4-21). Only quartz, montmorillonite and starkeyite are identified by all methods in sample IN13-P3 (Table 4-23). Potential blodite, alum-K and halite are the only minerals observed with all tools at IN13-P4 (Table 4-24). Atacamite and kaolinite were only identified from the ESEM analysis of the mounted secondary precipitates. None of the minerals are identified by all analytical methods in sample IN13-P5 (Table 4-25).

Figure 4-33 μ XRD element maps collected on thin section IN13-P1. μ XRD spots demonstrate that multiple elements are found even at the finer scale.

Table 4-21 List of minerals identified at IN13-P1 with μ XRD, XRD and ESEM (MSP).

IN13-P1		Identification Method		
Minerals	Formula	XRD	μXRD	ESEM
Albite	$(\text{Na}_{0.84}\text{Ca}_{0.16})\text{Al}_{1.16}\text{Si}_{2.84}\text{O}_8$		x	
Quartz	SiO_2	x	x	x
Loweite	$\text{Na}_{12}\text{Mg}_7(\text{SO}_4)_{13} \cdot 15(\text{H}_2\text{O})$		x	x
Blodite	$\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4(\text{H}_2\text{O})$	x	x	x
Alunite	$\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$		x	x
Hexahydrite	$\text{Mg}(\text{SO}_4) \cdot 6(\text{H}_2\text{O})$		x	
Gypsum	$\text{Ca}(\text{SO}_4) \cdot 2(\text{H}_2\text{O})$	x		x
Aphthitalite	$(\text{K},\text{Na})_3\text{Na}(\text{SO}_4)_2$			x
Halite	NaCl			x

Figure 4-34 ESEM images of IN13-P1 sample measured at 15 kV. (A) Flat hexagonal crystallites of Ca sulfates with evidence of Cu, euohedral intergrowths of Na K sulfate phase interpreted as potentially thenardite, irregularly shaped halite mass, euohedral intergrowth of varying sizes of Na Mg sulfate interpreted to be blodite, finer groundmass of probable alunite. (B) Irregularly shaped globular mass of halite, euohedral intergrowth of varying sizes of Na Mg sulfate interpreted to be blodite or loweite, finer groundmass of probably alunite forming crusts on the Na Mg sulfate phases. (C) Euohedral isometric aggregates of Na Mg sulfates with flattened terminations and intergrown nodules of alunite and quartz.

Figure 4-35 μ XRD elemental maps collected on thin section IN13-P2. Although the fluorescence map demonstrates enrichments in Cu yet no Cu minerals have been identified.

Figure 4-36 μ XRD 2D diffraction pattern of natrojarosite and associated 1D diffraction pattern with matched mineral profile (top right).

Table 4-22 List of minerals identified at IN13-P2 with μ XRD methods at the synchrotron, bulk XRD and ESEM.

IN13-P2 Minerals	Formula	Identification Method	
		XRD	μ XRD
Quartz	SiO_2		x
Halite	NaCl		x
Loweite	$\text{Na}_{12}\text{Mg}_7(\text{SO}_4)_{13} \cdot 15(\text{H}_2\text{O})$		x
Blodite	$\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4(\text{H}_2\text{O})$		x
Alunite	$\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$		x
Hematite	Fe_2O_3		x
Hexahydrate	$\text{Mg}(\text{SO}_4) \cdot 6(\text{H}_2\text{O})$		x
Gypsum	$\text{Ca}(\text{SO}_4) \cdot 2(\text{H}_2\text{O})$	x

Figure 4-37 μ XRD elemental maps collected on thin section IN13-P3.

Figure 4-38 ESEM images of IN13-P3 sample measured at 10 kV. (A) Isometric euhedral grains of halite with irregularly shaped amalgamation of Na, Mg sulfate forming within the structure. (B) Tabular to lamellar aggregate of Mg sulfate (probably starkeyite) surrounded by intergrown microcrystals of kaolinite, an unknown phase of Mg, Al, Cl sulfate (likely pickeringite), micronodules of Cu halite and irregularly shaped halide. (C) Isometric crystal of halite with irregular inclusion of unknown Mg, Al, Cl sulfate, surrounded by intergrown microcrystals of kaolinite, the same unknown phase of Mg, Al sulfate and irregularly shaped halite. (D) Growth of Na, Mg sulfate cubes covered by crusts of halite and probably pickeringite.

Table 4-23 List of minerals identified at IN13-P3 with μ XRD methods at the synchrotron, bulk XRD and ESEM.

IN13-P3		Identification Method			
Minerals	Formula	XRD	μ XRD	ESEM	
Quartz	SiO_2	X	X	X	
Orthoclase	$\text{K(AlSi}_3\text{)O}_8$	X	X		
Anorthite	$(\text{Na}_{0.45}\text{Ca}_{0.55})(\text{Al}_{1.55}\text{Si}_{2.45}\text{O}_8)$		X		
Montmorillonte	$\text{Na}_{0.3}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot x\text{H}_2\text{O}$	X	X	X	
Halite	NaCl		X	X	
Changoite	$\text{Na}_2\text{Zn(SO}_4\text{)}_2 \cdot 4(\text{H}_2\text{O})$		X		
Anhydrite	CaSO_4	X	X		
Starkeyite	$\text{Mg(SO}_4\text{)} \cdot 4(\text{H}_2\text{O})$	X	X	X	
Na Mg sulfate				X	
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$			X	
Pickeringite	$\text{MgAl}_2(\text{SO}_4)_4 \cdot 22(\text{H}_2\text{O})$			X	
Atacamite	$\text{Cu}_2\text{Cl(OH)}_3$			X

Figure 4-39 μ XRD elemental maps collected on thin section IN13-P4.

Table 4-24 List of minerals identified at IN13-P4 with μ XRD methods at the synchrotron, bulk XRD and ESEM.

IN13-P4		Identification Method			
Minerals	Formula	XRD	μ XRD	ESEM	
Quartz	SiO_2	x	x	x	
Halite	NaCl	x	x	x	
Albite	$(\text{Na}_{0.84}\text{Ca}_{0.16})\text{Al}_{1.16}\text{Si}_{2.84}\text{O}_8$		x	x	
Alum-K	$\text{KAl}(\text{SO}_4)_2 \cdot 12(\text{H}_2\text{O})$	x	x	x	
Magnesite	$\text{Mg}(\text{CO}_3)$		x		
Hexahydrite	$\text{Mg}(\text{SO}_4) \cdot 6(\text{H}_2\text{O})$	x	x		
Blodite	$\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4(\text{H}_2\text{O})$	x	x	x	
Montmorillonite	$\text{Na}_{0.3}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot x(\text{H}_2\text{O})$		x	x	
Gypsum	$\text{Ca}(\text{SO}_4) \cdot 2(\text{H}_2\text{O})$	x			
Atacamite	$\text{Cu}_2\text{Cl}(\text{OH})_3$			x	
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$			x

Figure 4-40 ESEM images of IN13-P4 sample measured at 10 kV. (A) Globular masses of Cu halide mineral presumed to be atacamite, surrounded by anhedral masses of quartz, Mg Al sulfate and probable montmorillonite. (B) Nodules of Cu halide mineral presumed to be atacamite, and probable microcrystalline alum-K, albite and a Na Mg sulfate (C) Amalgamated mass of probable atacamite with minor phase of probable kaolinite (D) Larger cube of halite with possible inclusions of microcrystalline Na Mg sulfates and kaolinite, bordering smaller cubic crystals of Na Mg sulfates.

Figure 4-41 μ XRD elemental maps collected on thin section IN13-P5.

Table 4-25 List of minerals identified at IN13-P5 with μ XRD methods at the synchrotron, bulk XRD and ESEM.

IN13-P5 Minerals	Formula	Identification Method		
		XRD	μ XRD	ESEM
Halite	NaCl	x		x
Gypsum	$\text{Ca}(\text{SO}_4) \cdot 2(\text{H}_2\text{O})$	x		x
Hexahydrite	$\text{Mg}(\text{SO}_4) \cdot 6(\text{H}_2\text{O})$	x	x	x
Muscovite	$\text{KAl}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2$	x	x	
Starkeyite	$\text{Mg}(\text{SO}_4) \cdot 4(\text{H}_2\text{O})$	x		x
Albite	$(\text{Na}_{0.622}\text{Ca}_{0.368})\text{Al}_{1.29}\text{Si}_{2.7}\text{O}_8$		x	
Quartz	SiO_2	x	x	
Bassanite	$\text{Ca}(\text{SO}_4) \cdot 0.5(\text{H}_2\text{O})$		x	
Loweite	$\text{Na}_{12}\text{Mg}_7(\text{SO}_4)_{13} \cdot 15(\text{H}_2\text{O})$		x	x
Anhydrite	$\text{Ca}(\text{SO}_4)$		x	x
Blodite	$\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4(\text{H}_2\text{O})$		x	x
d'ansite	$(\text{Zn}(\text{SO}_4))(\text{NaCl})_3(\text{Na}_2(\text{SO}_4))_9$		x

Figure 4-42 ESEM images of sample IN13-P5. (A) Euhedral crystals of probable blodite and halite enclosed in a mixture of microcrystallites of unidentified Mg sulfate, halite and sylvite (B) Microcrystals of cubic sylvite found alongside a larger cube of Mg Na sulfate (C) Intergrown aggregates of tabular Ca sulfate (gypsum or anhydrite), globules of subhedral to anhedral Al sulfates and euhedral Na Mg sulfates. (D) Crusts and nodules of Cu halide and traces of Mg. (E) Cubic crystals of halite and isometric crystals of probable blodite. (F) Spherical aggregates of tabular Na Mg Cl sulfate and anhedral globules of unidentified Mg sulfate. (G) Probable euhedral crystals of blodite, covered by crusts of halite and alongside crystals of unidentified subhedral Al sulfate minerals.

4.2.2.2 Lagunas Norte

4.2.2.2.1 LN-DAR-1

The water at DAR-1 was underdrain from waste rock pile leachate. One sample of brownish-red secondary precipitates was sampled. Hydroniumjarosite ($(\text{H}_3\text{O})\text{Fe}(\text{SO}_4)_2(\text{OH})_6$), quartz (SiO_2) and anorthoclase ($(\text{Na,K})\text{AlSi}_3\text{O}_8$) are identified (Table 4-27). Al, As, Ca, Fe, Mg, K, P and S are the most concentrated elements in this sample (Figure 4-43).

Figure 4-43 Concentration of elements in mg/kg in the solid sample LN-DAR01 from ICP-OES analysis.

4.2.2.2.2 LN-SP3

This sampling site is the third settling pond on site. Two wet precipitate samples were collected here: Fe oxides and some creamy white material. XRD analysis demonstrates that sample LN-SP3-P1 contains mainly quartz (SiO_2) and albite ($\text{NaAlSi}_3\text{O}_8$) with bulk analysis revealing highest concentrations in Al, Fe, Mg, K, S (Figure 4-44).

Figure 4-44 Concentration of elements in mg/kg in the solid sample LN-SP3 from ICP-OES analysis.

4.2.2.2.3 LN-PW1-P1

Precipitates were sampled along the pit wall and can be described as blue crusts. Sample bulk chemistry data shows highest concentrations of Ca, Cu, Fe and S (Figure 4-45). Minerals identified for this thin section in bulk analysis include chalcantite ($\text{Cu}(\text{SO}_4) \cdot 5(\text{H}_2\text{O})$) and gypsum. Thin section LN-PW1-P was made out of secondary precipitates collected from effluent mine drainage waters along the pit wall. Micro-XRD demonstrates a more diverse set of minerals present such as Cu, Fe, Fe-As, and SO_4 rich minerals. Copper-rich minerals potentially include poitevinite ($\text{Cu,Fe}^{2+},\text{Zn}(\text{SO}_4) \cdot (\text{H}_2\text{O})$), antlerite ($\text{Cu}_3(\text{SO}_4)(\text{OH})_4$), and chrysocolla ($(\text{Cu,Mg})(\text{SiO}_3) \cdot (\text{H}_2\text{O})$) (Table 4-26). Iron-rich minerals include fibroferrite ($\text{Fe}(\text{OH})(\text{SO}_4) \cdot 5(\text{H}_2\text{O})$) and scorodite ($\text{Fe}(\text{AsO}_4) \cdot 2(\text{H}_2\text{O})$) (Table 4-26). Gypsum ($\text{Ca}(\text{SO}_4) \cdot 2(\text{H}_2\text{O})$) was also present throughout the section. Poitevinite is a rare secondary mineral that may occur in the oxidized zone of hydrothermal mineral prospects (Schindler et al., 2006; Lottermoser, 2010c). Although poitevinite is closely related to the kieserite group, it is differentiated by the presence of Cu, Fe and Zn. Antlerite is a secondary mineral occurring in the oxidized zone of copper deposits in arid regions (Zvereva et al., 2015). Jarosite, is a straw-yellow mineral that is common found in the weathered zone of sulfide ore deposits

and in acid sulfate soils (Bigham et al., 2000). Chrysocolla is a commonly associated with other secondary copper minerals. Bonattite is also a common secondary mineral from a pyrite containing deposit. Scorodite is a common secondary mineral formed by the oxidation of arsenopyrite or other arsenic-bearing minerals (Triantafyllidis and Skarpelis, 2006; Jamieson et al., 2011).

This sample was also mounted on a stub and carbon coated to be analyzed by ESEM. The results demonstrate great variation in morphologies and chemical composition. At least 5 phases were identified by the ESEM (Figure 4-48): (1) intergrowths of sheet-like stacks of Fe Al sulfate interpreted to be aluminocopiapite, the aluminium (2) crystals of tabular gypsum (3) anhedral to subhedral tabular crystals of Cu sulfates with rounded terminations (4) anhedral Cu sulfate crystals showing evidence of desiccation (5) microcrystalline Cu silicate (likely chrysocolla). These results demonstrate that only chalcantite was identified by all methods, whereas the Al Fe sulfate phase likely aluminocopiapite, was only identified using the ESEM.

Figure 4-45 Concentration of elements in mg/kg in the solid sample LN-PW1-P1 and LN-PW1-P2 from ICP-OES analysis.

Synchrotron microanalysis was conducted on the sample LN-PW1-P1. The results are tabulated so as to show common phases with differing analytical methods (Table 4-26).

Figure 4-46 μ XRF elemental maps from the thin section made of sample LN-PW1-P1.

Figure 4-47 μ XRD 2D diffraction pattern (bottom left) of antlerite. The associated 1D diffraction pattern with matched mineral profiles is on the right.

Figure 4-48 ESEM images of sample LN-PW1-P1 mounted on a stub. (A) Intergrowths of sheet-like stacks of Fe-Al sulfate interpreted to be aluminocopiapite, crystals of tabular gypsum and anhydral to subhedral tabular crystals of Cu sulfates with rounded terminations. (B) Sheet-like aggregates of Cu and Fe sulfates surrounded by tabular Cu sulfate minerals. (C) Tabular euhedral crystal of Cu sulfates, as well as anhydral, larger Cu sulfate crystals showing evidence of desiccation. (D) Larger tabular subhedral crystal of unidentified Cu sulfate and smaller crystal of gypsum. (E) Anhydral tabular grain of Cu sulfate.

Table 4-26 List of minerals identified at LN-PW1-P1 with μ XRD methods at the synchrotron, bulk XRD and ESEM.

LN-PW1-P1		Identification Method		
Minerals	Formula	XRD	μ XRD	ESEM
Chalcanthite	$\text{CuSO}_4 \cdot 5(\text{H}_2\text{O})$	x	x	x
Antlerite	$(\text{Cu}_3(\text{OH})_4(\text{SO}_4))$		x	x
Chrysocolla	$(\text{Cu}, \text{Mg})\text{SiO}_3 \cdot (\text{H}_2\text{O})$		x	x
Scorodite	$\text{Fe}(\text{AsO}_4) \cdot 2(\text{H}_2\text{O})$		x	
Poitevinite	$\text{Cu}(\text{SO}_4) \cdot (\text{H}_2\text{O})$		x	x
Fibroferrite	$\text{Fe}(\text{OH})(\text{SO}_4) \cdot 5(\text{H}_2\text{O})$		x	
Aluminocopiapite	$\text{Al}_{2/3}\text{Fe}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20(\text{H}_2\text{O})$			x
Gypsum	$\text{Ca}(\text{SO}_4) \cdot 2(\text{H}_2\text{O})$		x	x

4.2.2.2.4 LN-VWD

Solid samples were collected next to the waste rock leachate before the collection in the Vizcachaz pond for treatment. Two white precipitate samples, and Fe oxide crust overlying the white material were sampled and analyzed. LN-VWD-P1 reveals high concentrations in Al, Ca, Fe, Mn, P, K, S (Figure 4-49). LN-VWD-P2 reveals high concentrations in Al, Ca, Fe, Mg, Mn, P, K, S (Figure 4-49). The occurrences of the following minerals are based on bulk chemistry, physical properties of the sample such as colour and XRD analyses: Ettringite ($\text{Ca}_6(\text{Al}(\text{OH})_6(\text{SO}_4)_3 \cdot 26(\text{H}_2\text{O}))$), calcite ($\text{Ca}(\text{CO}_3)$), quartz and alunogen were identified in LN-VWD-P1; gypsum, quartz and ettringite were identified at LN-VWD-P2 (Table 4-27). Ettringite is assumed to have an anthropogenic origin in the sample because of the nearby lime addition. Calcite may have possibly formed as a result of lime addition near this sampling location.

Figure 4-49 Concentration of elements in mg/kg in the solid sample LN-VWD-P1 and LN-VWD-P2 from ICP-OES analysis.

Table 4-27 Minerals identified with bulk XRD from samples collected at Lagunas Norte mine.

Sample	Minerals	Chemical Formula
LN-DAR01-P1	Quartz	SiO_2
	Hydroniumjarosite	$(\text{H}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$
	Anorthoclase	$\text{Na}_{0.7}\text{K}_{0.29}\text{AlSi}_3\text{O}_8$
LN-SP3-P1	Quartz	SiO_2
	Albite	$\text{NaAlSi}_3\text{O}_8$
	Muscovite	$\text{KAl}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2$
LN-PW1-P1	Chalcanthite	$\text{Cu}(\text{SO}_4) \cdot 5(\text{H}_2\text{O})$
LN-PW1-P2	Chalcanthite	$\text{Cu}(\text{SO}_4) \cdot 5(\text{H}_2\text{O})$
	Quartz	SiO_2
	Anorthite	$\text{CaAl}_2\text{Si}_2\text{O}_8$
	Alum-Na	$\text{NaAl}(\text{SO}_4)_2 \cdot 12(\text{H}_2\text{O})$
	Melanterite	$\text{Fe}^{+2}(\text{SO}_4) \cdot 7(\text{H}_2\text{O})$
LN-PW2-P1	Quartz	SiO_2
	Muscovite	$\text{KAl}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2$
	Gypsum	$\text{CaSO}_4 \cdot 2(\text{H}_2\text{O})$
LN-VWD-P1	Ettringite	$\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26(\text{H}_2\text{O})$
	Calcite	$\text{Ca}(\text{CO}_3)$
	Quartz	SiO_2
	Alunogen	$\text{Al}_2(\text{SO}_4)_3 \cdot 17(\text{H}_2\text{O})$
LN-VWD-P2	Gypsum	$\text{Ca}(\text{SO}_4) \cdot 2(\text{H}_2\text{O})$
	Quartz	SiO_2
	Ettringite	$\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26(\text{H}_2\text{O})$

4.2.2.3 Pierina

Secondary minerals identified at Pierina in a study conducted by Klohn Crippen Berger (2012) include alunite, calcite, gypsum, chalcantite, paracoquimbite, coquimbite, ferriocopiapite, zincocopiapite, brochantite and antlerite.

4.2.2.3.1 P-WRD

Three secondary precipitates were collected next to waste rock drainage water. These include Fe oxides, Fe oxides with some lighter coloured areas and some flaky darker brown pieces, and brown-beige colored precipitates. In this sample, quartz (SiO_2), jarosite, montmorillonite ($(\text{Na,Ca})_{0.3}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot x\text{H}_2\text{O}$) were identified based on the chemistry analyzed by Analytical Services Unit at Queen's University, physical properties of the sample such as colour and XRD analyses. Bulk chemistry results show high concentrations in Al, As, Ca, Fe, Mg, P, Na, S. All elements in this list are accounted for by identified mineralogy with the exception of As and P (Figure 4-50, Table 4-28).

Figure 4-50 Concentration of elements in mg/kg in the solid sample P-WRD-P1 from ICP-OES analysis.

4.2.2.3.2 P-EC

Secondary samples at P-EC were collected from water filled Emilio Cocha pit. These are brownish beige coloured with no obvious mineral structures. Minerals observed in P-EC-P1 include alunite ($K(Al_3(SO_4)_2(OH)_6)$), spangolite ($Cu_6Al(SO_4)(OH)_{12}Cl \cdot 3(H_2O)$), quartz (SiO_2) and montmorillonite ($((Na,Ca)_{0.3}(Al, Mg)_2Si_4O_{10}(OH)_2 \cdot x(H_2O))$) (Table 4-28). The most elevated elemental concentrations are in Al, Ca, Fe, Mg, Mn, K, P, S, Zn (Figure 4-51).

Figure 4-51 Concentration of elements in mg/kg in the solid sample P-EC from ICP-OES analysis.

4.2.2.3.3 P-PW

Mixed white, yellow and cream coloured secondary precipitates were collected from the pit wall. P-PW1-P-b and P-PW1-P-c show high concentrations of Al, As, Ca, Cu, Fe, and S (Figure 4-52). Minerals include romerite ($Fe^{2+}Fe^{3+}_2(SO_4)_4 \cdot 14(H_2O)$), coquimbite ($Fe_{1.62}Al_{0.38}(SO_4)_3 \cdot 9(H_2O)$), and quartz in P-PW1-P-b, and coquimbite ($Fe_{1.62}Al_{0.38}(SO_4)_3 \cdot (H_2O)_9$), romerite ($Fe^{2+}Fe^{3+}_2(SO_4)_4 \cdot 14(H_2O)$) and likely magnesiocopiapite in P-PW1-P-c (Table 4-28). Alunite is a common alteration mineral found at HS epithermal deposits. Coquimbite is a water soluble efflorescent mineral commonly produced by oxidation with Fe sulfide minerals (Romero et al., 2006). Romerite also forms from the oxidation of Fe sulfides (Chou et al., 2013).

ESEM analyses conducted on carbon coated mounted stubs from samples P-PW1-Pb and P-PW1-Pc. At least 3 distinct phases were identified from the MSP stubs of sample P-PW1-Pc, clearly demonstrating differing morphology and chemistry (Figure 4-53): (1) fine grained mass of Fe Al sulfate mineral (likely halotrichite) (2) microcrystalline of halite (3) euhedral radial intergrowth of Fe Al sulfate crystallites. Seven different phases were identified by ESEM within the sample P-PW1-Pb (Figure 4-54), including: (1) Platy, hexagonal crystallites of an Al sulfate mineral (2) Columnar Fe Al sulfate (3) stacked hexagonal and platy Fe Al sulfates with surficial crusts of Cu and As aggregates (4) hexagonal and platy Fe Al sulfate interpreted as the aluminium endmember of coquimbite, aluminocoquimbite, forming rosettes (5) Platy hexagonal Fe sulfates (6) fibrous and columnar aggregate of probable aluminocoquimbite (7) granular kaolinite.

Figure 4-52 Concentration of elements in mg/kg in the solid sample P-PW-Pb and P-PW-Pc from ICP-OES analysis.

Figure 4-53 ESEM images of P-PW1-Pc sample. (A) Fine grained mass of Fe Al sulfate mineral (likely halotrichite) (B) Crusts of halite forming on euhedral radial intergrowth of Fe Al sulfate crystallites. (C) Radial intergrowths of Fe Al sulfate minerals with trace amount of Mg, perhaps as a contaminant from the epoxy used.

Figure 4-54 ESEM images of sample P-PW1-Pb. (A) Platy, hexagonal crystallites of an Al sulfate mineral.(B) Columnar Fe Al sulfate seemingly growing on a rosette of Fe sulfate with less Al. (C) Intergrowth of stacked hexagonal and platy Fe Al sulfates with crusts of Cu aggregates forming on the surface of the minerals. (D) Platy hexagonal Fe Al sulfate interpreted as aluminocoquimbite forming rosettes (E) Platy hexagonal Fe sulfates on columnar Fe Al sulfate. Unidentified Fe sulfate minerals appear as larger subhedral aggregates. (F) Fibrous and columnar aggregate of probable aluminocoquimbite with granular kaolinite. (G) Columnar aggregates of Fe Al sulfate, smooth and bright phase are a mixture of Fe sulfates with Cu and quartz and platy hexagonal crystallites of Fe Al sulfates with evidence of As.

Table 4-28 Minerals identified with bulk XRD from samples collected at Pierina mine.

Sample	Minerals	Chemical Formula
P-EC-P1	Muscovite	$\text{KAl}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2$
	Quartz	SiO_2
	Gypsum	$\text{Ca}(\text{SO}_4) \cdot 2(\text{H}_2\text{O})$
P-PW1-P-a	No bulk XRD	
P-PW1-P-b	Romerite	$\text{Fe}^{2+}\text{Fe}^{3+}_2(\text{SO}_4)_4 \cdot 14(\text{H}_2\text{O})$
	Coquimbite	$(\text{Fe}_{1.62}\text{Al}_{0.38})(\text{SO}_4)_3 \cdot 9(\text{H}_2\text{O})$
	Quartz	SiO_2
P-PW1-P-c	Coquimbite	$(\text{Fe}_{1.54}\text{Al}_{0.46})(\text{SO}_4)_3 \cdot 9(\text{H}_2\text{O})$
	Romerite	$\text{Fe}^{2+}\text{Fe}^{3+}_2(\text{SO}_4)_4 \cdot 14(\text{H}_2\text{O})$
	Magnesiocoiapite	$\text{MgFe}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20(\text{H}_2\text{O})$
P-PW1-P-d	No bulk XRD	
P-WRD	Quartz	SiO_2
	Jarosite	$\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$
	Montmorillonite	$(\text{Na,Ca})_{0.3}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot x(\text{H}_2\text{O})$

4.2.3 Trace element association with minerals

Semi-quantitative amounts of trace elements associated with certain minerals were identified by the analysis of MCA spectra collected from the μ XRF maps. This analysis was conducted for spots where the mineral had already been identified by μ XRD. In order to calculate weight percentages of the trace elements given count values from the μ XRF maps, these were normalized to Fe or Cu depending on the spectra (Table 4-31). For the calculations, a matrix of either $\text{Cu}(\text{SO}_4)$ or $\text{Fe}(\text{SO}_4)$ was assumed based on the energy dispersive spectra. Furthermore, compositionally, almost all analyses are dominated by Cu or Fe. If the Fe phases here are oxides rather than sulfates, the uncertainty is very small since S and O have similar absorption at the energy of analysis. Sulfur and O concentrations are fixed at 20 and 40 weight percent. Results show that blodite is host to Cu, Mn, Zn, Ca, Co, Fe, and Ni in approximately decreasing order. Alunite is host to Cu, Zn, Ca, Mn, Fe, Ti, Co, Ni and As in decreasing order. Hexahydrite contains Cu, Zn, Fe, Mn, As, Ni, Ti or Ti, As, Co, and Ni in decreasing order. Goethite shows significant variation with regards to trace elements from one spot to the next. In fact, the order of elements is different in all 7 spots analyzed with goethite being identified as the primary mineral (Table 4-30). Copper and Zn, have been observed by Manceau et al. (2000) to be incorporated into the structure of goethite, which may also be the case here. However, it is also possible that the elements are associated with a different mineral if another phase, perhaps amorphous, is present but not identified through μ XRD analysis.

Table 4-29 Elements associated to blodite, alunite, hexahydrite and goethite in decreasing order within samples from El Indio.

Minerals	Associated elements
Blodite	Cu, Mn, Zn, Ca, Co, Fe, Ni
Alunite	Cu, Zn, Ca, Mn, Fe, Ti, Co, Ni
Hexahydrite	Cu, Zn, Fe, Mn, As, Ni, Ti
Goethite	Cu, K, Mn, As

Table 4-30 Elements associated to goethite in decreasing order within samples from El Indio.

Sample	Mineral μXRD	Associated elements
IN28-P2-04-xrd2	Goethite	Cu>Mn>K>Zn>Ca>As>Ti>Co
IN28-P4-01-xrd1		K>As>Ti>Mn>Co>Cu>Zn
IN28-P4-01-xrd2		Mn>As>K>Co>Ti>Ca>Cu>Ni
IN28-P4-01-xrd10		K>Ca>Ti>Mn>Ni>Br>Co>Cu>Zn>As
IN28-P4-02-xrd3		K>Ti>Mn>Co>Ca>Cu>Ni>Zn>As
IN28-P4-04-xrd1		K>Ca>Ti>Mn>Co>As>Cu
IN28-P4-04-xrd2		Ti>Mn>Co>Cu>As

Table 4-31 Trace elements determined with μ XRF (weight percent).

IN13-P1-03-XRD2			IN13-P1-07-xrd6			IN13-P3-01-xrd13		
Blodite			Blodite			Anhydrite		
Component	Wt%	Ratios (Cu)	Component	Wt%	Ratios (Cu)	Component	Wt%	Ratios (Cu)
Cu	40	1.0	Cu	40	1.0	Ca	150	3.8
Mn	28	0.7	Mn	22	0.55	Zn	115	2.9
Zn	14	0.35	Zn	10	0.26	Mn	70	1.8
Ca	3.5	0.087	Fe	0.99	0.025	Cu	40	1.0
Co	0.99	0.025				Ti	14	0.36
Fe	0.70	0.018				Fe	8.5	0.21
Ni	0.77	0.019				As	1.3	0.033
						Br	1.4	0.035
IN13-P1-05-XRD5			IN28-P2-04-xrd2			IN28-P4-01-xrd1		
Alunite			Goethite			Goethite		
Component	Wt%	Ratios (Cu)	Component	Wt%	Ratio(Fe)	Component	Wt%	Ratio(Fe)
Cu	40	1.0	Fe	40	1.0	Fe	40	1.0
Zn	17	0.42	Cu	6.0	0.15	K	2.8	0.071
Ca	13	0.32	Mn	5.0	0.12	As	1.9	0.046
Mn	12	0.31	K	2.2	0.056	Ti	0.78	0.020
Fe	4.8	0.12	Zn	1.2	0.031	Mn	0.74	0.019
Ti	2.0	0.050	Ca	0.80	0.020	Co	0.28	0.0069
Co	0.28	0.0070	As	0.68	0.017	Cu	0.19	0.0046
Ni	0.23	0.0058	Ti	0.59	0.015	Zn	0.021	0.00053
As	0.13	0.0031	Co	0.31	0.0078			
Rb	0.52	0.013						
IN28-P4-01-xrd2			IN28-P4-01-xrd10			IN28-P4-02-xrd3		
Goethite			Goethite			Goethite		
Component	Wt%	Ratio(Fe)	Component	Wt%	Ratio(Fe)	Component	Wt%	Ratio(Fe)
Fe	40	1.0	Fe	40	1.0	Fe	40	1.0
Mn	4.2	0.11	K	3.8	0.095	K	1.7	0.042
As	3.4	0.085	Ca	1	0.025	Ti	0.94	0.024
K	2.7	0.067	Ti	0.91	0.023	Mn	0.79	0.020
Co	0.96	0.024	Mn	0.83	0.021	Co	0.73	0.018
Ti	0.75	0.019	Ni	0.18	0.0044	Ca	0.57	0.014
Ca	0.64	0.016	Br	0.081	0.0020	Cu	0.18	0.0046
Cu	0.086	0.0022	Co	0.019	0.00047	Ni	0.018	0.00044
Ni	0.063	0.0016	Cu	0.01	0.00025	Zn	0.012	0.00031
			Zn	0.0078	0.00019	As	0.0052	0.00013
			As	0.001	0.00003			
IN28-P4-04-xrd1			IN28-P4-04-xrd2			IN28-P2-04-xrd6		
Goethite			Goethite			Hexahydrite		
Component	Wt%	Ratio(Fe)	Component	Wt%	Ratio(Fe)	Component	Wt%	Ratio (Cu)
Fe	40	1.0	Fe	40	1.0	Cu	40	1.0
K	2.0	0.049	Ti	0.53	0.013	Zn	16	0.41
Ca	0.81	0.020	Mn	0.36	0.0089	Fe	15	0.38
Ti	0.63	0.016	Co	0.50	0.012	Mn	6.7	0.17
Mn	0.55	0.014	Cu	0.050	0.0012	As	5.3	0.13
Co	0.56	0.014	As	0.038	0.00094	Ni	2.8	0.069
As	0.084	0.0021				Ti	1.0	0.026
Cu	0.037	0.00093						

Table 4-32 Trace elements determined with μ XRF (weight percent).

IN28-P2-04-xrd9 Hexahydrite			IN13-P1-01-XRD3 Loweite			IN13-P2-02-xrd1 Loweite		
Component	Wt%	Ratio(Cu)	Component	Wt%	Ratios (Cu)	Component	Wt%	Ratios (Cu)
Cu	40	1.0	Cu	40	1.0	Cu	40	1.0
Zn	18	0.46	Mn	33	0.83	Mn	29	0.73
Fe	12	0.30	Zn	4.4	0.11	As	8.1	0.20
Mn	11	0.27	Co	1.5	0.038			
Ti	0.81	0.020	Ni	1.3	0.032			
As	0.40	0.010	Fe	0.84	0.021			
Co	0.16	0.0039						
Ni	0.22	0.0055						
IN13-P5-01-xrd10 Loweite			IN13-P5-02-xrd10 Loweite			IN13-P5-03-xrd2 Loweite		
Component	Wt%	Ratios (Cu)	Component	Wt%	Ratios (Fe)	Component	Wt%	Ratio(Fe)
Cu	40	1.0	Fe	40	1.0	Fe	40	1.0
Fe	26	0.64	Ca	13	0.33	Cu	40	1.00
Zn	25	0.63	Cu	13	0.33	Mn	27	0.67
Mn	16	0.41	K	11	0.28	K	19	0.47
Ti	2.7	0.068	Mn	7.6	0.19	Ca	11	0.29
Co	1.7	0.042	Ti	5.1	0.13	Zn	4.3	0.11
Ni	1.2	0.030	Zn	1.7	0.042	Ti	1.4	0.034
			Ni	0.58	0.014	Co	1.2	0.030
			Co	0.49	0.012	As	0.23	0.0057
			As	0.12	0.0031			
			Br	0.027	0.00068			

Chapter 5

Discussion

5.1 Discussion of geochemical characterization of waters

5.1.1 Field parameters

Field parameters for surface waters collected at the 3 sites are listed in Table 4-7, Table 4-8, Table 4-9. At El Indio, conductivity measurements increased significantly downstream from 458 $\mu\text{S}/\text{cm}$ to 1789 $\mu\text{S}/\text{cm}$ suggesting that ions were being added to the solution over the course of the downstream flow. As such, attenuation processes for sequestering ions from the solution during the sampling period may be relatively ineffective as the stream increases concentrations of dissolved species. The Eh measurements at El Indio suggest that IN28 and IN2 have a slightly higher redox capacity (higher Eh values), a variation that may impact the mobility of certain elements in the river system. IN23 has the highest pH (7.31) as it represents a natural stream before it enters the mine site. The lowest temperature and pH are measured at IN2, the sampling site found closest downstream to the Pastos Largos settling pond. Otherwise, temperature is fairly consistent amongst measured sites. The pH of IN-13 increases 1-2 pH units as a result of surficial water input from a nearby stream. A correlation between temperature and pH or conductivity was not observed at this mine. Based on temporal data collected from Barrick Gold Corporation, sample site IN28 is representative of the largest single flow into the mine drainage system.

At Lagunas Norte, specific conductance is highest at LN-DAR-1. A large concentration of dissolved salts is expected in these waters because the sample site represents leachate from the waste rock pile. This sampling location also has the lowest pH out of all measured sites because of its direct association with the waste rock pile, which is of acid sulfates HS origin. The waters collected from the pit wall (LN-PW1 and LN-PW2) have near neutral pH measurements likely because they have not been exposed to acid sulfates and oxidizing sulfides that would acidify the waters. The ORP demonstrates that LN-DW-B-11 (1.74 V) and LN-PW2 (6.4 V) have the lowest Eh values, which decreases the mobility of elements such as

Pb, Cd, As, Mn, Al, Fe. At Pierina, specific conductance measurements are highest at P-WRD and pH is the lowest, consistent with the observation that this solution is representative of waste rock drainage. The temperature values are positively correlated with specific conductance measurements at this mine, implying that temperature should always be recorded as it controls and influences specific conductance measurements.

Although samples were collected during one field season, seasonal variations including rainfall, weathering rates and temperature changes are expected to have an influence on the field variable values collected. Temperature of these streams is expected to rise in the summer months, thereby potentially increasing the values of specific conductance of the streams. Moreover, research from Sracek et al. (2010) demonstrate the effects of seasonal changes such as humidity, precipitation and evaporation. Sracek et al. (2010) have studied precipitated efflorescent salts in Cu-Co chemical leaching plant wastes in Zambia, and their precipitation sequences in evaporation experiments. The acidic waters of Na-Mg-SO₄ type underwent evaporation and demonstrated gradual increase in the concentration of Na, Mg, and SO₄, a sharp increase in the concentration of K, and a decrease in the concentration of Ca. The changes in these concentrations during evaporation experiments demonstrate the control of certain elements by precipitation of specific phases. It is clear that evaporative concentration is a prominent process at these mine sites due to the presence of the various types of hydrated to dehydrated precipitates such as hexahydrate and starkeyite. Moreover, the variations in elemental concentrations in solution throughout the mines can be attributed to the types of primary minerals oxidizing, to the secondary minerals dissolving or (re)forming, as well as the varying affinities of trace elements and aqueous species to mineral surfaces. These secondary minerals will be further discussed in section 5.2. Finally, the field parameters are not uncommon for deposits with ARD but do show variability from site to site and between mines.

5.1.2 Comments on ultrafiltration and colloidal stability

Throughout the various sampling sites, trace metals and other elements in solution are thought to be partitioned between colloids and aqueous species. Studies by Hiemenz et al., 1997; Zanker et al. (2003) consider colloids to be part of the dissolved fraction ($<0.45 \mu\text{m}$), and smaller particles to be suspended particulate matter. Hiemenz and Rajagopalan (1997) and Zanker et al. (2003) further define colloids as suspended material in aqueous systems with linear dimensions between 10^{-6} m to 10^{-9} m . The colloids in this study have arbitrarily been defined as anything less than $0.45 \mu\text{m}$, which falls in the range of 10^{-6} m to 10^{-9} m . Colloids have large surface area to volume ratio resulting in a greater number of sites for reactivity and surface charge leading to an increased adsorption capacity, thereby facilitating the transport of particle reactive elements (Hassellöv et al., 2007).

In order for colloids to flocculate, settle out of solution and form secondary precipitates, their surface charge must be altered, or must be subjected to significant chemical or physical changes (Langmuir, 1997). Studies by Zanker et al. (2002) show that colloid particles are intermediates in the precipitate formation process, further increasing the importance of colloids in this study. The equation provided from Everett (1988) describes the numerous variables involved in the stability ratio of colloids (W).

$$\text{Log}W = V_{\text{max}}/kT$$

Equation 5.1

V_{max} is the free-energy barrier that prevents coagulation, k is the Boltzmann constant and T represents temperature in Kelvins. Change in chemistry, temperature or pressure of the solution can cause colloid instability. Colloidal instability is observed when $V_{\text{max}}=kT$. Coagulation for the formation of a colloid occurs most easily at a specific pH called the point of zero net proton charge (PZNPC). With the increase of ionic strength, coagulation over a broader range of pH is observed as a result of the compression of the diffuse layer reducing particle repulsion (Liang et al., 1990). The differences in elemental concentrations between the colloidal and dissolved phases from ultrafiltered and filtered samples at Pierina and Lagunas Norte can be attributed to variation in ionic strength. Ultrafiltered samples always show lower ionic strength

than filtered samples. Generally, it is observed that there are more colloids when the ionic strength is greater at Pierina (Table 4-10, Table 4-11) but such a statement does not hold true for samples from Lagunas Norte where no correlation is observed (Table 4-12, Table 4-13). This may be explained by the pronounced argillic alteration at Pierina which is absent at Lagunas Norte. If these clays are present as a colloidal fraction, it is possible for them to have ions adsorbed onto their surface and increasing the ionic strength of the solution by releasing them into the solution. Ions will be released should there be changes in chemistry, temperature or pressure of the solution.

Comparison of the filtered and ultrafiltered water demonstrates that colloids should be observed on the filters; however, the ESEM results do not show any. Although some of the samples filtered were orange-brown, no staining of filter paper was observed. It is also possible that colloids are not observed at Lagunas Norte and Pierina as a result of low relative concentrations (Table 5-1, Table 5-2). Masses expected on filters were calculated for 60 mL of sample; hence, concentrations from Table 4-11 and Table 4-13 were converted into ppm units and subsequently multiplied by 60. Finally, small sections of the filter paper were analyzed. It is a possibility that other parts of the filter paper did contain more colloids. The lack of colloids can be understood with the collection and analysis of more samples on site.

Table 5-1 Calculated mass of colloids present at each sampling site at Pierina.

Elements	Units	P-ARD-17-W	P-WRD-W	P-PD-W	P-EC-W
Al	mg	0.0030	1.0	0.26	0.1000
As	mg	0.00036	0.0028	0.024	NA
Ca	mg	0.0030	1.4	0.14	0
Cu	mg	0.0024	0.12	NA	0.0160
Fe	mg	0.033	1.4	0.80	0.1000
Mg	mg	0.0024	0.18	0.0080	0
Mn	mg	0.0060	2.2	0.16	0.42
K	mg	0.0060	NA	0.0020	0.0060
Na	mg	0.0060	0.060	0.0080	0.060
Sr	mg	0	0.016	0.00014	0.0024
S	mg	0	6.6	0.40	4.2
Zn	mg	NA	0.52	0.28	0.28
TOTAL	mg	0.0622	13.5	2.1	5.2

Table 5-2 Calculated mass of colloids present at each sampling site at Lagunas Norte.

Elements	Units	LN-SP3-W	LN-SP3-W2	LN-DW-B-11-W	LN-DAR-1-W	LN-BP	LN-PW2-W	LN-VWD-W
Al	mg	0.0014	0.21	0.12	0.80	0.027	0	0.60
As	mg	0	0	0.014	NA	0	0	0.0010
Ca	mg	0	0.60	0	1.2	0.24	0.80	2.4
Cu	mg	0.036	0.0027	0.60	0.080	0.012	0	0
Fe	mg	0.030	0.42	0	1.2	0.090	NA	2.7
Mg	mg	0.060	0.12	NA	0.40	0.018	0.0018	0.48
Mn	mg	0.034	0.024	0.0040	0.0030	0.0030	0	NA
K	mg	0.0060	NA	NA	0	0.0060	0.0020	NA
S	mg	1.2	9.0	0.20	6.0	9.0	50	NA
Zn	mg	0.010	0.0060	0.026	0	0.0010	0	0.030
TOTAL	mg	1.4	10.4	0.96	9.7	9.4	50.8	6.2

5.1.3 PHREEQC modelling

The results from PHREEQC modeling indicate which minerals may have precipitated. Many elements (Ag, Be, Ce, Co, Cr, Cs, Dy, Er, Eu, Ga, Gd, Ge, Hf, Ho, Ir, La, Lu, Mo, Nb, Nd, Pd, Pr, Pt, Rh, Re, Ru, Sb, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Tl, V, W, Y, Yb, Zr) were missing from the database and were subsequently not incorporated in the calculations; however, these are only present in trace amounts and are not expected to form secondary precipitates. The ESEM, μ XRF maps and μ XRD were methods used to identify trace elements that may be adsorbed onto precipitates or incorporated in the minerals structure. Furthermore, all the potentially oversaturated phases at the mines, identified by diffraction methods, are not present within the WATEQ database, which was used in this research. Commonly observed precipitates such as blodite, loweite, hexahydrate and magnesiopcopiapite are missing from the WATEQ database. These minerals were also missing from MINTEQ, PHREEQC and PITZER databases. In fact, even some minerals present in the WATEQ database were nonexistent in PHREEQC database (i.e. atacamite, alum-k, magnesite, scorodite, chalcantite, and antlerite). Specifically, only 21 of 38 minerals identified by a combination of XRD, μ XRD, ESEM and bulk geochemistry data are found in the WATEQ database (Table 5-3). The geochemical modeling of aqueous solutions is limited to the availability of thermodynamic data and underlying assumptions of geochemical equilibrium that apply (Hammarstrom et al., 2005).

The SI indices computed from filtered samples and ultrafiltered samples were compared and show similar oversaturated minerals in both cases, implying that the concentrations between the two sample types are similar. The precipitates identified from XRD, bulk chemical analyses from the sites are

compared to the oversaturated minerals from PHREEQC and demonstrate major differences. Although sulfates were the most commonly identified minerals, PHREEQC results only show the occurrence of only 2 sulfates: alunite and basaluminite. This is the result of many sulfates missing from the database. Oversaturated minerals modeled by PHREEQC are generally Fe-oxides, Cu and Fe oxides, Fe oxyhydroxides, Al oxyhydroxides. When comparing XRD identified minerals to bulk geochemistry results, there do not seem to be enough Al or Fe minerals identified that account for the measured amount of Al or Fe present in the sample. Most sampled sites at El Indio and Lagunas Norte do not show any Fe minerals even though they are the most concentrated elements. It is possible for these Fe and Al oxides to be present as amorphous material, which would explain why they are not identified with XRD analysis (Figure 5.1). An elevated background in the XRD pattern suggested some amorphous material may be present.

Figure 5-1 μ XRD spectra collected from sample IN28-P4 on XRD location 02-xrd1-001. The two identified minerals include goethite and montmorillonite. The elevated background is indicative of a third phase that is present but likely amorphous.

Results from forward modeling by concentrating waters 20-fold (Section 4.1.4: PHREEQC modelling) suggest an increased number of Fe, Al and Mn oxyhydroxides, as well as Cu and Fe sulfates formed from these concentrated waters. These concentrated solutions show more similarities with precipitates identified (i.e. anhydrite, gypsum, alunite, jarosite), since they show a greater mixture of minerals. However, there are still some precipitates observed commonly in this study that are missing

from the database such as romerite, coquimbite, magnesiocopiapite, antlerite, chalcantite, scorodite, blodite, loweite, etc. Many of the Fe-oxides, Mn oxyhydroxides, Cu and Fe oxides, Fe oxyhydroxides, Al oxyhydroxides are not as prominent in the secondary precipitates identified with diffraction methods. This may be attributed to that fact that many of these minerals are amorphous, as explained in the previous paragraph.

Table 5-3 List of all minerals identified at El Indio, Lagunas Norte and Pierina mines with respective mineral formulae and indications of whether they are found in the WATEQ database that was used in PHREEQC. This comparison demonstrates that about 45% of the minerals identified by alternative methods are unaccounted for in this database.

Mineral	Chemical formula	In WATEQ database?	Mineral	Chemical formula	In WATEQ database?
Albite	(Na _{0.84} Ca _{0.16}) Al _{1.16} Si _{2.84} O ₈	yes	Dietrichite	ZnAl ₂ (SO ₄) ₄ ·22(H ₂ O)	no
Alunite	KAl ₃ (SO ₄) ₂ (OH) ₆	yes	Scorodite	FeAsO ₄ ·2(H ₂ O)	yes
Anorthite	(Na _{0.45} Ca _{0.55})(Al _{1.55} Si _{2.45} O ₈)	yes	Ettringite	Ca ₆ (Al(OH) ₆ (SO ₄) ₃ ·26(H ₂ O)	no
Quartz	SiO ₂	yes	Magnesioaubertite	(Mg,Cu)Al(SO ₄) ₂ Cl·14(H ₂ O)	no
Halite	NaCl	yes	Chrysocolla	(Cu,Mg)SiO ₃ ·(H ₂ O)	no
Orthoclase	K(AlSi ₃)O ₈	yes	Magnesite	Mg(CO ₃)	yes
Montmorillonite	Na _{0.3} (Al,Mg) ₂ Si ₄ O ₁₀ (OH) ₂ ·x(H ₂ O)	yes	Goethite	FeO(OH)	yes
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	no	Fibroferrite	Fe(OH)(SO ₄)·5(H ₂ O)	no
Aphthitalite	(K,Na) ₃ Na(SO ₄) ₂	no	Hematite	Fe ₂ O ₃	yes
Changoite	Na ₂ Zn(SO ₄) ₂ ·4(H ₂ O)	no	Magnetite	Fe ₂ O ₃	yes
Atacamite	Cu ₂ Cl(OH) ₃	yes	Gibbsite	Al(OH) ₃	yes
Alunogen	Al ₂ (SO ₄) ₃ ·17(H ₂ O)	no	Bohemite	AlO(OH)	yes
Alum-K	KAl(SO ₄) ₂ ·12(H ₂ O)	yes	Chalcanthite	Cu(SO ₄)·5(H ₂ O)	yes
Alum-Na	NaAl(SO ₄) ₂ ·12(H ₂ O)	yes	Antlerite	(Cu ₃ (OH) ₄ (SO ₄)	yes
Natroalunite	(Na _{0.75} K _{0.25})Al ₃ (SO ₄) ₂ (OH) ₆	yes	Poitevinite	Cu(SO ₄)·(H ₂ O)	no
Natrojarosite	NaFe ₃ (SO ₄) ₂ (OH) ₆	yes	Bonattite	Cu(SO ₄)·3(H ₂ O)	no
Jarosite	KFe ³⁺ ₃ (OH) ₆ (SO ₄) ₂	yes	Starkeyite	Mg(SO ₄)·4(H ₂ O)	no
Magensiocopiapite	MgFe ₄ ⁺³ (SO ₄) ₆ (OH) ₂ ·20(H ₂ O)	no	Hexahydrite	Mg(SO ₄)·6(H ₂ O)	no
Romerite	Fe ²⁺ Fe ³⁺ ₂ (SO ₄) ₄ ·14(H ₂ O)	no	Epsomite	Mg(SO ₄)·7(H ₂ O)	no
Coquimbite	(Fe _{1.54} Al _{0.46})(SO ₄) ₃ ·9(H ₂ O)	no	D'ansite	Na ₂₁ Mg (SO ₄) ₁₀ Cl ₃	no
Melanterite	Fe(SO ₄)·7(H ₂ O)	yes	Loweite	Na ₁₂ Mg ₇ (SO ₄) ₁₃ ·15(H ₂ O)	no
Aluminocopiapite	Al _{2/3} Fe ₄ (SO ₄) ₆ (OH) ₂ ·20(H ₂ O)	no	Blodite	Na ₂ Mg(SO ₄) ₂ ·4(H ₂ O)	no
Gypsum	Ca(SO ₄)·2(H ₂ O)	yes	Boyleite	(Zn,Mg)(SO ₄)·4(H ₂ O)	no
Anhydrite	Ca(SO ₄)	yes			

5.1.4 Bulk geochemistry and comparison to effluent regulations

The analyzed waters (i.e streams within mines, waste rock leachate, pit wall drainage) demonstrate that El Indio, Lagunas Norte and Pierina are producing ARD with low pH, high electrical conductivity, high sulfate, high TDS and high metal concentrations. The metals present in solution are reflective of the solid-phase metals identified and the primary mineralogy. The primary mineral contributing to ARD at Pierina is mainly pyrite, as well as jarosite and alunite. As the jarosite and alunite dissolve, the Al and Fe hydrolyze and contribute to acidity. Elevated concentrations of Al, Ca, Fe, Cu, Mg, Mn, K, Na, SO₄ and Zn are present dissolved in solution. The known enrichments of As, Cu and Zn, in the primary minerals suggest that these elements were also expected in relatively high concentrations in solution (Klohn Crippen Berger, 2012a). The dissolved ions Na⁺, Al³⁺, Ca²⁺, Mg²⁺ and K⁺, are likely derived through chemical weathering of plagioclase, anorthite, hornblende, biotite identified in the dacite flow-dome complex, the andesite and the rhyodacitic domes (Spencer, 2000). The minerals that may be formed from these waters depend on the ratios of cations in solution and on the relative solubility of the primary sulfide and sulfate minerals. The results of geochemical modelling from this study and a previous study from Klohn Crippen Berger (2012), both classify Pierina waters as Al-SO₄ waters and Ca-SO₄ waters with secondary minerals that can control the Pb, Zn and Cu aqueous concentrations.

The elemental concentrations of waters were compared to the effluent regulations in Peru and Chile to have an understanding of exceedances and mitigation efforts (i.e., appropriate water treatment technology). The values stated below will only exceed regulations once they leave Barrick Gold Corporation property. Various elements demonstrate exceedances in effluent regulations of Chile and Peru respectively (Table 5-4); however, comparisons to regulations are only for reference as some active and passive water treatments are currently in place to mitigate these effluent concentrations before reaching compliance points. Comparison to effluent guidelines provides some indication of how much treatment is required. The following comparison exercise is a typical first step in assessing the level of

mitigation required prior to discharge. At Lagunas Norte, As exceeds its Peruvian limits by 2 orders of magnitude at LN-DW-B-11, by a single order of magnitude at LN-DAR-1 and LN-VWD. Cadmium is very near its exceedance limit at LN-SP3, and 1 order of magnitude greater at sample sites LN-DW-B-11, LN-DAR-1 and LN-VWD. Chromium exceeds the Peruvian effluent guidelines by a few units at sites LN-DAR-1 and LN-VWD. Both Cu and Fe concentrations are 2 to 4 orders of magnitude higher than limits at all sites except those collected from the pit wall. Lead only shows exceedances at LN-DW-B-11. Finally, Zn shows exceedances of 2 orders of magnitude or less except at LN-PW1 and LN-PW2. These samples represent untreated leachate and exact concentrations may be found in Table 4-3 and Table 4-4.

At Pierina, the samples demonstrate exceedances in As limits of 1 to 2 orders of magnitude at all sample sites except P-EC and P-ARD-17. Concentrations may be found in Table 4-5 and Table-4-6. All samples except for P-ARD17 are 1-2 orders of magnitude higher than the Peruvian limits. All chromium concentrations are below Peruvian effluent guidelines and all Fe concentrations are above these guidelines. Zinc exceedances exist at all site, Cu exceedances exist at all sites except at P-PD whereas lead exceedances only exist at P-PD and P-EC. Waters were not analyzed post treatment at this site. Active HDS treatment via oxidation and lime addition is the normally effective treatment technology for the suite of parameters listed in Tables 5-4 and Table 5-5, and is the current technology used at both Pierina and Lagunas Norte. These plants are also presently being upgraded to include a reverse osmosis (RO) stage. As previously mentioned, mitigation at El Indio consists of cover placements, water diversions and passive treatment at the Pastos Largos pond via gravity settling. The El Indio water quality permit has been grandfathered in and this mine site is regulated for pH, As, Fe and Cu based on a dry and wet year basis.

Table 5-4 Peruvian effluent guidelines for mine sites in mg/L from 2010 (Klohn Crippen Berger, 2012a).

Peruvian effluent guidelines			
	Units	Maximum	Average annual
Field pH		6 to 9	6 to 9
TSS	mg/L	50	25
As	mg/L	0.1	0.08
Cd	mg/L	0.05	0.04
Cr	mg/L	0.1	0.08
Cu	mg/L	0.5	0.4
Fe	mg/L	2	1.6
Hg	mg/L	0.002	0.0016
Pb	mg/L	0.2	0.16
Zn	mg/L	1.5	1.2

5.1.5 Comparison with published values

Water chemistry results sampled from El Indio, Lagunas Norte and Pierina were plotted against values from other HS epithermal deposits summarized by Plumlee et al. (1999) including Summitville and Red Mountain Pass in Colorado, Goldfield and Paradise Peak in Nevada, and Mount Macintosh in British Columbia.

Figure 5-2 Comparison of data collected from El Indio (orange), Lagunas Norte (blue) and Pierina (yellow), compared to HS deposits studied by Plumlee et al. (1999) for elements As, Ca, Cd, Co, Cu, Fe, Mg, Mn, Ni.

Figure 5-2 demonstrates that water chemistry at sample sites are similar to data collected from Plumlee et al. (1999) and are therefore typical of HS epithermal deposits. Approximately 60-70% of the data points collected from the mine sites are similar to values collected by Plumlee (1999). This research has contributed to a wider range of pH values that were not observed at other HS epithermal deposits. Water treatment methods at El Indio, Lagunas Norte and Pierina should continue with current treatment such as neutralization of effluent by HDS production via hydrated lime addition and sedimentation, as well as planned reverse osmosis.

5.2 Discussion of secondary precipitate occurrences and characterization

5.2.1 Elemental correlations

Spearman correlation matrices were created with the bulk ICP-MS data in order to observe relationships between major, minor and trace elements, and to interpret elemental association and possible substitution mechanisms. The standard error of the coefficient (σ) was determined by Pearson in 1907 and follows equation 5.2.

$$\sigma = 0.6325 / \sqrt{n - 1} \quad \text{Equation 5.2}$$

This value is used to measure the precision of the estimate of the coefficient, where larger values imply less precision. The variable n represents the sample size. As such, with a smaller sample size, there is an increase in standard error of coefficient. The sample size is 20 at El Indio, 6 at Lagunas Norte and 5 at Pierina. These sample sizes yield standard errors of coefficient of 0.1454, 0.2836 and 0.3163 for El Indio, Lagunas Norte and Pierina respectively. As a result, the correlations from El Indio are the most reliable ones.

The secondary minerals identified account for most of the elemental correlations at Lagunas Norte, Pierina and El Indio. Moderate to strong positive correlations between Fe and As, Zn and Cd, and Na and Mg at El Indio are likely the result of the occurrence and dissolution of primary minerals such as pyrite, enargite, sphalerite, chalcopyrite and covellite (source), and the resulting formation of secondary

precipitates (sink). Based on the minerals identified at El Indio, the correlation of elements Fe and As can be related to the occurrences of scorodite ($\text{FeAsO}_4 \cdot \text{H}_2\text{O}$) which is known to be secondary because it is intergrown with other phases, and the occurrence of melanterite with adsorbed As. The association of arsenic with melanterite was also noted in research conducted by Cheng et al. (2009) that studies the geochemical processes controlling the release, speciation, and distribution of inorganic As in mine drainage. Similarly, the correlation between Na and Mg is likely a result of positively identified Na-Mg sulfates such as blodite, loweite. Jamieson et al. (1999) have documented the occurrence of some Fe-sulfate minerals that precipitate from acid mine waters and incorporate substantial amounts of Zn and other elements in solid solution at Iron Mountain, California. It is assumed that Zn and Cd can enter the crystal lattice preferentially because of their higher ionic potential, and our results do show a very strong correlation in the Spearman matrix created for El Indio, suggesting they would be hosted in the same phases. The correlations observed at the mines studied for this research agree with the findings by Jamieson et al. (1999) that state that potentially hazardous elements such as Zn, Cu, Cd and As are commonly sequestered in secondary minerals by substitution and adsorption. Since SEM-EMPA analysis was not conducted to show how the secondary precipitates incorporate trace elements, this statistical information was used to make inferences. The Cu-Zn correlations ($R=0.84$), Cu-Ni ($R=0.76$) and Cu-Mn ($R=0.69$), suggest that the Cu-Cl mineral identified at El Indio through ESEM as probable atacamite, may store Zn, Ni and Mn. The Mg-Mn ($R=0.78$), Mg-Ni ($R=0.73$), Mg-K ($R=0.76$) correlations suggest that Mg or Mg-Na sulfates identified at El Indio may store Mn, Ni, and K. Research by Sracek et al. (2010) has identified Co and Mn in blodite from samples collected at a leaching plant in Zambia. Cobalt, Zn and Cu are known to be sequestered as solid solution within Fe- and Fe-Al sulfate minerals (Hammarstrom et al., 2005).

Moreover, elements demonstrating correlations may also be due to elements entering solution at the same time as a result of dissolution. For example, the oxidation of pyrite and enargite can release

many elements of interest into solution together, which may coprecipitate within the sulfate system. Table 5-5 modified from Lottermoser et al. (2000) lists common sulfides, as well as the minor and trace elements that may substitute within the structure. Table 5-6 from Smith (1999) lists the pH ranges that are usually equivalent to observed adsorption edges for divalent metal sorption (Cu, Pb, Hg, Zn, Co, Ni, Cd, Mn, Mg, Ca, Sr) on Fe or Al-oxide minerals, the critical ranges, which were identified at all mine sites (a majority through PHREEQC analysis). Hence, any of the elements listed may show strong positive correlations with Fe or Al depending on the pH of the solution, which typically ranged values from less than 3 to greater than 6. The critical range of sorption of anions will be closer to the neutral range (i.e. As, Se). Negative correlations of elements may be indicative of competitive substitution where the inclusion of an element prevents another from entering the mineral structure. This may be observed between Fe and Mg at El Indio (-0.89). These two elements fit Goldschmidt's rules of substitution since their charges are identical and their atomic radii differ less than 15%.

Table 5-5 Sulfide minerals, chemical formulas and minor or trace elements that may partake in cation substitution (Lottermoser et al., 2010).

Mineral name	Chemical Formula	Minor and trace element substitution
Chalcopyrite	CuFeS ₂	Ag,As,Bi,Cd,Co,Cr,In,Mn,Mo,Ni,Pb,Sb,Se,Sn,Tn,V,Zn
Galena	PbS	Ag,As,Bi,Cd,Cu,Fe,Hg,Mn,Ni,Sb,Se,Sn,Tl,Zn
Marcasite	FeS ₂	As,Hg,Se,Sn,Ti,Tl,Pb,V
Pyrite	FeS ₂	Ag,As,Au,Bi,Cd,Co,Ga,Ge,Hg,In,Mo,Ni,Pb,Sb,Se,Sn,Ti,Tl,V
Pyrrhotite	Fe _{1-x} S	Ag,As,Co,Cr,Cu,Mo,Ni,Pb,Se,Sn,V,Zn
Sphalerite	ZnS	Ag,As,Ba,Cu,Cd,Co,Cr,Fe,Ga,Ge,Hg,In,Mn,Mo,Ni,Sb,Se,Sn,Tl,V

Table 5-6 The critical ranges for sorption of divalent metal cations on hydrous Fe and Al oxides (Smith, 1999).

Cation	Critical pH Range
Cu, Pb, Hg	3 to 5
Zn, Co, Ni, Cd	5 to 6.5
Mn	6.5 to 7.5
Mg, Ca, Sr	6.5 to 9

The Spearman correlation matrix created for Lagunas Norte highlights the strongest correlations between elements as Zn and Cd, and S and Ni. The correlation of Zn and Cd, two elements of similar charge and ionic radii, is explained by the fact that both may be sequestered in secondary minerals by substitution or adsorption. Also, both Zn and Cd originate in the same mineral (sphalerite) and are commonly found substituting each other. The source of Ni and S at Lagunas Norte is likely pyrite, and since no Ni-sulfate minerals were identified, this information suggests that Ni is either adsorbed on a sulfate mineral, or substituting another element within the crystal lattice, likely Cu or Fe.

Statistical analyses at Pierina revealed various strong correlations, notably between Ca and Cd, Mg and Cd, Mn and Cd, Zn and Cd, Ca and Mg, Ca and Mn, Al and Cu, Al and Ag, Al and S, Fe and As, Cu and S. Out of these numerous pairs of correlated elements, Al and S can be explained by the presence of coquimbite, Fe and As can be explained by the presence of romerite and jarosite and the sorption of As on these minerals, Ca and Mg by the presence of montmorillonite, Zn, Cu and Cd as elements that commonly sequestered in secondary minerals by substitution and adsorption. Unaccounted pairs might be a result of minimal precision of the Spearman matrix due to the low number of sample numbers from Pierina.

The GSECARS X-ray Map Viewer software from synchrotron microanalysis also incorporates statistical analyses to make correlation plots. This data can be used occasionally to see trends, but can also lead to data misinterpretation. Often, the assumption that ROI counts directly relate to elemental abundance is made. This supposition is false, as other variable such as thickness of the sample and self-absorption effects will give differing fluorescence counts. As such, statistical analyses were not conducted on the micron scaled data collected from the synchrotron.

5.2.2 Secondary minerals identified in ARD

The interaction between mine waters and the secondary precipitates formed is representative of a dynamic system. Hypergene processes in the deposit ore bodies have resulted in the formation of highly

concentrated solutions, from which secondary minerals were crystallized. The mineralogical and chemical compositions of the secondary minerals identified reflect the composition of the waters from which they form. For example, ettringite can only form from Al-Ca-SO₄-rich waters. Subsequently, these minerals can undergo transformations resulting from decreasing moisture or increasing temperatures (Buckby et al., 2003). Authors such as Jambor et al. (2000), and Nordstrom & Alpers (1999) describe the paragenetic sequence relating to the Fe-sulfate minerals that form from evaporating acid mine drainage. Nordstrom & Alpers (1999) demonstrates a paragenetic sequence of Fe-sulfate minerals from pyrite oxidation as early to late rozenite, copiapite, romerite, coquimbite, jarosite. A similar sequence was expected within this study, but cannot be confirmed. It is a possibility that only a portion of this sequence is present since we do not have the whole range of conditions at the sites.

The secondary precipitates at the mine sites studied here likely formed by a combination of several processes including: the oxidation and hydrolysis of dissolved cations, mixing of acid mine waters with neutral pH waters, oxidation of sulfides in humid air and the concentration of mine water due to evaporation (Lottermoser, 2010c; Carbone et al., 2013; Romero et al., 2006; Frau, 2000). The oxidation of the primary minerals, which are mostly sulfides, at El Indio, Lagunas Norte and Pierina deposits, the hydrolysis of Fe and Al leached from primary minerals, as well as the low buffering capacity of the host rocks has created ARD. The results of mineralogical analyses indicate that the mineralogy of the secondary minerals forming at these three settings is variable but the most common minerals can be placed into 3 broad groups: 1) hydrous Na-, Mg-, Ca-, and other metal-sulfates such as blodite, hexahydrate and gypsum 2) Fe-oxides, oxyhydroxides and oxyhydroxysulphates such as ferrihydrites, goethite, scorodite and jarosite 3) other metal rich, low crystalline phases such as basaluminite-like Al minerals, and few oxides, hydroxide, arsenates, carbonates and silicates in decreasing order. All identified minerals are listed in Table 5-3, and those discussed in the following section can be observed in Table 5-7.

Table 5-7 Names and formulae of minerals discussed in following sections.

<i>Fe-sulfates and Al-sulfates</i>		<i>Fe-Al oxyhydroxides</i>	
Minerals	Formula	Minerals	Formula
Alunogen	$\text{Al}_2(\text{SO}_4)_3 \cdot 17(\text{H}_2\text{O})$	Scorodite	$\text{Fe}(\text{AsO}_4) \cdot 2(\text{H}_2\text{O})$
Alum-K	$\text{KAl}(\text{SO}_4)_2 \cdot 12(\text{H}_2\text{O})$	Goethite	$\text{FeO}(\text{OH})$
Alum-Na	$\text{NaAl}(\text{SO}_4)_2 \cdot 12(\text{H}_2\text{O})$	Fibroferrite	$\text{Fe}(\text{OH})(\text{SO}_4) \cdot 5(\text{H}_2\text{O})$
Natrojarosite	$\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$	Hematite	Fe_2O_3
Jarosite	$\text{KFe}^{3+}_3(\text{OH})_6(\text{SO}_4)_2$	Magnetite	Fe_2O_3
Magensicopiapite	$\text{MgFe}_4^{+3}(\text{SO}_4)_6(\text{OH})_2 \cdot 20(\text{H}_2\text{O})$	Gibbsite	$\text{Al}(\text{OH})_3$
Romerite	$\text{Fe}^{2+}\text{Fe}^{3+}_2(\text{SO}_4)_4 \cdot 14(\text{H}_2\text{O})$	Bohemite	$\text{AlO}(\text{OH})$
Coquimbite	$(\text{Fe}_{1.54}\text{Al}_{0.46})(\text{SO}_4)_3 \cdot 9(\text{H}_2\text{O})$		
Melanterite	$\text{Fe}(\text{SO}_4) \cdot 7(\text{H}_2\text{O})$		
Aluminocopiapite	$\text{Al}_{2/3}\text{Fe}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20(\text{H}_2\text{O})$		
Alunite	$\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$		
<i>Na-Mg-K-Ca sulfates</i>		<i>Cu-sulfates</i>	
Minerals	Formula	Minerals	Formula
Starkeyite	$\text{Mg}(\text{SO}_4) \cdot 4(\text{H}_2\text{O})$	Chalcanthite	$\text{Cu}(\text{SO}_4) \cdot 5(\text{H}_2\text{O})$
Hexahydrate	$\text{Mg}(\text{SO}_4) \cdot 6(\text{H}_2\text{O})$	Antlerite	$(\text{Cu}_3(\text{OH})_4)(\text{SO}_4)$
Epsomite	$\text{Mg}(\text{SO}_4) \cdot 7(\text{H}_2\text{O})$	Poitevinite	$\text{Cu}(\text{SO}_4) \cdot (\text{H}_2\text{O})$
Gypsum	$\text{Ca}(\text{SO}_4) \cdot 2(\text{H}_2\text{O})$	Bonattite	$\text{Cu}(\text{SO}_4) \cdot 3(\text{H}_2\text{O})$
Anhydrite	$\text{Ca}(\text{SO}_4)$		
D'ansite	$\text{Na}_{21}\text{Mg}(\text{SO}_4)_{10}\text{Cl}_3$		
Loweite	$\text{Na}_{12}\text{Mg}_7(\text{SO}_4)_{13} \cdot 15(\text{H}_2\text{O})$		
Blodite	$\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4(\text{H}_2\text{O})$		
Boyleite	$(\text{Zn,Mg})(\text{SO}_4) \cdot 4(\text{H}_2\text{O})$		

Hence, the most common secondary minerals observed include simple hydrous metals sulfates with divalent metal cations, simple hydrous metals sulfates with trivalent metal cations, mixed divalent-trivalent hydrous metal sulfates in order of occurrence. The most commonly occurring secondary minerals at Lagunas Norte were identified as gypsum, chalcanthite and alum-Na. Various phases were identified through μXRD including antlerite, chrysocolla, scorodite and poitevinite. As observed by their mineral formulae, chalcanthite, antlerite and poitevinite are hydrated or less hydrated versions of one another. At El Indio, blodite, loweite, gypsum, halite, hexahydrate, starkeyite, and magnesicopiapite secondary minerals are amongst the most common. The most ubiquitous secondary precipitates at Pierina are romerite, coquimbite, magnesicopiapite and jarosite. These efflorescent minerals thereby exhibit a range of crystal habits appearing to be related to their morphology. These results are in agreement with

previous studies on post-mining secondary minerals found in sulfidic mine wastes (Lottermoser, 2010c). The occurrence of the soluble precipitates provides valuable information about the reactions that have occurred, as well as the compositions of the solutions from which they formed and the types of primary minerals that likely weathered, leading to their formation (Jambor et al., 2000).

Although the waters were enriched in Fe, as a result of the primary pyrite minerals as well as other Al or Fe minerals being oxidized, most of the secondary precipitates identified from El Indio, Lagunas Norte and Pierina mines were Na and Mg hydrated sulfates. Goethite and hematite, the most common forms of ferric oxide and oxyhydroxide respectively, are known to have slow growth kinetics at surficial temperatures observed at El Indio, Lagunas Norte and Pierina, and are therefore poorly crystalline (Carbone et al., 2005; Keith et al., 2001; Lottermoser, 2010b). As explained by Lottermoser et al. (2010b), all precipitates will not be crystalline. In fact, many can be poorly crystalline or amorphous. Furthermore, the first minerals that precipitate have the tendency of being poorly crystalline, metastable phases that may transform into more stable phases over time, explaining why minimal Fe minerals were identified (Carbone et al., 2005; Jönsson et al., 2006). This further explains the presence of few Al-minerals identified (Nordstrom et al., 1999; Nordstrom, 2011). Nevertheless, PHREEQC modeling using the WATEQ database identifies a number of Fe and Al oxyhydroxydes that may be representative of the minerals present at these sites. Non-crystalline Fe and Al minerals are present in these samples, as per PHREEQC modeling and geochemical information, but were not identified by diffraction methods. Hydrous sulfates may also dehydrate to less hydrous compositions such as the case of observed minerals hexahydrite and starkeyite at El Indio.

This thesis further supports statements made in research by Buckby et al., (2003) Jambor et al., (2000) in that the composition of the secondary minerals reflects the composition of the waters from which they precipitated, and that the composition of waters directly influences the mineralogy of secondary precipitates, particularly in arid settings (Spencer, 2000). In the case of the mines characterized

for this study, PHREEQC modeling demonstrated an additional set of secondary precipitates, most likely present as secondary precipitates, yet left unidentified due to their amorphous nature. In all mines, the secondary precipitates formed act as sinks of various elements during the dry season; however, they also act as sources of elemental loading as they become dissolved during the wet season (Klohn Crippen Berger, 2012b). Nordstrom et al. (1999), have created a list of common secondary minerals whose solubilities can control the amount of metals found in solution. It may be observed in Table 5-8 that many of those minerals are also found at Lagunas Notre, El Indio, or Pierina as per analytical tests conducted on solid samples and forward modelling of solutions.

Table 5-8 Minerals whose solubilities are likely to control metal concentrations in mine waters (Nordstrom et al., 1999). The minerals names highlighted in red represent minerals identified on site.

Solubility equilibrium likely	Solubility equilibrium possible
<i>alunogen</i>	<i>alunite</i>
anglesite	ankerite
<i>basaluminite</i>	<i>antlerite</i>
calcite	<i>atacamite, paratacamite</i>
cerussite	azurite
<i>chalcantite</i>	bronchantite
<i>epsomite</i>	<i>chrysocolla</i>
<i>ferrihydrite</i>	<i>goethite</i>
<i>gibbsite</i>	hemimorphite
goslarite	<i>hematite</i>
<i>gypsum</i>	hydrozincite
halotrichite	<i>jarosite</i>
<i>manganese oxides</i>	kaolinite
<i>melanterite</i>	kutnohorite
otavite	malachite
rhodochrosite	natroalunite
schwertmannite	<i>natrojarosite</i>
<i>scorodite</i>	plumbojarosite
siderite	
silica	
smithsonite	
witherite	

5.2.2.1 Na-Mg-K- Ca sulfates

Many of the minerals at El Indio are Na-Mg sulfate minerals that have been described by Lottermoser (2010c) as post-mining secondary minerals identified in mine waste. Hydrated Mg-sulfates and Na-Mg sulfates have also been identified on irrigated paddy soils in the Soudano-Sahelian region of Niger that are unrelated to mining (Ducloux et al., 1994). Leduc (2010) states that Na-Mg hydrates sulfate are commonly found in inland saline lake systems and are known to occur in various hydration states, depending on temperature, relative humidity and brine concentration. Demartin et al. (2012) have recorded similar minerals forming from fumaroles, which are modern day analogues of epithermal deposits. The source of Na, Mg, K and S are probably the primary minerals formed at El Indio such as pyrite, enargite, alunite, feldspars, pyroxenes and hornblende. The Na-K-Ca-Mg sulfate salts found at the mines in this study are variable and range from simple anhydrous salt anhydrite, to simple hydrous salts such as gypsum, to variably hydrated Mg-sulfates such as hexahydrate, epsomite and starkeyite, to mixed salts of cation pairs (Jambor et al., 2000). The secondary precipitates identified during this study include gypsum, loweite, Mg and Zn endmembers of the blodite group (blodite, changoite), hexahydrate and starkeyite (Table 5-7). The most common simple Ca sulfate salts such as gypsum and anhydrite are the least soluble out of all minerals in this section (Spencer, 2000), but can also be dehydration products of some samples. Finding anhydrite is unusual because this mineral tends to form at temperatures above 40°C (Jambor et al., 2000); however, its identification is supported by μ XRD. Solubility of minerals in grams per kilogram were calculated by Spencer (2000) using thermochemical model of Harvie et al. (1984) and temperatures below 25°C. The solubility of mixed cation minerals varies and will likely fall between the solubility values of the cations involved.

A sudden rainfall event can cause the dissolution of the minerals previously formed. The Na-Mg or Ca-sulfates identified are not acid forming upon precipitation or dissolution (Buckby et al., 2003), therefore cannot contribute to the low pH measured throughout El Indio. However, their dissolution

following is known to be responsible for the high contents of dissolved salts in the measured streams (Buckby et al., 2003). Blodite-type compounds have the chemical formula $\text{Na}_2\text{Me}(\text{SO}_4)(\text{H}_2\text{O})_4$ where K may replace some Na and $\text{Me} = \text{Mg, Co, Ni, Zn}$ (Spencer, 2000). Blodite-type structures are built of $[\text{Me}(\text{H}_2\text{O})_4(\text{SO}_4)_2]^{2-}$ molecules that are linked NaO_6 polyhedra and hydrogen bonds (Stoilova and Wildner, 2004). Changoite is also in the blodite group but contains Zn in its mineral formula instead of Mg. Hexahydrate is a mineral from the hexahydrate group of monoclinic sulfates of the type $\text{Me}^{2+}\text{SO}_4 \cdot 6(\text{H}_2\text{O})$ and has been formed by Mg-rich waters (Jambor et al., 2000). Although generally, the minerals of this group are found as the oxidation product of sulfide deposits, hexahydrate has been identified as a precipitate in various settings (i.e. diamond mine waste, saline lakes, soils, weathered mine wastes) (Jambor et al., 2000; Rollo and Jamieson, 2006; Peterson, 2011; Whittig et al., 1982). At El Indio sample site IN13, hexahydrate has likely dehydrated to starkeyite since both mineral are observed at the same location. The dehydration may have occurred at the sampling site or during transportation prior to sample preparation. Hexahydrate may hydrate to epsomite, or dehydrate to kieserite as demonstrated in Figure 5-3. In this figure, the relative humidity (45-90%) and temperature variation (5-30°) conditions at El Indio are represented, showing potential phases that may occur. From research conducted east-southeast of Calingasta, Argentina, Peterson (2011) has identified hexahydrate veins with soft surficial dusting of starkeyite as a result of dehydration. Hence, this study is in agreement with observations by Peterson (2011). Also in agreement with Peterson (2011), the hydrated Mg-sulfate minerals are commonly found as mixtures. Chou and Seal (2003) have further reviewed literature relating to the epsomite-hexahydrate-vapor equilibrium.

Figure 5-3 Hydrogenetic grids for hydrated metal-sulfate salts kieserite, hexahydrite, and epsomite. The curves are representative of experimentally determined dehydration reactions to temperature and relative humidity conducted by Hammarstrom et al. (2005). The questions marks indicate uncertain reaction phase boundaries. The red box represents approximate temperature and humidity conditions at El Indio (Barrick Gold Corporation, personal communication).

Similar minerals to those at El Indio (i.e. gypsum, hexahydrite, starkeyite, loweite, blodite) have been identified in the Upper Colorado River Basin as efflorescences on the Mancos Shale. These minerals reflect the compositions of the solutions from which they have precipitated. As such, solutions that formed these minerals at Mancos Shale, were enriched in SO_4 , Na, Mg, K, Ca and Zn and these minerals are important sinks of these elements during the dry season.

5.2.2.2 Cu-sulfates and Cu-silicates

This group of secondary precipitates was amongst the most common at Lagunas Norte and was also observed at El Indio. The minerals in this section are expected to be soluble because they are simple hydrous metal sulfates (Lottermoser, 2010c). The oxidation of primary minerals such as chalcocite (Cu_2S), bornite (Cu_5FeS_4), digenite (Cu_9S_5) at El Indio to the formation of these various sulfates of Cu. The primary Cu-mineral identified Lagunas Norte and Pierina is enargite. The Lagunas Norte and Pierina deposits represent mineralization formed

closer to the surface than that at the El Indio deposit, explaining the abundance of Cu-sulfides that tend to mineralize at greater depths (Arribas, 1995).

The Cu sulfates at El Indio were only identified using ESEM analysis of the mounted bulk sample. Due to the significant amount of primary Cu minerals present at El Indio, a larger amount of secondary Cu sulfate minerals were expected to have been identified in the field. Selective sampling and specific sampling period could have influenced the amount of Cu minerals identified in the field. It was only possible to collect from a few locations, perhaps leading to missed Cu minerals. It is also likely that the Cu minerals at El Indio were dissolved due to rainfall.

Copper-sulfates were identified in 2 out of 3 samples collected from the pit-wall at the Lagunas Norte Mine and include antlerite, chalcantite and poitevinite (Table 5-7). Antlerite ($\text{Cu}_3(\text{OH})_4(\text{SO}_4)$) is a mineral metastable at ambient temperature. Chalcantite is the Cu endmember of the triclinic Cu, Mg, Mn and Fe pentahydrates of the chalcantite group, and is generally of common occurrence (Jambor et al., 2000). Solid-solution incorporation of Mg or Zn has been observed at 25°C by Balarew et al. (1975). Poitevinite is formed as a result of the dehydration of chalcantite. Hence, this mineral could have formed after it was sampled. Antlerite, chalcantite, and poitevinite must have formed from Cu-rich waters, and are all important in the retention of Cu at the respective sites in which they occur. Based on superposition

of El Indio temperature and humidity conditions onto hydrogenetic grids, it becomes evident that chalcantite would likely occur at El Indio.

Figure 5-4 Hydrogenetic grids for hydrated metal-sulfate salts bonattite and chalcantite. The curves are representative of experimentally determined dehydration reactions to temperature and relative humidity conducted by Hammarstrom et al. (2005). The red box represents approximate temperature and humidity conditions at El Indio (Barrick Gold Corporation, personal communication).

5.2.2.3 Fe-Al oxyhydroxides

XRD analyses have allowed identifying Fe-oxyhydroxides and Fe-oxides that are likely found at El Indio, Lagunas Norte and Pierina mines. Geochemical modeling has also predicted that similar minerals would precipitate in these settings. These minerals were rarely identified through XRD or μ XRD because of their microcrystalline or amorphous nature, or selective sampling. The source of Fe is expected to have entered into waters through the oxidation of primary minerals such as the ubiquitous pyrite and other Fe-sulfides. Fe-oxyhydroxides are commonly occurring ARD minerals (Buckby et al., 2003; Jönsson et al., 2006; Romero et al., 2011; Jambor et al., 2000; Nordstrom et al., 1999).

Figure 5-5 pE-pH diagram, showing the stable solid phases in Fe-S-K-O-H system at $T=25^{\circ}\text{C}$ and 1 bar. The activities are $a_{\text{iron}}=10^{-1.0}$, $a_{\text{sulfur}}=10^{-1.7}$, $a_{\text{potassium}}=10^{-2.6}$ and are congruent with activities observed in collected samples. The stability from A to B, there are changes in activities of elements in play (modified from Alpers and Brimhall, 1989). The range of pe and pH conditions for each mine vary and is displayed in orange (El Indio), blue (Pierina), purple (Lagunas Norte) based on collected field data. Increasingly reducing conditions may dissolve Fe-sulfates and encourage the precipitation of Fe-sulfides. Increasingly acidic and/reducing conditions will reduce the stability of ferrihydrite and jarosite, leading to dissolution or alteration to other phases.

Munk et al. (2006) have conducted laboratory experiments studying the geochemical evolution of solutions derived by experimental weathering of sulfide-bearing rocks. Their results indicate that changes in pH and the formation of Fe and Al oxyhydroxides affect the chemical composition of the solution. Specifically, these authors have stated that an increase in pH to a value of around 5.1 causes Fe and Al oxyhydroxides to precipitate, which would scavenge cations from solution via sorption. Thus, their presence can significantly affect water quality as they promote attenuation of metals. However, if more acidic conditions are created, then metals may desorb and will be released in solution (Schwertmann et al., 1983). Based on geochemical modeling, scorodite, goethite, hematite, magnetite, gibbsite, diaspore,

bohemite are likely precipitated at El Indio (Table 5-7). Scorodite, fibroferrite, hematite, magnetite, gibbsite, bohemite likely precipitated at Lagunas Norte and goethite, hematite, magnetite, gibbsite, diaspore, bohemite show $SI > 0$ at Pierina (Table 5-7). Few of these minerals (i.e scorodite, goethite, hematite) were identified by diffraction methods; however, given the chemistry of the studied secondary precipitates and waters, we assume that these minerals are actually present. Goethite is found in low-temperature environments. This mineral is formed through the weathering of other Fe-rich minerals. Goethite forms under surface conditions since its precipitation is a result of Fe oxidation from $2+$ to $3+$. The disintegration or oxidation of arsenopyrite, pyrite and other sulfides leads to the precipitation of Fe such as scorodite and ferrihydrite. Scorodite is commonly found in hydrothermal deposits as a weathering product of arsenopyrite in mine waste (DeSisto et al., 2011). Ferrihydrite is a common host for metal sorption in aqueous systems (Klohn Crippen Berger, 2012b; Dzombak and Morel, 1990). Schwertmann and Murad (1983) have stated that ferrihydrite dissolves and reprecipitates as goethite outside of a pH range of 5 and 9.

The presence of abundant Fe oxides at El Indio, Lagunas Norte and Pierina mines suggests that the waters in which they precipitated are well oxidized, and this is supported by the ORP measurements collected in the field (Table 4-7, Table 4-8, Table 4-9). Ferric minerals are representative of a more advanced stage of oxidation relative to the Fe^{2+} sulfates. The secondary precipitates discussed in this section have generally been formed from Fe- or Al- rich waters, and retain Fe and Al, and other elements that may be adsorbed on them. More Fe and Al oxides were identified by a combination of XRD and μ XRD methods, at all mine sites. Selective sampling and the amorphous nature of some of these precipitates may explain the lack of such minerals identified with methods measuring diffraction.

5.2.2.4 Fe-Al sulfates or hydroxysulfates

Iron-sulfates commonly occur at El Indio, Lagunas Norte and Pierina mines. Melanterite, magnesiocopiapite, jarosite, natrojarosite were identified at El Indio (Table 5-7). Aluminocopiapite,

melanterite and hydroniumjarosite were found at Lagunas Norte and romerite, coquimbite, jarosite and magnesiocopiapite were present at Pierina (Table 5-7). Magnesiocopiapite is a mineral of the copiapite group with the general formula $A^{2+}R^{3+}_4(SO_4)_6(OH)_2 \cdot 20H_2O$ where R is represented by Fe^{3+} , and is likely formed by Fe^{2+} -poor waters. Substitution of Al and Fe^{3+} in the A^{2+} is a possibility, which is trivalent instead of mixed divalent. Magnesiocopiapite minerals from the Richmond Mine at Iron Mountain have been identified under the ESEM as 10-50 μ m plate crystals (Jamieson et al., 2005; Jambor et al., 2000). Minerals from the copiapite group are likely to be precipitated from solutions with pH>2.0, but can also form as an alteration product of mineral precipitates (Buckby et al., 2003). According to Jambor et al. (2000), coquimbite ($Fe_2(SO_4)_3 \cdot 9H_2O$) and alunogen ($Al_2(SO_4)_3 \cdot 17H_2O$) are the most commonly occurring secondary precipitates with trivalent cations. The stream waters that formed coquimbite were likely Fe^{3+} rich; coexisting waters were rich in Fe. Vaniman et al. (2004) have studied the hydration and dehydration of hydrous Fe^{3+} sulfates, notably coquimbite, kornelite and botryogen. Specifically, it is discovered that although coquimbite, botryogen and kornelite structures all contain independent H_2O molecules, reversible dehydration reactions similar to the epsomite to hexahydrate reaction for Mg-sulfates was not observed. The lack of botryogen and kornelite at the mine sites in this study further confirm this theory as the three minerals may have been identified if reversible dehydration reactions did take place. In samples collected from IN28, Na has substituted for K, creating a mineral called natroalunite. Sracek et al. (2010) have identified that melanterite and rozenite may store significant amounts of Cu, Co and Zn. Alunite $KAl_3(SO_4)_2(OH)_6$ is an alteration mineral that occurs at HS epithermal deposits in volcanic rocks. Alunite is a version of jarosite where Al has replaced Fe^{3+} . Alunite is a primary mineral and is ubiquitous throughout HS epithermal deposits, including Pierina, but can also be a secondary mineral (Rainbow, 2009). As described by Jensen et al. (1971), stable sulfur isotopes can be used to distinguish between the primary and secondary alunite, where S of the primary alunite will be enriched in S^{34} . The secondary precipitates discussed in this section have generally been formed from Fe- or Al- rich waters, and are

essential for the retention and storage of Fe, Al, As and SO_4 . Jarosite and melanterite represent an important family of hydrated Fe- SO_4 minerals that are commonly found in acid environments (Nordstrom and Alpers, 1999; Jamieson et al., 2005; Kohn Crippen Berger, 2012a). The relative humidity and temperature conditions of rozenite and melanterite are displayed on Figure 5-6 with relative humidity and temperature conditions at El Indio highlighted. Based on this diagram, both rozenite and melanterite may be observed at El Indio.

Figure 5-6 Hydrogenetic grids for hydrated metal-sulfate salts rozenite and melanterite. The curves are representative of experimentally determined dehydration reactions to temperature and relative humidity conducted by Hammarstrom et al. (2005). The question marks indicate uncertain reaction phase boundaries. The red box represents approximate temperature and humidity conditions at El Indio (Barrick Gold Corporation, personal communication).

Studies conducted by Carrero et al., (2015) study the sorption capacity of trace elements in solution by Fe and Al-hydroxysulfates. Less research pertaining to sorption has been conducted on Al-hydroxysulfates formed in ARD settings because they are less common than Fe-hydroxysulfates. Carrero and his coauthors reconfirm the affinity of basaluminite with Si and Cu, and of schwertmannite for As and Cr, and discover previously unidentified affinity of basaluminite for As and Cr. Basaluminite from El Indio, Lagunas Norte, and Pierina may demonstrate similar results.

5.2.3 Comparison of analytical methods

Through the analysis of bulk samples with ESEM, various morphologies of minerals were observed as well as identification of elements, providing a semi-quantitative analysis of minerals. Targeting textures or morphologies of interest allowed quick identification of the major elements. The hydration state could not be measured with the ESEM. Also, some elements have similar K or L X-ray adsorption energies, including Pb with As, Mg with As and As with Sb. Hence, an overlap of their peaks was an issue while attempting to identify these elements on the spectra. Previous research on Fe and Al hydroxysulfate minerals by Bigham and Nordstrom (2000) states that crystal morphology of most minerals is variable and therefore not a reliable tool for identification. Most of these minerals could not be positively identified only with the use of the ESEM. A number of morphologies were observed and associated with corresponding groups of minerals. For example, Na-Mg sulfates tend to occur as euhedral isometric clusters.

Synchrotron-based analyses including μ XRD and μ XRF were indispensable to mineral identification and elemental associations. A significant number of unknown phases from samples collected at El Indio were identified through μ XRD analysis with HighScoreTM peak matching software. The elemental mapping by μ XRF, led to the identification of trace elements in some minerals. The association of trace elements with minerals was only conducted on spots analyzed by μ XRD spots that show a single identified phase. The observed diffraction of assumed single phase does not mean that no other phases exist within the 2 μ m volume of the beam size, and it is possible that there are amorphous phases or those coarse to diffract under these conditions. Furthermore, not all phases could be identified because of complex mineral mixtures present in samples. Peak overlap such as that observed for ESEM spectra was also an issue for the MCA spectra collected from μ XRF maps.

Bulk XRD analysis identified the most common and most coarsely-crystalline phases in the powdered samples. MicroXRD analysis showed that each sample with intergrowths of multiple phases observed. Hence, the resolution of bulk XRD analysis is not great enough to identify all phases present in

the sample. The differences observed between bulk XRD and μ XRD can be explained by the differing resolutions of the tools used, types of samples analyzed, scales of analysis and sample preparation. The micron-scaled beam used at the synchrotron and the μ XRF maps created allow for target selection whereas the bulk results only show the most abundant and crystalline phases. The analytical methods used for this study complemented one another, improving the quality of results.

X-ray fluorescence maps were created at selected areas of the thin section (Figure 4-26, Figure 4-27, Figure 4-33, Figure 4-35, Figure 4-36) and XRF spectra, as well as μ XRD were compared at all sites. The objective of comparing minerals identified by μ XRD to elements occurring in the μ XRF spectra was to identify which elements are associated with the identified minerals, including those not in the mineral formulae. Of these 185 sites, only 26 sites showed a single phase and were used to observe element-mineral associations. Since mixtures of minerals are observed through μ XRD and μ XRF, and are also evident through ESEM analysis, it is also likely that some elements are from nearby minerals due to the resolution of the beam. The spot size of the incident beam is 2 microns. Although we have seen the diffraction pattern of a single mineral, phases may exist within that 2 μ m volume that are amorphous or too coarse to identify by μ XRD. Synchrotron microanalysis was useful but limited by beamtime availability.

5.3 Predicted metal mobility in mine waste conditions

Analysis of the results from El Indio, Lagunas Norte and Pierina has demonstrated that the release of major, minor and trace elements into stream water depends on the pH-Eh conditions, and the precipitation and dissolution of mineral phases. The mobility of major, minor and trace elements are also controlled by the formation of highly soluble sulfate minerals identified. It is shown that a number of elements are attenuated by secondary mineral precipitation at El Indio, Lagunas Norte, and Pierina mines. A great number of cations can be incorporated in synthetic goethite, including: Al, Ni, Zn, Cd, Cr, Ga, V, Mn, Co, Sc, Pb, Ge and Si (Inouye et al., 1972; Lim-Numez and Gilkes, 1985; Stiers and Schwertmann, 1985; Vandenberghe et al., 198; Cornell and Giovanoli, 1987; Diaz et al, 1989). Micro-XRF spot analysis was

conducted on goethite sampled from El Indio, and has shown an association with Cu, K, Mn, Ti, Zn, As, K, Co, Br, Ca, Ni. These elements are assumed to be adsorbed onto the mineral, incorporated within the crystal structure or to be associated with other phases and accidentally detected by the synchrotron beam. The critical ranges of sorption of these elements are listed in Table 5-6 and match the pH conditions of the solutions at the sample sites. Based on results from μ XRF spot analysis of samples from El Indio and Lagunas Norte, the elements Cu, Mn, Zn, Ca, Co, Fe, and Ni are attenuated by the precipitation of blodite whereas Cu, K, Zn, Ca, Mn, Fe, Ti, Co, Ni and As are attenuated by alunite. Hexahydrite contains Cu, Zn, Fe, Mn, As, Ni, Ti or Ti, As, Co, and Ni and may control their mobility. Its precipitation will decrease the mobility of the listed elements. The lower values of K in some waters show that this element has been retained likely a result of the precipitation of jarosite. Studies by Romero et al. (2011) further demonstrate that Na and Pb could be retained by jarosite when these elements substitute for K to form natrojarosite and plumbojarosite. Cadmium and Zn can be easily released in HS epithermal settings as they are highly mobile in very acidic environments (Romero et al., 2011; Nordstrom et al., 1999; Plumlee, 1999); however, Pb is a very immobile element. Sulfate is attenuated throughout all mines with the formation of the various sulfate minerals. Arsenate is also known to substitute for sulfate in the jarosite structure (Dutrizac et al., 1987; Savage et al., 2005).

5.4 Implications of research to water treatment at sites

Both passive and active water treatment present are effective methods in attenuating metal concentrations in waters flowing out of the mine sites. If traditional water treatment fails to meet parameter requirements, Barrick Gold Corporation can consider capturing the sulfate-rich secondary precipitates by mechanically enhanced pond-evaporation and precipitation of efflorescent salts, methods which have shown to contain trace metals and may allow to efficiently capture elements of interest. Significant pre-treatment is required for volume reduction and quality control (MEND, 2014). This method may prove to be expensive as a result of disposal costs of the highly soluble metal sulfate salts present, as

well as due to the requirement for a significantly high amount of energy required as a result of abundant rainfall or snowfall at the Peruvian sites and seasonal snowmelt at El Indio.

Most secondary minerals identified at the mine sites are sulfates, and the waters also demonstrate significant concentrations of sulfate. Due to the lower environmental risks and regulatory standards for sulfate comparatively to those for acidity and dissolved metals, minimal attention is given to the mitigation of sulfate in ARD treatment (Lorax Environmental, 2003). However, sulfate has recently become an important indicator of environmental compliance to the mining industry as concern is increasing over the impact sulfate can have on the salinity of receiving waters (Philippe et al., 2015). Furthermore, issues associated with excess sulfate in mine process waters include reduction to toxic HS gas, scale formation, decreased metallurgical production recovery, and increase in cost related to mitigation, control and treatment (Philippe et al., 2015). Recovering sulfate from solution will decrease all of these.

The long-term objective of this research project was to investigate methods of extracting metals from acid mine waste in order to minimize the environmental impact of the drainage and offset remediation costs. Hence, the price of the extracted commodity will also be taken into account to further understand extraction viability (i.e., market conditions). To determine whether an element will be of economic value, the mass of metal that could be recovered was calculated and compared to commodity prices. A few important assumptions were made including that the flow rate is constant, that an average concentration of elements can be used, that there are only 7 elements that can be recovered (Al, Cu, Mg, Mn, Ni Pb, Zn), and that the commodity price is unchanged throughout the year. Furthermore, capital expenditure is not included in this section, but will also have significant impact on offsetting treatment costs depending on applied flow technology. This analysis focuses primarily on operational costs.

Commodity prices were collected on October 14th, 2015 and were used for calculations (Table 5-9). These values are subject to change, inferring that values calculated in this section are only estimates.

Water treatment costs (i.e HDS, ion exchange, nanofiltration and RO) are estimated at 0.20\$-1.00\$ per cubic meter for ARD and recovery costs are generally similar (MEND, 2014). The average flow rates are calculated at 9,555,723,360 L/year at El Indio; 493,061,049 L/year at Lagunas Norte, and 128,107,116 L/year. According to these numbers, water treatment costs will fall between \$1,911,144-\$9,555,723 at El Indio, \$98,612- \$493,061 at Lagunas Norte, \$25,621-\$128,107 at Pierina. Recovery costs will be similar, but additional to water treatment costs. The averaged values of recoverable metals, assuming 100% recovery, were calculated at approximately \$6,160,703 at El Indio; \$1,434,913 at Lagunas Norte, and \$21,987 at Pierina (Table 5-10, Table 5-11, Table 5-12). The averaged values of recoverable metals, assuming 85% recovery, were also calculated at approximately \$2,565,367 at El Indio; \$121,164 at Lagunas Norte, and \$5,318 at Pierina. However, since the best case scenario was calculated, 100% recovery values were used. The treatment costs and average value of recoverable metals were calculated from data provided by Barrick Gold Corporation.

Table 5-9 List of economic prices of elements analysed at mine sites as per stock values on October 14th, 2015. Prices are provided in units of \$/kg and then converted to \$/mg to compare and calculate average annual income through assuming 100% recovery. The commodity prices collected on October 14th, 2015 were used for calculations and were retrieved from www.infomine.com.

Element	Unit	Price
Al	\$/kg	1.61
Cu	\$/kg	6.91
Mg	\$/kg	2.07
Mn	\$/kg	1.75
Ni	\$/kg	16.96
Pb	\$/kg	1.80
Zn	\$/kg	1.84

Annual flow rates (L/Year) are multiplied by the concentration of elements in solution (mg/L), which are subsequently multiplied by the price of the commodity, providing us with a value of recoverable element per site. The profit per year is averaged between each sampled site, assuming a closed system, and values for each element are summed to provide a grossly estimated total in USD per year (Table 5-12). Since the goal is cost reduction, net treatment cost per year was averaged because if metals are removed

from one site, this will influence the quantity at the next site. These values were then compared to the water treatment costs provided earlier. The net treatment cost was calculated by subtraction water treatment costs (WTC) and recovery costs (RC) from the summed total metal value (Equation 5.3).

$$\text{Net treatment cost} = (WTC + RC) - MV \quad \text{Equation 5.3}$$

Even in the best case scenario of 100% metal recovery, values indicate that Barrick Gold Corporation cannot significantly offset treatment costs from the recovery of elements Al, Cu, Mg, Mn, Ni, Pb, and Zn at any of the sites. In fact, assuming that recovery costs are greater than treatment costs, the company may lose substantial capital by recovering these metals. Nevertheless, water treatment must decrease the values of these elements to environmentally acceptable concentrations, as described in section 5.1.5. The values of metal concentration can change in the waters depending on mining activities, changes in climate and precipitation. It is also important to note that the previous calculations are preliminary analysis conducted on bulk averages for the abovementioned suite of metals and flow. Barrick Gold Corporation should consider looking at seasonal flows to potentially recover metals part of the year. Although a plant startup cost, a capital cost, is associated with this strategy, strategic recovery may allow to offset water costs. Moreover, targeting the recovery of the most valuable metals on the market and cheapest for recovery may aid in offsetting costs. The calculations in this section are not selective in this regard.

Table 5-10 Sampling sites, flow rates, and elemental concentrations (Al, Cu, Fe, Mg, Mn, Ni, Pb, Zn) as per collection data provided by Barrick Gold Corporation between 1900-2014.

		Sampling location						
	Units	IN12	IN13	IN2	IN21	IN23	IN28	IN3
Average Flow	L/s	275	774	285	34	63	191	499
	L/year	8.7.E+09	2.4.E+10	9.0.E+09	1.1.E+09	2.0.E+09	6.0.E+09	1.6.E+10
Elements								
Al	mg/L	15	25	78	44	0.029	46	40
Cu	mg/L	0.066	14	33	4.8	0.014	70	23
Fe	mg/L	2.5	6.0	37	42	0.14	86	17
Mg	mg/L	43	49	47	46	9.2	33	49
Mn	mg/L	3.5	5.3	8.5	15.0	0.0080	8	7
Ni	mg/L	0.042	0.057	0.099	0.094	0.019	0.19	0.060
Pb	mg/L	0.0012	0.0027	0.0024	0.0020	0.0015	0.0044	0.0023
Zn	mg/L	0.47	2.3	4.7	7.2	0.013	3.7	3.6

Table 5-11 Amount of recoverable metals from each sampled site in mg/year by multiplying concentration with annual flow rate.

Elements	Units	IN12	IN13	IN2	IN21	IN23	IN28	IN3
Al	kg/year	127,135	598,025	699,865	48,111	58	278,921	629,320
Cu	kg/year	567	343,925	297,801	5,223	28	424,419	361,859
Mg	kg/year	374,650	1,192,877	421,444	49,682	18,285	198,988	764,624
Mn	kg/year	30,658	128,636	75,819	16,264	16	50,109	102,264
Ni	kg/year	364	1,379	886	102	38	1,123	947
Pb	kg/year	10	66	22	2	3	27	36
Zn	kg/year	4,097	56,873	42,171	7,786	26	22,157	56,009

Table 5-12 Amount in USD per year was calculated by multiplying mg/year values from Table 5-10 with appropriate economic prices in Table 5-8.

		Sampling location								
Elements	Units	IN12	IN13	IN2	IN21	IN23	IN28	IN3	AVERAGE	
Al	\$/year	204,306	961,026	1,124,682	77,314	93	448,226	1,011,317	\$	546,709
Cu	\$/year	3,920	2,376,906	2,058,138	36,096	190	2,933,206	2,500,847	\$	1,415,615
Mg	\$/year	775,525	2,469,255	872,389	102,842	37,850	411,905	1,582,771	\$	893,219
Mn	\$/year	53,651	225,114	132,683	28,463	28	87,691	178,963	\$	100,942
Ni	\$/year	6,167	23,384	15,016	1,727	649	19,040	16,059	\$	11,720
Pb	\$/year	19	119	39	4	5	48	65	\$	43
Zn	\$/year	7,557	104,900	77,783	14,360	47	40,867	103,306	\$	49,831
TOTAL									\$	3,018,079

El Indio mitigation has been cover placements, water diversions and passive treatment at Pastos Largos gravity settling pond. pH adjustment via lime addition and sedimentation are practiced at Pierina

with HDS. Reverse osmosis (RO) plants are currently being built (Thomaz, 2006; BGC, 2014b). Active treatment via lime neutralization and (HDS) generation is conducted at Lagunas Norte (Thomaz, 2006; BGC, 2014b). Plants at this site are being upgraded for RO due to changes in environmental legislation. The most common form of chemical treatment, which is currently used at Lagunas Norte and Pierina, is the addition of lime in order to precipitate sulfate in the form of gypsum. Lime can be added as limestone (CaCO_3), calcium oxide, calcium hydroxide (Ca(OH)_2), and hydrated lime. Soda ash (Na_2CO_3) is also required at times to balance the precipitation reaction. The process produces low density (LDS) or HDS containing gypsum and iron oxyhydroxides with adsorbed metals. ARD at Pierina has been calculated by Klohn Crippen Berger (2012) to persist for several decades to hundreds of years after closure based on the available sulfur. Since the majority of the acidity generated is related to the dissolved Fe and Al concentrations, precipitating these two elements out of solution can have significant impact on the quality of effluent waters at all sites (Klohn Crippen Berger, 2012a). Based on mineralogy observed at El Indio, K, As, Al, SO_4 , Ca, Cu, Fe, Zn, Cu, Co, Mn, Al, Na, Pb and Mn can be attenuated by precipitation of secondary minerals and ideal lattice substitutions and/or sorption of these elements. Based on mineralogy observed at Lagunas Norte and Pierina, Cu, Fe, SO_4 , Ca, Na, As, Mg, and K, Al, Ca, Fe, SO_4 , Mg respectively can be attenuated by ideal lattice substitutions and/or sorption. Finally, selective removal of elements can be conducted by ion exchange. This method would be ideal for elements that are not removed by lime neutralization, such as As. The high toxicity of this element acts as a strong incentive for removing it rather than allowing its precipitation in sludge (MEND Treatment Committee, 2013). Elements that behave similarly to As remain in solution and must be removed by other treatment methods such as ion exchange.

Chapter 6

Conclusions

The main objective of this study was to characterize the waters and secondary precipitates from El Indio, Lagunas Norte and Pierina mines. The trace element contents of the secondary sulfate minerals were documented with μ XRF analyses. An idea of potential adsorption or substitutions was also observed through elemental correlations from Spearman diagrams. The following conclusions are based on selected sample sites.

Conclusion 1: No one instrument or method can be used to identify secondary precipitates from mine drainage and determine the trace element content of those precipitates (Table 4-20, Table 4-27, Table 4-28). In this study, minerals were identified with the use of bulk diffraction and their chemical composition was studied with the use of semi-quantitative μ XRF analyses. Several geochemical analytical techniques were used to obtain data at various scales, thereby providing the researcher with a more accurate and holistic understanding of the geochemistry of studied mines. Analyses by ICP-MS and ICP-OES were essential in understanding the bulk composition of the samples collected. The characterization of textures and their associated elements was accomplished through ESEM analysis conducted on unpolished bulk samples, mounted on stubs. Conventional X-ray diffraction analyses were instrumental in the general description of the most common and crystalline phases within the samples analyzed. The synchrotron (μ XRF and μ XRD) was a critical tool that identified previously unobserved phases, and gave insight on the distribution of elements within certain secondary precipitates. Images and chemical information collected with the ESEM demonstrate the wide array of morphologies of Na-Mg sulfates, and other sulfate salts. This research demonstrates that morphology, in itself, cannot be used to identify the precipitates observed at our sites. As such, the data collected from each analytical technique complemented the other, and the combined use of these methods and techniques increased the quality of results. For future reference, microprobe analysis should be conducted prior to lifting of thin sections.

Conclusion 2: These secondary precipitates pose analytical challenges as a result of their complex chemistry, instability with varying temperature and humidity conditions, and the intergrowths of multiple phases from the micron to bulk scales. Specifically, the μ XRD analyses are collected from an area of approximately 2 μ m in diameter, and over 90% of these analyzed spots show 2 or more positively identified phases. The ESEM observations of the unpolished, mounted samples also indicate complex mixtures at the micron scale (refer to figures that show this). Moreover some of the phases observed may not represent those stable under field conditions as a result of changes in humidity in the laboratory or within the analytical instruments.

Conclusion 3: Sulfate salts incorporate or host, as adsorbed species, a specific suite of minor and trace metals or elements of concern. Based on the samples analyzed by μ XRF, blodite is host to Cu, Mn, Zn, Ca, Co, Fe, and Ni in approximately decreasing order. Alunite is host to Cu, K, Zn, Ca, Mn, Fe, Ti, Co, Ni and As in decreasing order. Hexahydrite contains Cu, Zn, Fe, Mn, As, Ni, Ti or Ti, As, Co, and Ni in decreasing order. Spearman correlations suggest the other minerals host specific elements, but this requires further testing. Considerable amounts of metals can also be attenuated by the precipitation and formation of chrysocolla, boyleite, hexahydrite, starkeyite, epsomite, magnesiocopiapite, dietrichite, melanterite and scorodite at El Indio, chalcantite, hydroniumjarosite, antlerite, scorodite, poitevinite, and fibroferrite at Lagunas Norte, and romerite, coquimbite, jarosite and magnesiocopipiate at Pierina. These minerals are likely only temporary storage sites for the elements that compose them as a result of the relatively high solubility of these elements and their sensitivity to changes in pH.

Conclusion 4: Geochemical modeling provided information on poorly-crystalline phases not detected by XRD. Although PHREEQC databases do not include thermodynamic information on many of the minerals observed as precipitates at these sites, the software predicted that Fe and Al oxyhydroxide would precipitate. Bulk chemical data were in agreement with these results but their amorphous nature meant that they were not recognized by diffraction tools.

Conclusion 5: Generally, the waters and secondary precipitates are characteristic of HS epithermal deposits, although a few minerals are very rare or not previously recognized in this setting (i.e. blodite, loweite). According to the Piper diagrams, analyzed waters are of the Ca-SO₄ type and typical of mine drainage. The pH range was acidic (3.4-6.7 at El Indio, 2.9 to 6.2 at Lagunas Norte, 2.6-3.1 at Pierina) at all sample sites with the exception of IN23 at El Indio (pH 6.7), and LN-PW2 at Lagunas Norte (pH 6.2). Major elements in waters sampled from El Indio include Ca and S, minor elements include Al, Cu, Mg, Mn, K, Fe and Na, and trace elements are As, Co, Ni, Sr, Pb, Cd, and Zn. Differences in elemental concentrations are observed at Lagunas Norte where major elements consist of Al, Ca, Fe, and S, minor elements comprise Cu, Mn, Na, Zn and Mg, and trace elements are As, Pb, Ni and K. Iron, Ca and S are the most concentrated elements at Pierina, with Al, Cu, Mg, Zn and Mn as minor elements and As, Cd, Co, Pb, K, Na as trace elements.

Conclusion 6: Mined HS epithermal deposits such as El Indio, Lagunas Norte and Pierina provide the right conditions to allow the development of a wide variety of highly soluble secondary precipitates that were previously unidentified at these mines. The mineralogy of the secondary minerals forming at these three settings is variable but can be placed into 3 broad groups: 1) hydrous Na-, Mg-, Ca-, Cu- and other metal-sulfates such as blodite, hexahydrate and gypsum 2) Fe-oxides, oxyhydroxides and oxyhydroxysulfates such as ferrihydrites, goethite, scorodite and jarosite 3) other metal rich, low crystalline phases such as basaluminite-like Al minerals, and few oxides, hydroxide, arsenates, carbonates and silicates in decreasing order. The first group is predominant at El Indio, the second group was most common at El Indio and Pierina, and Cu-sulfates were ubiquitous at Lagunas Norte.

Conclusion 7: The precipitates formed in the streams, stream beds and the surface of rocks are dependent on the chemical variations of the circulating solution during their formation. The most concentrated ions are generally similar in secondary precipitates and in solution. For example, at sample site IN28, both water and secondary precipitates are most heavily concentrated in Al, Ca, Fe, Cu, Na, Zn

and S. This sampling reflects a specific and single point in space and time. Furthermore, concentration of solutions using PHREEQC modeling has demonstrated an expected change in secondary precipitates forming through evaporation, presumably through time. An increased number of Fe, Al and Mn oxyhydroxides, as well as Cu and Fe sulfates formed from modeling of these concentrated waters; others, not found in the database are also expected to precipitate.

Conclusion 8: The occurrence of secondary precipitates stands as evidence purporting that sulfide oxidation at these mine sites is ongoing. The sulfide rich geology in these studied mines and resulting sulfide wastes are presently being oxidized to be leaving such a high signature of sulfate in the analyzed streams. The dissolution of primary Fe and Al minerals from the original lithology is also adding to the acidity of these streams.

Conclusion 9: Calculations demonstrate that quantities of economic metals that may be recovered from waters are not substantial enough to significantly offset water treatment costs when considering operational expenditure. Based on calculations, Barrick Gold Corporation may lose money on recovery costs; however, it is recommended that specific elements with high economic value and low recovery cost be targeted for a greater return margin, and that metal recovery be conducted during a specific temporal timeframe. Assumptions included a constant flow rate, an average concentration of elements, that there are only 7 recoverable elements and that the commodity price is unchanged throughout the year. Furthermore, capital expenditure was not taken into account, and the focus of the calculations was solely on operational expenditure.

6.1 Future work

Although this work provides researchers with insight into the aqueous and secondary precipitate geochemistry, as well as some controls of elemental mobility at El Indio, Lagunas Norte and Pierina, some uncertainties remain. The concentrations of elements measured by the several analytical techniques and statistical analyses give an understanding about the minerals that may be hosting important elements.

However, there is an uncertainty related to these correlations on how representative they may be of the overall chemistry of all secondary precipitates present at the mine sites. It is suggested that more samples be collected, specifically from Lagunas Norte and Pierina during the dry season, for a representative sample size decreasing the standard error value.

From field sampling, selection of sample to be made into thin sections, selection of areas and specific spots analyzed for μ XRF and μ XRD, sampling methods and sample preparation introduce bias to the analysis at various stages of the project. Most of the samples chosen to be made into thin sections were based on the abundances of peaks observed in bulk XRD, since these were interpreted as potentially representative of mixtures that would be more easily identified by finer scaled analyses. This decision skewed mineralogical results towards giving an impression that Na-Mg oxyhydroxide sulfates are more omnipresent than they actually are. This was caused by the fact that the Na-Mg oxyhydroxide sulfates had an elevated number of peaks. A more varied selection could have been more representative if it captured the nature of other minerals present. In future work, samples with many peaks and some with fewer peaks should be considered to be made into thin sections. Moreover, because of this limitation on the number of samples that could be analyzed and the types of analysis conducted, the researchers were unable to observe element-mineral associations for many of the minerals present throughout the mines. This decreases the degree to which these results may be extrapolated to the respective deposit. Semi-quantitative element analysis was conducted on samples collected from 2 sites at El Indio and 1 from Lagunas Norte. The number of samples made and analyzed depended on time required to make thin sections prior to synchrotron work. Time was also a factor during synchrotron analysis, limiting the number of samples that could be semi-quantitatively characterized to 2 days. Furthermore, not all elemental correlations that were made could be explained, and further mineralogical work should be conducted to understand them.

To address these questions and uncertainties, a number of other experiments and analyses are suggested:

- A representative amount of thin sections from each mine should be made and analyzed at various scales. Petrographic work will be necessary to conduct prior to thin section lifting for synchrotron analysis, in order to identify any genetic relationships visible. Additional analysis with EXAFS (extended X-ray absorption fine structure spectroscopy), which can be measured at the synchrotron can provide information on bond length and distances between atoms allowing to identify molecular structures and elemental inclusions in the mineral structures (Foster et al., 1998). Such analyses will allow a better understanding of solid solutions, as well as speciation of elements. Hence, the association of elements to minerals can be further described allowing for a better understanding of element mobility.
- Multiple site visits and additional collection of water and solid samples from all mines throughout the wet and dry seasons would be necessary to document the seasonal changes in water quality and secondary metal-salt sulfates. Long-term water quality monitoring is also of importance in order to identify the seasons with peak metal concentrations to develop efficient remediation methods.
- A portable X-ray diffractometer should be used in future work, in order to distinguish minerals while conducting field work, as demonstrated by Peterson (2011). It may be more difficult to identify all minerals in mixtures since peaks are wider on the portable XRD, but will still provide a general understanding of the types of minerals observed.
- EMPA analyses should be conducted on polished thin sections. The ESEM work provided semi-quantitative data and would be well complemented with quantitative data from the microprobe.
- Further modeling using PHREEQC could be used to predict and understand the formation of precipitates. The thermodynamic data for more minerals, specifically sulfate hydrates can be

added to the database. The log-K_{sp} values from solubility diagrams could be used in PHREEQC to see how this alters the potential occurrence of minerals. With regards to PHREEQC, geochemical modeling can be further used to understand how responsive different acid water compositions may be to active or passive treatment (Plumlee et al., 1999). The chemistry of waters can be modeled to demonstrate progressive neutralization by lime addition or dilution to estimate the types of precipitates formed. As such, the optimal pH of waters from mines can be identified to which they would be treated. Research by Wanty et al. (1990) and Plumlee et al. (1990) state that some metals such as As or Mo that form oxyanions or strong carbonate complexes (i.e. U) can desorb at high pH values. As such, treatment to very high pH values can lead to the release of these harmful elements.

- Reitveld analysis of the XRD and μ XRD spectra should be conducted to understand the quantity of the secondary minerals present within the collected samples. The focus of this specific research was based on the identification and not quantification.

Chapter 7

References

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Appendix A: Sampling site locations

Table 0-1: List of sample types and sampling dates for specific locations

Sample Site	Sampling Date	Type of Sample procured
IN-23	May 7, 2014	Water, secondary precipitates, RNA, DNA
IN-28	May 7, 2014	Water, secondary precipitates, RNA, DNA
RMATR	May 7, 2014	Water, secondary precipitates, RNA, DNA
IN-2	May 7, 2014	Water, secondary precipitates, RNA, DNA
IN-13	May 8, 2014	Water, secondary precipitates, RNA, DNA

Table 0-2: Sample UTM coordinates and elevation

Sample Site	Elevation (m)	UTM (N)	UTM (E)
IN-23	4100	6709647	0407489
IN-28	3650	6705697	0405670
RMATR	3550	6704938	0404246
IN-2	3250	6699644	0401358
IN-13	2080	6760128	0365587

Table 0-3: List of sample types and sampling dates for specific locations at Lagunas Norte

Sample Site	Sampling Date	Type of Sample procured
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LN-DAR-1	May 13, 2014	Water (full suite), secondary precipitates, RNA, DNA
LN-SP-3	May 13, 2014	Water (full suite), secondary precipitates, RNA, DNA
LN-DW-B-11	May 13, 2014	Water (full suite)
ARD Water treatment plant	May 14, 2014	Sludge sample, RNA, DNA
LN-SP-3	May 14, 2014	Water resampled (full suite)
LN-PW-1	May 14, 2014	Water (UA only)
LN-BP	May 14, 2014	Water (full suite), secondary precipitates, RNA, DNA
LN-PW-2	May 14, 2014	Water (full suite), secondary precipitates, RNA, DNA
LN-VWD	May 14, 2014	Water (full suite), secondary precipitates, RNA, DNA

Table 0-4: Sample UTM coordinates and elevation at Lagunas Norte

Sample Site	Elevation (m)	UTM (N)	UTM (E)
LN-DAR-1	4200	9119899	0807547
LN-SP-3	4007	9111805	0810251
LN-DW-B-11	3903	9111696	0796497
LN-PW-1	3683	9124710	0803521
LN-BP	3951	9119813	0806361
LN-PW-2	3926	9120600	0804039
LN-VWD	3951	9122653	0803623

Table 0-5: List of sample types at Pierina and sampling dates for specific locations

Sample Site	Sampling Date	Type of Sample procured
P-WRD-stream1	17-May-14	YSI only
P-WRD-stream2	17-May-14	YSI only
P-WRD	17-May-14	Water (full suite), secondary precipitates, RNA, DNA
P-ARD-17 (tunnel)	17-May-14	Water (full suite), RNA, DNA
P-PD (trucks)	18-May-14	Water (full suite), secondary precipitates
P-EC	18-May-14	Water (full suite), secondary precipitates, RNA, DNA

Table 0-6: Pierina sample UTM coordinates and elevation

Sample Site	Elevation (m)	UTM (N)	UTM (E)
P-WRD	4104	8952826	215121
P-ARD-17	3867	8952904	216985
P-PD	3842	8954442	216053
P-PW1	3847	8954451	216072
P-PW2	3851	8955127	216235
P-EC	3813	8955127	216225

Appendix B: PHREEQC modeling minerals with $SI \geq 0$

Electrical imbalance greater than 10% can be created by laboratory error or sampling error. Electrical balance of waters from field sites calculated by PHREEQC shows values below 10% for all samples, except for FA triplicate of sample P-EC-W (78%) and FA duplicate of LN-VWD-W (28%). These samples were discarded from future analysis and interpretation.

IN23-W UA No43		IN23-W UA No44		IN23-W UA No45		IN28-W UA No46 *		IN28-W UA No47		IN28-W UA No48	
Ba3(AsO4)2		Ba3(AsO4)2		Ba3(AsO4)2		Alunite	KAl3(SO4)2(OH)6	Alunite	KAl3(SO4)2(OH)6	Alunite	KAl3(SO4)2(OH)6
Basaluminite	Al4(OH)10SO4	Boehmite	AlOOH	Boehmite	AlOOH	Basaluminite	Al4(OH)10SO4	Basaluminite	Al4(OH)10SO4	Basaluminite	Al4(OH)10SO4
Boehmite	AlOOH	CupricFerrite	CuFe2O4	Diaspore	AlOOH	Boehmite	AlOOH	Boehmite	AlOOH	Boehmite	AlOOH
CupricFerrite	CuFe2O4	CuprousFerrite	CuFeO2	Fe(OH)2.7Cl.3		Cupricferrite	CuFe2O4	Cupricferrite	CuFe2O4	Cupricferrite	CuFe2O4
CuprousFerrite	CuFeO2	Diaspore	AlOOH	Fe(OH)3(a)		Cuprousferrite	CuFeO2	Cuprousferrite	CuFeO2	Cupricferrite	CuFeO2
Diaspore	AlOOH	Fe(OH)2.7Cl.3		Fe3(OH)8		Diaspore	AlOOH	Diaspore	AlOOH	Diaspore	AlOOH
Fe(OH)2.7Cl.3		Fe(OH)3(a)		Gibbsite	Al(OH)3	Fe(OH)2.7Cl		Fe(OH)2.7Cl		Fe(OH)2.7Cl	
Fe(OH)3(a)		Fe3(OH)8		Goethite	FeOOH	Gibbsite	Al(OH)3	Gibbsite	Al(OH)3	Gibbsite	Al(OH)3
Gibbsite	Al(OH)3	Gibbsite	Al(OH)3	Maghemite	Fe2O3	Goethite	FeOOH	Goethite	FeOOH	Goethite	FeOOH
Goethite	FeOOH	Goethite	FeOOH	Magnetite	Fe3O4	Maghemite	Fe2O3	Maghemite	Fe2O3	Maghemite	Fe2O3
Hematite	Fe2O3	Hematite	Fe2O3			Hematite	Fe2O3	Hematite	Fe2O3	Hematite	Fe2O3
Maghemite	Fe2O3	Maghemite	Fe2O3			Magnetite	Fe3O4	Magnetite	Fe3O4	Magnetite	Fe3O4
Magnetite	Fe3O4	Magnetite	Fe3O4								
IN-RMATR-W FA No49		IN-RMATR-W FA No50		IN-RMATR-W FA No51		IN2-W FA No52		IN2-W FA No53		IN2-W FA No54	
CuprousFerrite	CuFeO2	CuprousFerrite	CuFeO2	CuprousFerrite	CuFeO2	CuprousFerrite	CuFeO2	CuprousFerrite	CuFeO2	CuprousFerrite	CuFeO2
Hematite	Fe2O3	Hematite	Fe2O3	Hematite	Fe2O3	Hematite	Fe2O3	Hematite	Fe2O3	Hematite	Fe2O3
Jurbanite	AlOHSO4	Jurbanite	AlOHSO4	Jurbanite	AlOHSO4						
IN13-W FA No55		IN13-W FA No56		IN13-W FA No57							
Alunite	KAl3(SO4)2(OH)6	Alunite	KAl3(SO4)2(OH)6	Alunite	KAl3(SO4)2(OH)6						
Basaluminite	Al4(OH)10SO4	Basaluminite	Al4(OH)10SO4	Basaluminite	Al4(OH)10SO4						
Boehmite	AlOOH	Boehmite	AlOOH	Boehmite	AlOOH						
Cupricferrite	CuFe2O4	Cupricferrite	CuFe2O4	Cupricferrite	CuFe2O4						
Cupricferrite	CuFeO2	Cupricferrite	CuFeO2	Cupricferrite	CuFeO2						
Diaspore		Diaspore	AlOOH	Diaspore	AlOOH						
Fe(OH)2.7Cl		Fe(OH)2.7Cl		Fe(OH)2.7Cl							
Gibbsite	Al(OH)3	Gibbsite	Al(OH)3	Gibbsite	Al(OH)3						
Goethite	FeOOH	Goethite	FeOOH	Goethite	FeOOH						
Magnetite	Fe3O4	Hematite	Fe2O3	Hematite	Fe2O3						
		Magnetite	Fe3O4	Magnetite	Fe3O4						

LN-SP3-W FA No1		LN-DW-B-11-W FA No2		LN-DW-B-11-W FA No3		LN-DW-B-11-W FA No4		LN-SP3-W FA No5		LN-SP3-W FA No6	
CuprousFerrite	CuFeO2	As		As		As		CuprousFerrite	CuFeO2	CuprousFerrite	CuFeO2
Fe(OH)2.7Cl.3		Cu		Cu		Cu		Fe(OH)2.7Cl.3		Fe(OH)2.7Cl.3	
Goethite	FeOOH	Cuprite	Cu2O	Cuprite	Cu2O	Cuprite	Cu2O	Goethite	FeOOH	Goethite	FeOOH
Hematite	Fe2O3	CuprousFerrite	CuFeO2	CuprousFerrite	CuFeO2	CuprousFerrite	CuFeO2	Hematite	Fe2O3	Hematite	Fe2O3
		U4O9(c)	U4O9(c)	U4O9(c)	U4O9(c)						
		Uraninite	UO2	Uraninite	UO2	Uraninite	UO2				
LN-DAR-1-W FA No8		LN-DAR-1-W FA No9		LN-DAR-1-W FA No10		LN-BP-W FA No11*		LN-BP-W FA No12		LN-PW2-W FA No13	
CuprousFerrite	CuFeO2	CuprousFerrite	CuFeO2	CuprousFerrite	CuFeO2	CuprousFerrite	CuFeO2	CuprousFerrite	CuFeO2	Basaluminite	Al4(OH)10SO4
Fe(OH)2.7Cl.3		Fe(OH)2.7Cl.3		Fe(OH)2.7Cl.3		Fe(OH)2.7Cl.3		Fe(OH)2.7Cl.3		Boehmite	AlOOH
Goethite	FeOOH	Goethite	FeOOH	Goethite	FeOOH	Goethite	FeOOH	Goethite	FeOOH	Cu	
Hematite	Fe2O3	Hematite	Fe2O3	Hematite	Fe2O3	Hematite	Fe2O3	Hematite	Fe2O3	Cuprite	Cu2O
Magnetite	Fe3O4	Magnetite	Fe3O4	Magnetite	Fe3O4					CuprousFerrite	CuFeO2
										Diaspore	AlOOH
										Gibbsite	Al(OH)3
										UO2(a)	
										Uraninite	UO2
LN-PW2-W FA No14		LN-PW2-W FA No15		LN-VWD-W FA No16		LN-VWD-W FA No17		LN-SP3-W2 FA No18		LN-SP3-W2 FA No19	
Basaluminite	Al4(OH)10SO4	Basaluminite	Al4(OH)10SO4	CuprousFerrite	CuFeO2	CuprousFerrite	CuFeO2	CuprousFerrite	CuFeO2	CuprousFerrite	CuFeO2
Boehmite	AlOOH	Boehmite	AlOOH	Fe(OH)2.7Cl.3		Fe(OH)2.7Cl.3		Fe(OH)2.7Cl.3		Fe(OH)2.7Cl.3	
Cu		Cu		Goethite	FeOOH	Goethite	FeOOH	Goethite	FeOOH	Goethite	FeOOH
Cuprite	Cu2O	Cuprite	Cu2O	Hematite	Fe2O3	Hematite	Fe2O3	Hematite	Fe2O3	Hematite	Fe2O3
CuprousFerrite	CuFeO2	CuprousFerrite	CuFeO2	Magnetite	Fe3O4	Magnetite	Fe3O4			Magnetite	Fe3O4
Diaspore	AlOOH	Diaspore	AlOOH								
Gibbsite	Al(OH)3	UO2(a)									
UO2(a)		Uraninite	UO2								
Uraninite	UO2										
LN-DW-B-11-W FFA No21		LN-PW2-W FFA No22		LN-SP3-W FFA No23		LN-DAR-1-W FFA No24		LN-BP-W FFA No25		LN-SP3-W2 FFA No26	
Arsenic	AS	Boehmite	AlOOH	CuprousFerrite	CuFeO2	CuprousFerrite	CuFeO2	CuprousFerrite	CuFeO2	CuprousFerrite	CuFeO2
Copper	Cu	Copper		Fe(OH)2.7Cl.3		Fe(OH)2.7Cl.3		Fe(OH)2.7Cl.3		Fe(OH)2.7Cl.3	
Cuprite	Cu2O	Gibbsite	Al(OH)3	Goethite	FeOOH	Goethite	FeOOH	Goethite	FeOOH	Goethite	FeOOH
CuprousFerrite	CuFeO2	UO2	amorph			Hematite	Fe2O3	Hematite	Fe2O3	Hematite	Fe2O3
U4O9		Uraninite	UO2			Magnetite	Fe3O4			Magnetite	Fe3O4
Uraninite	UO2										

LN-VWD-W		LN-DAR-1-W		LN-DAR-1-W		LN-DW-B-11-W		LN-DW-B-11-W		LN-SP3-W	
FFA		UA		UA		UA		UA		UA	
No27 *		No28		No29 *		No30		No31		No32	
CuprousFerrite	CuFeO2	CuprousFerrite	CuFeO2	CuprousFerrite	CuFeO2	As		As		CuprousFerrite	CuFeO2
Fe(OH)2.7Cl3		Fe(OH)2.7Cl3		Fe(OH)2.7Cl3		Cu		Cu		Fe(OH)2.7Cl3	
Goethite	FeOOH	Goethite	FeOOH	Goethite	FeOOH	Cuprite	Cu2O	Cuprite	Cu2O	Goethite	FeOOH
Hematite	Fe2O3	Hematite	Fe2O3	Hematite	Fe2O3	Cuprous ferrite	CuFeO2	Cuprous ferrite	CuFeO2	Hematite	Fe2O3
Magnetite	Fe3O4	Magnetite	Fe3O4	Magnetite	Fe3O4	U4O9(c)		U4O9(c)		Magnetite	Fe3O4
LN-SP3-W		LN-SP3-W2		LN-PW-W		LN-BP-W		LN-BP-W		LN-PW2-W	
UA		UA		UA		UA		UA		UA	
No33		No35		No36		No37		No38		No39	
CuprousFerrite	CuFeO2	Cuprous ferrite	CuFeO2	Al(OH)3(a)		Cuprous ferrite	CuFeO2	Cuprous ferrite	CuFeO2	Al(OH)3(a)	
Fe(OH)2.7Cl3		Fe(OH)2.7Cl3		Boehmite	AlOOH	Fe(OH)2.7Cl3		Fe(OH)2.7Cl3		Basaluminite	Al4(OH)10SO4
Goethite	FeOOH	Goethite	FeOOH	CuMetal	Cu	Goethite	FeOOH	Goethite	FeOOH	Boehmite	AlOOH
Hematite	Fe2O3	Hematite	Fe2O3	CupricFerrite	CuFe2O4	Hematite	Fe2O3	Hematite	Fe2O3	CuMetal	Cu
Magnetite	Fe3O4	Magnetite	Fe3O4	Cuprite	Cu2O					Cuprite	Cu2O
				Cuprous ferrite	CuFeO2					Cuprous ferrite	CuFeO2
				Diaspore	AlOOH					Diaspore	AlOOH
				Gibbsite	Al(OH)3					Gibbsite	Al(OH)3
				Goethite	FeOOH					UO2(a)	
				Hematite	Fe2O3					Uraninite(c)	UO2
				Magnetite	Fe3O4						
				U4O9(c)							
				Uraninite(c)	UO2						
LN-PW2-W		LN-VWD-W									
UA		UA									
No40		No41									
Al(OH)3(a)		Cuprousferrite	CuFeO2								
Basaluminite	Al4(OH)10SO4	Goethite	FeOOH								
Boehmite	AlOOH	Fe(OH)2.7Cl3									
CuMetal	Cu	Hematite	Fe2O3								
Cuprite	Cu2O	Magnetite	Fe3O4								
Cuprous ferrite	CuFeO2										
Diaspore	AlOOH										
Gibbsite	Al(OH)3										
UO2(a)											
Uraninite(c)	UO2										

P-ARD17-W		P-EC-W		P-WRD-W		P-PD-W		P-ARD17-W		P-WRD-W	
FFA		FFA		FFA		FFA		UA		UA	
No60		No61		No62		No63		No65 *		No66	
CuprousFerrite	CuFeO2	Alunite	KAl3(SO4)2(OH)6	CuprousFerrite	CuFeO2	CuprousFerrite	CuFeO2	CuprousFerrite	CuFeO2	CuprousFerrite	CuFeO2
Goethite	FeOOH	Basaluminite	Al4(OH)10SO4	Fe(OH)2.7Cl3		Goethite	FeOOH	Goethite	FeOOH	Hematite	Fe2O3
		Boehmite	AlOOH	Goethite	FeOOH	Hematite	Fe2O3	Hematite	Fe2O3		
		CupricFerrite	CuFe2O4	Magnetite	Fe3O4						
		CuprousFerrite	CuFeO2								
		Diaspore	AlOOH								
		Fe(OH)2.7Cl3									
		Gibbsite	Al(OH)3								
		Goethite	FeOOH								
		Hematite	Fe2O3								
		Magnetite	Fe3O4								
P-ARD17-W		P-WRD-W		P-EC-W		P-EC-W		P-PD-W		P-PD-W	
UA		UA		UA		UA		UA		UA	
No67		No68		No69		No70		No71		No72	
CuprousFerrite	CuFeO2	CuprousFerrite	CuFeO2	Alunite	KAl3(SO4)2(OH)6	Alunite	KAl3(SO4)2(OH)6	CuprousFerrite	CuFeO2	CuprousFerrite	CuFeO2
Fe(OH)2.7Cl3		Fe(OH)2.7Cl3		Basaluminite	Al4(OH)10SO4	Basaluminite	Al4(OH)10SO4	Goethite	FeOOH	Goethite	FeOOH
Goethite	FeOOH	Goethite	FeOOH	Boehmite	AlOOH	Boehmite	AlOOH	Hematite	Fe2O3	Hematite	Fe2O3
Hematite	Fe2O3	Magnetite	Fe3O4	CupricFerrite	CuFe2O4	CupricFerrite	CuFe2O4				
Magnetite	Fe3O4			CuprousFerrite	CuFeO2	CuprousFerrite	CuFeO2				
				Diaspore	AlOOH	Diaspore	AlOOH				
				Fe(OH)2.7Cl3		Fe(OH)2.7Cl3					
				Gibbsite	Al(OH)3	Gibbsite	Al(OH)3				
				Goethite	FeOOH	Goethite	FeOOH				
				Hematite	Fe2O3	Hematite	Fe2O3				
				Magnetite	Fe3O4	Magnetite	Fe3O4				
P-ARD-17-W		P-ARD-17-W		P-WRD-W		P-WRD-W		P-WRD-W		P-PD-W	
FA		FA		FA		FA		FA		FA	
No73		No74		No76		No77		No78		No79	
CuprousFerrite	CuFeO2	CuprousFerrite	CuFeO2	CuprousFerrite	CuFeO2	CuprousFerrite	CuFeO2	CuprousFerrite	CuFeO2	CuprousFerrite	CuFeO2
Goethite	FeOOH	Goethite	FeOOH	Fe(OH)2.7Cl3		Fe(OH)2.7Cl3		Fe(OH)2.7Cl3		Goethite	FeOOH
Hematite	Fe2O3	Hematite	Fe2O3	Goethite	FeOOH	Goethite	FeOOH	Goethite	FeOOH	Hematite	Fe2O3
				Hematite	Fe2O3	Hematite	Fe2O3	Hematite	Fe2O3		
				Magnetite	Fe3O4	Magnetite	Fe3O4	Magnetite	Fe3O4		

P-PD-W		P-PD-W		P-EC-W		P-EC-W		P-EC-W	
FA		FA		FA		FA		FA	
No 80		No 81		No 82		No 83		No84 *	
CuprousFerrite	CuFeO2	CuprousFerrite	CuFeO2	Alunite	KAl3(SO4)2(OH)6	Alunite	KAl3(SO4)2(OH)6	CupricFerrite	CuFe2O4
Goethite	FeOOH	Goethite	FeOOH	Basaluminite	Al4(OH)10SO4	Basaluminite	Al4(OH)10SO4	CuprousFerrite	CuFeO2
Hematite	Fe2O3	Hematite	Fe2O3	Boehmite	AlOOH	Boehmite	AlOOH	Diaspore	AlOOH
				CupricFerrite	CuFe2O4	CupricFerrite	CuFe2O4	Fe(OH)2.7Cl.3	
				CuprousFerrite	CuFeO2	CuprousFerrite	CuFeO2	Gibbsite	Al(OH)3
				Diaspore	AlOOH	Diaspore	AlOOH	Goethite	FeOOH
				Fe(OH)2.7Cl.3		Fe(OH)2.7Cl.3		Hematite	Fe2O3
				Gibbsite	Al(OH)3	Gibbsite	Al(OH)3	Magnetite	Fe3O4
				Goethite	FeOOH	Goethite	FeOOH		
				Hematite	Fe2O3	Hematite	Fe2O3		
				Magnetite	Fe3O4	Magnetite	Fe3O4		

Appendix C: PHREEQC modeling with SI≥0 in solutions concentrated 20 fold

LN-SP3-W				LN-DW-B-11-W				LN-DAR-1-W			
Conc.1X		Conc.20X		Conc.1X		Conc.20X		Conc.1X		Conc.20X	
CuprousFerrite	CuFeO2	Al(OH)3(a)		As		As2S3(am)		CuprousFerrite	CuFeO2	CuprousFerrite	CuFeO2
Fe(OH)2.7Cl.3		Alunite	KAl3(SO4)2(OH)6	Cu		As		Fe(OH)2.7Cl.3		Fe(OH)2.7Cl.3	
Goethite	FeOOH	Barite	BaSO4	Cuprite	Cu2O	Blaubleil	Cu0.9Cu0.2S	Goethite	FeOOH	Goethite	FeOOH
Hematite	Fe2O3	Basaluminite	Al4(OH)10SO4	CuprousFerrite	CuFeO2	Chalcocite	Cu2C	Hematite	Fe2O3	Hematite	Fe2O3
		Boehmite	AlOOH	U4O9(c)	U4O9(c)	Chalcopyrite	CuFeS2	Magnetite	Fe3O4		
		Birnessite	MnO2	Uraninite	UO2	Cu					
		Bixbyite	Mn2O3			Cuprite	Cu2O				
		Boehmite	AlOOH			CuprousFerrite	CuFeO2				
		Bronchantite	Cu4(OH)6SO4			Djurleite	Cu0.066Cu1.868S				
		Cu(OH)2				Galena	PbS				
		Cu3(AsO4)2·6H2O				Greenockite	CdS				
		CuprousFerrite	CuFeO2			Orpiment	As2S3				
		Diaspore	AlOOH			Sphalerite	ZnS				
		Fe(OH)2.7Cl.3				Uraninite	UO2				
		Fe(OH)3									
		Fe3(OH)8									
		Gibbsite	Al(OH)3								
		Goethite	FeOOH								
		Hausmannite	Mn3O4								
		Hematite	Fe2O3								
		Jarosite-K	KFe3(SO4)2(OH)6								
		Jarosite-Na	NaFe3(SO4)2(OH)6								
		Jarosite-H	(H3O)Fe3(SO4)2(OH)6								
		Jurbanite	AlOHSO4								
		Maghemite	Fe2O3								
		Magnetite	Fe3O4								
		Manganite	MnOOH								
		Langite	Cu4(OH)6SO4·H2O								
		Nsutite	MnO2								
		Tenorite	CuO								

LN-BP-W				LN-PW2-W				LN-VWD-W			
Conc.1X		Conc.20X		Conc.1X		Conc.20X		Conc.1X		Conc.20X	
CuprousFerrite	CuFeO ₂	Birnessite	MnO ₂	Basaluminite	Al ₄ (OH) ₁₀ Al(OH)3(a)			CuprousFerrite	CuFeO ₂	CuprousFerrite	CuFeO ₂
Fe(OH)2.7Cl.3		CupricFerrite	CuFe2O ₄	Boehmite	AlOOH	Alunite	KAl3(SO ₄)2(OH)6	Fe(OH)2.7Cl.3		Fe(OH)2.7Cl.3	
Goethite	FeOOH	Fe(OH)2.7Cl.3		Cu		Barite	BaSO ₄	Goethite	FeOOH	Goethite	FeOOH
Hematite	Fe2O ₃	Goethite	FeOOH	Cuprite	Cu ₂ O	Basaluminite	Al ₄ (OH) ₁₀ SO ₄	Hematite	Fe2O ₃	Hematite	Fe2O ₃
		Jarosite(ss)		CuprousFerrite	CuFeO ₂	Boehmite	AlOOH	Magnetite	Fe3O ₄	Magnetite	Fe3O ₄
		Maghemite	Fe2O ₃	Diaspore	AlOOH	Birnessite	MnO ₂				
		Nsutite	MnO ₂	Gibbsite	Al(OH) ₃	Bixbyite	Mn2O ₃				
		Pyrolusite	MnO ₂	UO2(a)		CuprousFerrite	CuFeO ₂				
				Uraninite	UO ₂	CupricFerrite	CuFe2O ₄				
						Diaspore	AlOOH				
						Fe(OH)2.7Cl.3					
						Fe(OH)3(a)					
						Gibbsite	Al(OH)3				
						Goethite	FeOOH				
						Hausmannite	Mn3O ₄				
						Hematite	Fe2O ₃				
						Maghemite	Fe2O ₃				
						Magnetite	Fe3O ₄				
						Manganite	MnOOH				
						Nsutite	MnO ₂				
						Pyrolusite	MnO ₂				

LN-SP3-W2				IN-RMATR-W				IN2-W			
Conc.1X		Conc.20X		Conc.1X		Conc.20X		Conc.1X		Conc.20X	
CuprousFerrite	CuFeO ₂	CuprousFerrite	CuFeO ₂	CuprousFerrite	CuFeO ₂	Alunite	KAl3(SO ₄)2(OH)6	CuprousFerrite	CuFeO ₂	Fe(OH)2.7Cl	
Fe(OH)2.7Cl.3		Fe(OH)2.7Cl.3		Hematite	Fe2O ₃	Anhydrite	CaSO ₄	Hematite	Fe2O ₃	Hematite	Fe2O ₃
Goethite	FeOOH	Goethite	FeOOH	Jurbanite	AlOHSO ₄	Barite					
Hematite	Fe2O ₃	Hematite	Fe2O ₃			Birnessite					
		Jarosite(ss)	(K0.77Na0.03H0.2)Fe3(SO ₄)2(OH)6			Celestite	SrSO ₄				
		Maghemite	Fe2O ₃			Cupricferrite					
		Magnetite	Fe3O ₄			Cuprousferrite	CuFeO ₂				
						Diaspore	AlOOH				
						Fe(OH)2.7Cl					
						Goethite					
						Gypsum	CaSO ₄ ·2H ₂ O				
						Hematite	Fe2O ₃				
						Jarosite(ss)	(K0.77Na0.03H0.2)Fe3(SO ₄)2(OH)6				
						Jarosite-K	KFe3(SO ₄)2(OH)6				
						Jarosite-Na	NaFe3(SO ₄)2(OH)6				
						Jurbanite	AlOHSO ₄				
						Maghemite	Fe2O ₃				
						Magnetite	Fe3O ₄				
						Manganite	MnOOH				
						Nsutite	MnO ₂				
						Pyrolusite	MnO ₂				

IN13-W		P-WRD-W		P-PD-W	
Conc.1X	Conc.20X	Conc.1X	Conc.20X	Conc.1X	Conc.20X
Alunite	KAl ₃ (SO ₄) ₂ (OH)·Al(OH) ₃ (a)	Cuprous Ferrite	CuFeO ₂	Cuprous Ferrite	CuFeO ₂
Basaluminite	Al ₄ (OH) ₁₀ SO ₄	Alunite	Fe(OH) ₂ ·7Cl ₂ ·3	Goethite	FeOOH
Boehmite	AlOOH	Ba ₃ (AsO ₄) ₂	Goethite	Hematite	Fe ₂ O ₃
Cupric ferrite	CuFe ₂ O ₄	Boehmite	AlOOH		Magnetite
Cuprous ferrite	CuFeO ₂	Birnessite	MnO ₂		Fe ₃ O ₄
Diaspore	AlOOH	Bixbyite	Mn ₂ O ₃		
Fe(OH) ₂ ·7Cl		Cupric ferrite	CuFe ₂ O ₄		
Gibbsite	Al(OH) ₃	Cupric ferrite	CuFeO ₂		
Goethite	FeOOH	Diaspore	AlOOH		
Magnetite	Fe ₃ O ₄	Fe(OH) ₂ ·7Cl			
		Fe(OH) ₃ (a)			
		Fe ₃ (OH) ₈			
		Gibbsite	Al(OH) ₃		
		Goethite	FeOOH		
		Hematite	Fe ₂ O ₃		
		Jarosite(ss)	(K _{0.77} Na _{0.03} H _{0.2})Fe ₃ (SO ₄) ₂ (OH) ₆		
		Jarosite-K	KFe ₃ (SO ₄) ₂ (OH) ₆		
		Jarosite-Na	NaFe ₃ (SO ₄) ₂ (OH) ₆		
		Jurbanite	AlOHSO ₄		
		Maghemite	Fe ₂ O ₃		
		Magnetite	Fe ₃ O ₄		
		Manganite	MnOOH		
		Nsutite	MnO ₂		
		Pyrolusite	MnO ₂		
P-EC-W					
Conc.1X	Conc.20X				
Alunite	KAl ₃ (SO ₄) ₂ (OH)·Alunite	Alunite	KAl ₃ (SO ₄) ₂ (OH) ₆		
Basaluminite	Al ₄ (OH) ₁₀ SO ₄	Barite	BaSO ₄		
Boehmite	AlOOH	Birnessite	MnO ₂		
Cupric Ferrite	CuFe ₂ O ₄	Bixbyite	Mn ₂ O ₃		
Cuprous Ferrite	CuFeO ₂	Cupric Ferrite	CuFe ₂ O ₄		
Diaspore	AlOOH	Diaspore	AlOOH		
Fe(OH) ₂ ·7Cl ₂ ·3		Fe(OH) ₂ ·7Cl ₂ ·3			
Gibbsite	Al(OH) ₃	Fe(OH) ₃			
Goethite	FeOOH	Gibbsite	Al(OH) ₃		
Hematite	Fe ₂ O ₃	Goethite	FeOOH		
Magnetite	Fe ₃ O ₄	Hematite	Fe ₂ O ₃		
		Jarosite(ss)	(K _{0.77} Na _{0.03} H _{0.2})Fe ₃ (SO ₄) ₂ (OH) ₆		
		Jarosite-K	KFe ₃ (SO ₄) ₂ (OH) ₆		
		Jarosite-Na	NaFe ₃ (SO ₄) ₂ (OH) ₆		
		Maghemite	Fe ₂ O ₃		
		Magnetite	Fe ₃ O ₄		
		Manganite	MnOOH		
		Nsutite	MnO ₂		
		Pyrolusite	MnO ₂		

Appendix D: Comparison of methods ICP-MS & ICP-OES

The two types of analyses conducted for bulk chemical characterization of secondary precipitates and waters were ICP-MS and ICP-OES. Filtered and acidified samples from all mines were combined for the following comparative graphics. Major elements (Al, Ca, Mg, Fe, Na, Cu, S) were plotted as a scatterplot with the concentration of the element as measured by ICP-OES on the Y-axis, and the concentration of the element as measured by ICP-MS on the X-axis. A 1:1 trend-line, as well as R^2 values were added. There is a high degree of correlation between the results from the two methods. Hence, results from both analyses for the major elements can be used without any discrepancy. Due to higher detection limits for ICP-OES, results from ICP-MS were used for interpretation and discussion of major, minor and trace elements.

Digiprep LS Block (72 position) with disposable digitubes was used for these analyses. 6mL of HCl and 2mL of nitric acid were used with approximately 0.5g of sample for digestion. 7mL of water was then added and the samples heated at 90°C for a period of 5 hours reducing the volume to fewer milliliters. The temperature is controlled using an attached controller unit. Samples were then covered with disposable plastic watch-glasses when they were being digested. This prevented contamination from the fume hood, and also helped slow down the loss of acid fumes. Since the controller has a shut off feature, the samples were digested for exactly the same time and temperature on each run. The block was preheated before the samples were added. Samples were then filtered using Whatman No 42 filter papers and the filtrate was diluted by a factor of 10 for analysis on the IC-PMS (Agilent 7700x). There was no dilution necessary for ICP-OES (Varian Vista Pro - Axial) analysis.

Figure 0-1: Plots comparing the concentrations determined by ICP-MS (x-axis) and ICP-OES (y-axis) for major elements Al, Ca, Mg and Fe.

Figure 0-2: Plots comparing the concentrations determined by ICP-MS (x-axis) and ICP-OES (y-axis) for major elements Na, Cu and S.

Appendix E: QAQC & chemistry of secondary precipitates

Sample blanks, standard reference material, as well as experimental replicates were included for the lab QA/QC. Lab blanks show trace amounts of contamination of Cu, Li, K, Na and S as a result of carryover from samples with high concentrations; however, because the concentrations of these elements are extremely high this contamination is considered minor and does not affect the results. Reagent blanks were used as laboratory blanks that are the same acid concentration as for samples. These blanks get digested in the same containers as the samples and are also filtered in the same way as the samples to provide us with the method blanks. The method blank is multiplied by the same nominal dilution factor as the samples for ICP-OES and ICP-MS. These samples may have been contaminated by elements present in the laboratory setting.

Precision was determined by calculating the relative percent difference (RPD) of lab duplicates. QA/QC results for metals and anions confirm that all lab duplicates are within 20% precision with the exceptions of trace elements B, P, Be, Ce, Eu, Ga, Tb, and Y.

All Mine Sites						
	Symbol	Units	Detection limit	Blank	Blank	%Diff Blanks
Aluminium	Al	ug/g	10	23	19	19%
Antimony	Sb	ug/g	1	1	1	0%
Arsenic	As	ug/g	1	1	0.5	0%
Barium	Ba	ug/g	1	1	1.0	0%
Beryllium	Be	ug/g	0	0	0.05	0%
Boron	B	ug/g	20	20	20	0%
Cadmium	Cd	ug/g	0	0	0.05	0%
Calcium	Ca	ug/g	100	100	100	0%
Cerium	Ce	ug/g	0	0	0.05	0%
Cesium	Cs	ug/g	-	-	-	-
Chromium	Cr	ug/g	1	1	1	0%
Cobalt	Co	ug/g	0	0	0.1	0%
Copper	Cu	ug/g	2	2	42.0	182%
Dysprosium	Dy	ug/g	0	0	0.025	0%
Erbium	Er	ug/g	0	0	0.025	0%
Europium	Eu	ug/g	0	0	0.025	0%
Gadolinium	Gd	ug/g	0	0	0.025	0%
Gallium	Ga	ug/g	1	1	0.5	0%
Germanium	Ge	ug/g	5	5	5	0%
Hafnium	Hf	ug/g	-	-	-	-
Holonium	Ho	ug/g	0	0	0.025	0%
Iridium	Ir	ug/g	0	0	0.1	0%
Iron	Fe	ug/g	20	20	20	0%
Lanthanum	La	ug/g	0	0	0.05	0%
Lead	Pb	ug/g	1	1	1	0%
Lithium	Li	ug/g	1	0.62	2.5	121%
Lutetium	Lu	ug/g	0	0	0.025	0%
Magnesium	Mg	ug/g	20	20	20	0%
Manganese	Mn	ug/g	1	1	1.0	0%
Molybdenum	Mo	ug/g	1	1	0.5	0%
Neodymium	Nd	ug/g	0	0	0.025	0%
Nickel	Ni	ug/g	1	1	0.5	0%
Niobium	Nb	ug/g	0	0	0.05	0%
Palladium	Pd	ug/g	-	-	-	-
Phosphorus	P	ug/g	20	20	20	0%
Platinum	Pt	ug/g	0	0	0.05	0%
Potassium	K	ug/g	50	50	89	56%
Praseodymium	Pr	ug/g	0	0	0.025	0%
Rhenium	Re	ug/g	0	0	0.05	0%
Rhodium	Rh	ug/g	0	0	0.05	0%
Rubidium	Rb	ug/g	0	0	0.25	0%
Ruthenium	Ru	ug/g	0	0	0.05	0%
Samarium	Sm	ug/g	0	0	0.0	0%
Selenium	Se	ug/g	0	0	0.25	0%
Silver	Ag	ug/g	0	0	0.1	0%
Sodium	Na	ug/g	75	75	100	29%
Strontium	Sr	ug/g	1	1	1	0%
Sulfur	S	ug/g	25	25	35	33%
Tantalum	Ta	ug/g	0	0	0.025	0%
Terbium	Tb	ug/g	0	0	0.025	0%
Tellurium	Te	ug/g	0	0	0.1	0%
Thalium	Tl	ug/g	0	0	0.025	0%
Thorium	Th	ug/g	-	-	-	-
Thulium	Tm	ug/g	0	0	0.025	0%
Tin	Sn	ug/g	0	0	0.2	0%
Titanium	Ti	ug/g	1	1	1	0%
Tungsten	W	ug/g	0	0	0.1	0%
Uranium	U	ug/g	0	0	0.025	0%
Vanadium	V	ug/g	0	0	0.1	0%
Ytterbium	Yb	ug/g	0	0	0.0	0%
Yttrium	Y	ug/g	0	0	0.3	0%
Zinc	Zn	ug/g	5	5	5.3	6%
Zirconium	Zr	ug/g	1	1	0.5	0%

	Symbol	Units	Sample name	IN13-P2	IN13-P2	%Diff
			Detection limit	Lab Duplicate		
Aluminium	Al	ug/g	10	11000	11000	0%
Antimony	Sb	ug/g	1	7.4	7.2	3%
Arsenic	As	ug/g	1	5.5	5.6	2%
Barium	Ba	ug/g	1	1.0	1	0%
Beryllium	Be	ug/g	0	2.9	3.0	3%
Boron	B	ug/g	20	470	760	47%
Cadmium	Cd	ug/g	0	10	11	10%
Calcium	Ca	ug/g	100	1300	1400	7%
Cerium	Ce	ug/g	0	0.40	0.37	8%
Cesium	Cs	ug/g	-	-	-	-
Chromium	Cr	ug/g	1	1	1	0%
Cobalt	Co	ug/g	0	44	44	0%
Copper	Cu	ug/g	2	4800	5500	14%
Dysprosium	Dy	ug/g	0	0.20	0.20	0%
Erbium	Er	ug/g	0	0.22	0.23	4%
Europium	Eu	ug/g	0	0	0	0%
Gadolinium	Gd	ug/g	0	0.14	0.14	0%
Gallium	Ga	ug/g	1	1	1	0%
Germanium	Ge	ug/g	5	5	5	0%
Hafnium	Hf	ug/g	-	-	-	-
Holonium	Ho	ug/g	0	0.055	0.061	10%
Iridium	Ir	ug/g	0	0	0	0%
Iron	Fe	ug/g	20	220	220	0%
Lanthanum	La	ug/g	0	0.22	0.23	4%
Lead	Pb	ug/g	1	0.62	0.69	11%
Lithium	Li	ug/g	1	1400	1400	0%
Lutetium	Lu	ug/g	0	0.048	0.047	2%
Magnesium	Mg	ug/g	20	39000	40000	3%
Manganese	Mn	ug/g	1	4500	4900	9%
Molybdenum	Mo	ug/g	1	1	1	0%
Neodymium	Nd	ug/g	0	0.22	0.19	15%
Nickel	Ni	ug/g	1	29	30	3%
Niobium	Nb	ug/g	0	0	0	0%
Palladium	Pd	ug/g	-	-	-	-
Phosphorus	P	ug/g	20	130	100	26%
Platinum	Pt	ug/g	0	0	0	0%
Potassium	K	ug/g	50	8400	8900	6%
Praseodymium	Pr	ug/g	0	0.047	0.045	4%
Rhenium	Re	ug/g	0	0.21	0.23	9%
Rhodium	Rh	ug/g	0	0	0	0%
Rubidium	Rb	ug/g	0	54	59	9%
Ruthenium	Ru	ug/g	0	0	0	0%
Samarium	Sm	ug/g	0	0.048	0.044	9%
Selenium	Se	ug/g	0	0.25	0	0%
Silver	Ag	ug/g	0	0	0	0%
Sodium	Na	ug/g	75	130000	140000	7%
Strontium	Sr	ug/g	1	31	30	3%
Sulfur	S	ug/g	25	110000	120000	9%
Tantalum	Ta	ug/g	0	0	0	0%
Terbium	Tb	ug/g	0	0.027	0	8%
Tellurium	Te	ug/g	0	0	0	0%
Thalium	Tl	ug/g	0	0.18	0.20	11%
Thorium	Th	ug/g	-	-	-	-
Thulium	Tm	ug/g	0	0.036	0.034	6%
Tin	Sn	ug/g	0	0	0	0%
Titanium	Ti	ug/g	1	5.1	5.6	9%
Tungsten	W	ug/g	0	0	0	0%
Uranium	U	ug/g	0	4.6	5.0	8%
Vanadium	V	ug/g	0	0.38	0.40	5%
Ytterbium	Yb	ug/g	0	0.27	0.25	8%
Yttrium	Y	ug/g	0	2.5	2.5	0%
Zinc	Zn	ug/g	5	1400	1600	13%
Zirconium	Zr	ug/g	1	1	1	0%

	Symbol	Units	Sample name	P-PW-Pc	P-PW-Pc	%Diff
			Detection limit	Lab Duplicate		
Aluminium	Al	ug/g	10	4400	4400	0%
Antimony	Sb	ug/g	1	2.1	2.1	0%
Arsenic	As	ug/g	1	270	240	12%
Barium	Ba	ug/g	1	27	22	20%
Beryllium	Be	ug/g	0	0.093	0.067	33%
Boron	B	ug/g	20	20	20	0%
Cadmium	Cd	ug/g	0	1.3	1.3	0%
Calcium	Ca	ug/g	100	730	920	23%
Cerium	Ce	ug/g	0	2.6	2.3	12%
Cesium	Cs	ug/g	-	-	-	-
Chromium	Cr	ug/g	1	3.4	3.0	13%
Cobalt	Co	ug/g	0	40	37	8%
Copper	Cu	ug/g	2	1800	1600	12%
Dysprosium	Dy	ug/g	0	0.21	0.20	5%
Erbium	Er	ug/g	0	0.10	0.097	3%
Europium	Eu	ug/g	0	0.071	0.049	37%
Gadolinium	Gd	ug/g	0	0.25	0.21	17%
Gallium	Ga	ug/g	1	5.1	4.1	22%
Germanium	Ge	ug/g	5	5	5	0%
Hafnium	Hf	ug/g	-	-	-	-
Holonium	Ho	ug/g	0	0.040	0.034	16%
Iridium	Ir	ug/g	0	0	0	0%
Iron	Fe	ug/g	20	170000	150000	13%
Lanthanum	La	ug/g	0	1.3	1.1	17%
Lead	Pb	ug/g	1	120	120	0%
Lithium	Li	ug/g	1	2.7	2.1	25%
Lutetium	Lu	ug/g	0	0	0	0%
Magnesium	Mg	ug/g	20	500	480	4%
Manganese	Mn	ug/g	1	220	230	4%
Molybdenum	Mo	ug/g	1	0.53	1	6%
Neodymium	Nd	ug/g	0	1.3	1.2	8%
Nickel	Ni	ug/g	1	22	20	10%
Niobium	Nb	ug/g	0	0.066	0.060	10%
Palladium	Pd	ug/g	-	-	-	-
Phosphorus	P	ug/g	20	150	150	0%
Platinum	Pt	ug/g	0	0	0	0%
Potassium	K	ug/g	50	380	330	14%
Praseodymium	Pr	ug/g	0	0.32	0.28	13%
Rhenium	Re	ug/g	0	0	0	0%
Rhodium	Rh	ug/g	0	0	0	0%
Rubidium	Rb	ug/g	0	1.7	1.5	13%
Ruthenium	Ru	ug/g	0	0	0	0%
Samarium	Sm	ug/g	0	0.26	0.24	8%
Selenium	Se	ug/g	0	1.0	1.1	10%
Silver	Ag	ug/g	0	0.23	0.21	9%
Sodium	Na	ug/g	75	140	130	7%
Strontium	Sr	ug/g	1	6.1	5.3	14%
Sulfur	S	ug/g	25	120000	110000	9%
Tantalum	Ta	ug/g	0	0	0	0%
Terbium	Tb	ug/g	0	0.035	0.028	22%
Tellurium	Te	ug/g	0	1.2	1.2	0%
Thalium	Tl	ug/g	0	1.8	1.7	6%
Thorium	Th	ug/g	-	-	-	-
Thulium	Tm	ug/g	0	0	0	0%
Tin	Sn	ug/g	0	2.9	2.7	7%
Titanium	Ti	ug/g	1	12	13	8%
Tungsten	W	ug/g	0	0.20	0.18	11%
Uranium	U	ug/g	0	1.3	1.2	8%
Vanadium	V	ug/g	0	9.2	8.2	11%
Ytterbium	Yb	ug/g	0	0.091	0.080	13%
Yttrium	Y	ug/g	0	1.1	0.86	24%
Zinc	Zn	ug/g	5	89	94	5%
Zirconium	Zr	ug/g	1	2.3	1.9	19%

	Sample name						
	Symbol	Units	Detection limit	IN13-P1	IN13-P3	IN13-P4	IN13-P5
Aluminium	Al	ug/g	10	10000	5800	6300	8500
Antimony	Sb	ug/g	1	220	6.7	2.5	1.1
Arsenic	As	ug/g	1	11	18	46	30
Barium	Ba	ug/g	1	3.8	4.7	13	6.3
Beryllium	Be	ug/g	0	1.7	1.0	1.4	3.0
Boron	B	ug/g	20	140	690	130	160
Cadmium	Cd	ug/g	0	7.5	7.9	11	9.1
Calcium	Ca	ug/g	100	19000	9800	20000	22000
Cerium	Ce	ug/g	0	2.6	2.3	6.3	5.0
Cesium	Cs	ug/g	-	-	-	-	-
Chromium	Cr	ug/g	1	1	1	1.4	1
Cobalt	Co	ug/g	0	49	50	43	51
Copper	Cu	ug/g	2	3100	3400	3000	4800
Dysprosium	Dy	ug/g	0	0.66	0.41	0.66	1.1
Erbium	Er	ug/g	0	0.43	0.25	0.39	0.63
Europium	Eu	ug/g	0	0.13	0.11	0.19	0.23
Gadolinium	Gd	ug/g	0	0.72	0.43	0.86	1.1
Gallium	Ga	ug/g	1	1	1	1.6	0.63
Germanium	Ge	ug/g	5	5	5	5	5
Hafnium	Hf	ug/g	-	-	-	-	-
Holmium	Ho	ug/g	0	0.15	0.086	0.14	0.22
Iridium	Ir	ug/g	0	0	0	0	0
Iron	Fe	ug/g	20	1500	1600	5900	2600
Lanthanum	La	ug/g	0	1.2	0.97	2.9	2.4
Lead	Pb	ug/g	1	1.0	1.3	3.8	1.7
Lithium	Li	ug/g	1	570	1000	890	1100
Lutetium	Lu	ug/g	0	0.057	0.042	0.048	0.095
Magnesium	Mg	ug/g	20	39000	45000	38000	39000
Manganese	Mn	ug/g	1	4500	8000	4500	5000
Molybdenum	Mo	ug/g	1	1	1	1	1
Neodymium	Nd	ug/g	0	1.7	1.4	3.4	3.2
Nickel	Ni	ug/g	1	32	35	27	37
Niobium	Nb	ug/g	0	0	0	0.18	0.068
Palladium	Pd	ug/g	-	-	-	-	-
Phosphorus	P	ug/g	20	91	110	200	130
Platinum	Pt	ug/g	0	0	0	0	0
Potassium	K	ug/g	50	7800	6800	6600	10000
Praseodymium	Pr	ug/g	0	0.39	0.32	0.83	0.72
Rhenium	Re	ug/g	0	0.13	0.24	0.13	0.24
Rhodium	Rh	ug/g	0	0	0	0	0
Rubidium	Rb	ug/g	0	68	58	49	69
Ruthenium	Ru	ug/g	0	0	0	0	0
Samarium	Sm	ug/g	0	0.47	0.36	0.74	0.78
Selenium	Se	ug/g	0	0	0.52	0	0.56
Silver	Ag	ug/g	0	0	0.32	0.29	0
Sodium	Na	ug/g	75	120000	120000	120000	110000
Strontium	Sr	ug/g	1	130	49	100	140
Sulfur	S	ug/g	25	140000	83000	98000	130000
Tantalum	Ta	ug/g	0	0	0	0	0
Terbium	Tb	ug/g	0	0.12	0.062	0.12	0.17
Tellurium	Te	ug/g	0	0	0	0	0
Thallium	Tl	ug/g	0	0.18	0.63	0.31	0.21
Thorium	Th	ug/g	-	-	-	-	-
Thulium	Tm	ug/g	0	0.060	0.038	0.053	0.091
Tin	Sn	ug/g	0	0.32	0	0	0
Titanium	Ti	ug/g	1	42	45	140	54
Tungsten	W	ug/g	0	0	0	0.13	0
Uranium	U	ug/g	0	2.8	3.5	3.4	4.9
Vanadium	V	ug/g	0	1.9	3.0	9.8	4.7
Ytterbium	Yb	ug/g	0	0.40	0.24	0.31	0.58
Yttrium	Y	ug/g	0	4.9	3.0	4.3	8.0
Zinc	Zn	ug/g	5	1100	2700	1500	1400
Zirconium	Zr	ug/g	1	0.64	1	1.6	0.86

	Sample name							
	Symbol	Units	Detection limit	IN28-P2	IN28-P4	IN2-P1	IN2-P2	IN2-P3
Aluminium	Al	ug/g	10	39000	4300	11000	14000	23000
Antimony	Sb	ug/g	1	5.4	6.8	32	37	18
Arsenic	As	ug/g	1	230	200	1600	950	610
Barium	Ba	ug/g	1	16	36	77	120	33
Beryllium	Be	ug/g	0	2.4	0.099	0.34	0.52	2.1
Boron	B	ug/g	20	25	31	<20	<20	98
Cadmium	Cd	ug/g	0	12	0.080	0.12	0.27	11
Calcium	Ca	ug/g	100	1200	520	2200	3800	39000
Cerium	Ce	ug/g	0	2.7	2.4	11	17	8.8
Cesium	Cs	ug/g	-	-	-	-	-	-
Chromium	Cr	ug/g	1	5.5	1.9	11	16	4.5
Cobalt	Co	ug/g	0	35	0.39	4.7	6.5	51
Copper	Cu	ug/g	2	14000	420	640	740	6900
Dysprosium	Dy	ug/g	0	1.4	0.11	0.68	0.96	1.6
Erbium	Er	ug/g	0	0.82	0.056	0.30	0.41	0.75
Europium	Eu	ug/g	0	0.20	0.043	0.30	0.44	0.41
Gadolinium	Gd	ug/g	0	1.1	0.14	0.95	1.4	1.8
Gallium	Ga	ug/g	1	1.5	0.98	5.4	8.0	3.5
Germanium	Ge	ug/g	5	5	5	<5.0	<5.0	<5.0
Hafnium	Hf	ug/g	-	-	-	-	-	-
Holonium	Ho	ug/g	0	0.28	0	0.11	0.15	0.27
Iridium	Ir	ug/g	0	0	0	<0.1	<0.1	<0.1
Iron	Fe	ug/g	20	30000	270000	320000	300000	100000
Lanthanum	La	ug/g	0	1.0	1.2	5.2	8.1	3.7
Lead	Pb	ug/g	1	8.5	22	30	43	15
Lithium	Li	ug/g	1	190	4.6	11	16	220
Lutetium	Lu	ug/g	0	0.085	0	0.033	0.041	0.073
Magnesium	Mg	ug/g	20	21000	340	3700	5300	23000
Manganese	Mn	ug/g	1	6700	240	440	550	4400
Molybdenum	Mo	ug/g	1	1	1	7.5	9.4	2.2
Neodymium	Nd	ug/g	0	1.8	1.1	5.3	7.9	5.0
Nickel	Ni	ug/g	1	27	0.92	2.9	9.4	38
Niobium	Nb	ug/g	0	0	0.073	0.33	0.57	0.42
Palladium	Pd	ug/g	-	-	-	-	-	-
Phosphorus	P	ug/g	20	400	430	630	560	360
Platinum	Pt	ug/g	0	0	0	<0.05	<0.05	<0.05
Potassium	K	ug/g	50	440	1200	1300	2100	2900
Praseodymium	Pr	ug/g	0	0.36	0.29	1.3	2.0	1.2
Rhenium	Re	ug/g	0	0.057	0	<0.05	<0.05	0.13
Rhodium	Rh	ug/g	0	0	0	<0.05	<0.05	<0.05
Rubidium	Rb	ug/g	0	4.1	7.2	9.5	16	26
Ruthenium	Ru	ug/g	0	0	0	<0.05	<0.05	<0.05
Samarium	Sm	ug/g	0	0.64	0.23	1.0	1.7	1.3
Selenium	Se	ug/g	0	0.59	0.34	2.0	1.7	1.1
Silver	Ag	ug/g	0	0.44	0.43	0.26	0.60	1.5
Sodium	Na	ug/g	75	1400	310	340	730	22000
Strontium	Sr	ug/g	1	9.9	28	46	67	150
Sulfur	S	ug/g	25	140000	22000	32000	31000	120000
Tantalum	Ta	ug/g	0	0	0	<0.025	<0.025	<0.025
Terbium	Tb	ug/g	0	0.20	0	0.14	0.18	0.26
Tellurium	Te	ug/g	0	0.77	0.39	1.7	2.9	3.6
Thalium	Tl	ug/g	0	0.032	0.36	0.10	1.1	0.10
Thorium	Th	ug/g	-	-	-	-	-	-
Thulium	Tm	ug/g	0	0.11	0	0.036	0.052	0.095
Tin	Sn	ug/g	0	0.32	0.27	0.64	1.2	0.46
Titanium	Ti	ug/g	1	17	72	450	590	440
Tungsten	W	ug/g	0	0.34	0.35	2.9	2.8	0.82
Uranium	U	ug/g	0	7.8	0.32	0.59	0.93	6.4
Vanadium	V	ug/g	0	8.2	47	34	48	22
Ytterbium	Yb	ug/g	0	0.67	0.037	0.22	0.31	0.60
Yttrium	Y	ug/g	0	8.4	0.39	2.7	4.3	7.7
Zinc	Zn	ug/g	5	4600	49	52	74	2000
Zirconium	Zr	ug/g	1	1	0.55	2.7	5.8	3.0

	Symbol	Units	Sample name				
			Detection limit	LNPW2-P1	LNPW1-P2	LNPW1-P1	LN-VWD-P2
Aluminium	Al	ug/g	10	15000	250	250	8900
Antimony	Sb	ug/g	1	90	45	66	1.1
Arsenic	As	ug/g	1	490	130	200	15
Barium	Ba	ug/g	1	95	43	2.4	36
Beryllium	Be	ug/g	0	1.8	<0.05	0	3.3
Boron	B	ug/g	20	<20	<20	20	<20
Cadmium	Cd	ug/g	0	3.1	1.4	1.7	6.4
Calcium	Ca	ug/g	100	10000	4000	2400	200000
Cerium	Ce	ug/g	0	42	0.66	0.50	21
Cesium	Cs	ug/g	-	-	-	-	-
Chromium	Cr	ug/g	1	4.9	2.3	2.5	20
Cobalt	Co	ug/g	0	10	110	120	43
Copper	Cu	ug/g	2	150	180000	210000	950
Dysprosium	Dy	ug/g	0	2.2	0.037	0.054	1.4
Erbium	Er	ug/g	0	0.65	<0.025	0.026	0.75
Europium	Eu	ug/g	0	1.0	<0.025	0	0.45
Gadolinium	Gd	ug/g	0	3.4	0.072	0.065	1.8
Gallium	Ga	ug/g	1	6.8	<0.5	1	3.6
Germanium	Ge	ug/g	5	<5.0	<5.0	5	<5.0
Hafnium	Hf	ug/g	-	-	-	-	-
Holonium	Ho	ug/g	0	0.26	<0.025	0	0.26
Iridium	Ir	ug/g	0	<0.1	<0.1	0	<0.1
Iron	Fe	ug/g	20	59000	42000	19000	30000
Lanthanum	La	ug/g	0	19	0.37	0.18	8.1
Lead	Pb	ug/g	1	370	110	4.4	2.9
Lithium	Li	ug/g	1	11	0.63	1.8	1.7
Lutetium	Lu	ug/g	0	0.072	<0.025	0	0.088
Magnesium	Mg	ug/g	20	3500	230	170	8200
Manganese	Mn	ug/g	1	610	75	82	1700
Molybdenum	Mo	ug/g	1	110	2.6	0.70	<0.5
Neodymium	Nd	ug/g	0	20	0.37	0.36	8.0
Nickel	Ni	ug/g	1	6.4	37	39	44
Niobium	Nb	ug/g	0	0.13	<0.05	0	0.57
Palladium	Pd	ug/g	-	-	-	-	-
Phosphorus	P	ug/g	20	340	<20	420	460
Platinum	Pt	ug/g	0	<0.05	<0.05	0	<0.05
Potassium	K	ug/g	50	1600	150	81	470
Praseodymium	Pr	ug/g	0	4.8	0.086	0.078	1.9
Rhenium	Re	ug/g	0	<0.05	<0.05	0	<0.05
Rhodium	Rh	ug/g	0	<0.05	0.099	0.083	<0.05
Rubidium	Rb	ug/g	0	11	0.28	0	2.4
Ruthenium	Ru	ug/g	0	<0.05	<0.05	0	<0.05
Samarium	Sm	ug/g	0	4.0	0.072	0.083	1.7
Selenium	Se	ug/g	0	2.5	35	39	0.63
Silver	Ag	ug/g	0	2.0	2.6	0.49	<0.1
Sodium	Na	ug/g	75	330	170	170	160
Strontium	Sr	ug/g	1	130	4.7	2.4	150
Sulfur	S	ug/g	25	4400	120000	120000	130000
Tantalum	Ta	ug/g	0	<0.025	<0.025	0	<0.025
Terbium	Tb	ug/g	0	0.42	<0.025	0	0.24
Tellurium	Te	ug/g	0	0.84	6.0	15	0.16
Thalium	Tl	ug/g	0	0.99	0.20	0.40	0.13
Thorium	Th	ug/g	-	-	-	-	-
Thulium	Tm	ug/g	0	0.081	<0.025	0	0.092
Tin	Sn	ug/g	0	6.1	2.9	0.52	0.38
Titanium	Ti	ug/g	1	45	3.2	1	280
Tungsten	W	ug/g	0	1.3	<0.1	0	0.15
Uranium	U	ug/g	0	2.0	0.24	0.095	1.5
Vanadium	V	ug/g	0	39	1.2	0.27	12
Ytterbium	Yb	ug/g	0	0.54	<0.025	0	0.63
Yttrium	Y	ug/g	0	8.8	<0.25	0	8.0
Zinc	Zn	ug/g	5	290	100	170	180
Zirconium	Zr	ug/g	1	1.9	<0.5	1	9.9

	Sample name					
	Symbol	Units	Detection limit	LN-VWD-P1	LN-DAR01	LN-SP3-P1
Aluminium	Al	ug/g	10	7900	5200	13000
Antimony	Sb	ug/g	1	1.5	32	5.5
Arsenic	As	ug/g	1	21	460	60
Barium	Ba	ug/g	1	73	98	46
Beryllium	Be	ug/g	0	0.46	0.12	0.19
Boron	B	ug/g	20	<20	<20	<20
Cadmium	Cd	ug/g	0	0.13	0.16	0.094
Calcium	Ca	ug/g	100	420000	2600	180
Cerium	Ce	ug/g	0	10	11	9.8
Cesium	Cs	ug/g	-	-	-	-
Chromium	Cr	ug/g	1	36	4.2	<1.0
Cobalt	Co	ug/g	0	1.9	2.4	0.42
Copper	Cu	ug/g	2	42	48	32
Dysprosium	Dy	ug/g	0	0.76	0.54	0.21
Erbium	Er	ug/g	0	0.41	0.22	0.075
Europium	Eu	ug/g	0	0.20	0.24	0.20
Gadolinium	Gd	ug/g	0	0.82	0.82	0.49
Gallium	Ga	ug/g	1	2.9	5.2	3.6
Germanium	Ge	ug/g	5	<5.0	<5.0	<5.0
Hafnium	Hf	ug/g	-	-	-	-
Holonium	Ho	ug/g	0	0.13	0.085	0.035
Iridium	Ir	ug/g	0	<0.1	<0.1	<0.1
Iron	Fe	ug/g	20	6500	67000	28000
Lanthanum	La	ug/g	0	5.2	5.2	5.2
Lead	Pb	ug/g	1	2.0	30	88
Lithium	Li	ug/g	1	2.6	2.7	2.8
Lutetium	Lu	ug/g	0	0.055	0.026	<0.025
Magnesium	Mg	ug/g	20	14000	1700	1900
Manganese	Mn	ug/g	1	130	180	110
Molybdenum	Mo	ug/g	1	0.69	3.0	5.6
Neodymium	Nd	ug/g	0	4.8	5.4	4.5
Nickel	Ni	ug/g	1	7.1	2.0	<0.5
Niobium	Nb	ug/g	0	0.53	0.35	0.34
Palladium	Pd	ug/g	-	-	-	-
Phosphorus	P	ug/g	20	560	1200	360
Platinum	Pt	ug/g	0	<0.05	<0.05	<0.05
Potassium	K	ug/g	50	760	1400	730
Praseodymium	Pr	ug/g	0	1.2	1.4	1.2
Rhenium	Re	ug/g	0	<0.05	<0.05	<0.05
Rhodium	Rh	ug/g	0	<0.05	<0.05	<0.05
Rubidium	Rb	ug/g	0	3.2	4.2	4.9
Ruthenium	Ru	ug/g	0	<0.05	<0.05	<0.05
Samarium	Sm	ug/g	0	0.92	1.0	0.77
Selenium	Se	ug/g	0	0.66	3.5	3.8
Silver	Ag	ug/g	0	<0.1	0.41	0.14
Sodium	Na	ug/g	75	150	520	120
Strontium	Sr	ug/g	1	150	57	10
Sulfur	S	ug/g	25	18000	9800	750
Tantalum	Ta	ug/g	0	<0.025	<0.025	<0.025
Terbium	Tb	ug/g	0	0.12	0.10	0.056
Tellurium	Te	ug/g	0	<0.1	0.94	0.59
Thalium	Tl	ug/g	0	<0.025	0.038	0.13
Thorium	Th	ug/g	-	-	-	-
Thulium	Tm	ug/g	0	0.063	0.028	<0.025
Tin	Sn	ug/g	0	0.54	2.0	1.3
Titanium	Ti	ug/g	1	440	340	63
Tungsten	W	ug/g	0	0.19	0.14	<0.1
Uranium	U	ug/g	0	1.6	0.27	0.13
Vanadium	V	ug/g	0	15	38	13
Ytterbium	Yb	ug/g	0	0.37	0.18	0.056
Yttrium	Y	ug/g	0	4.3	2.2	0.71
Zinc	Zn	ug/g	5	26	38	24
Zirconium	Zr	ug/g	1	15	1.8	<0.5

	Sample name						
	Symbol	Units	Detection limit	RMATR-P1	RMATR-P2	RMATR-P3	RMATR-P4
Aluminium	Al	ug/g	10	26000	15000	18000	8000
Antimony	Sb	ug/g	1	2.4	14	6.5	1.9
Arsenic	As	ug/g	1	140	520	570	66
Barium	Ba	ug/g	1	33	19	38	22
Beryllium	Be	ug/g	0	3.5	1.3	1.8	0.52
Boron	B	ug/g	20	30	22	51	<20
Cadmium	Cd	ug/g	0	15	6.6	8.2	3.4
Calcium	Ca	ug/g	100	24000	66000	11000	150000
Cerium	Ce	ug/g	0	3.3	9.8	6.3	7.2
Cesium	Cs	ug/g	-	-	-	-	-
Chromium	Cr	ug/g	1	3.0	5.1	12	1.8
Cobalt	Co	ug/g	0	59	36	41	20
Copper	Cu	ug/g	2	15000	7900	8100	3600
Dysprosium	Dy	ug/g	0	1.6	2.8	0.82	3.3
Erbium	Er	ug/g	0	0.95	1.3	0.48	1.5
Europium	Eu	ug/g	0	0.31	0.71	0.23	0.76
Gadolinium	Gd	ug/g	0	1.4	3.2	1.0	3.5
Gallium	Ga	ug/g	1	1.3	2.3	3.0	1.2
Germanium	Ge	ug/g	5	<5.0	<5.0	<5.0	<5.0
Hafnium	Hf	ug/g	-	-	-	-	-
Holonium	Ho	ug/g	0	0.31	0.48	0.16	0.57
Iridium	Ir	ug/g	0	<0.1	<0.1	<0.1	<0.1
Iron	Fe	ug/g	20	16000	57000	75000	12000
Lanthanum	La	ug/g	0	1.2	3.5	2.6	2.3
Lead	Pb	ug/g	1	11	36	30	31
Lithium	Li	ug/g	1	380	120	260	53
Lutetium	Lu	ug/g	0	0.12	0.12	0.057	0.11
Magnesium	Mg	ug/g	20	31000	15000	22000	8900
Manganese	Mn	ug/g	1	6100	2500	3900	960
Molybdenum	Mo	ug/g	1	2.5	3.8	1.6	4.2
Neodymium	Nd	ug/g	0	2.5	7.1	3.4	6.1
Nickel	Ni	ug/g	1	43	24	40	13
Niobium	Nb	ug/g	0	<0.05	0.097	0.51	0.064
Palladium	Pd	ug/g	-	-	-	-	-
Phosphorus	P	ug/g	20	77	290	590	86
Platinum	Pt	ug/g	0	<0.05	<0.05	<0.05	<0.05
Potassium	K	ug/g	50	4400	1400	2600	5400
Praseodymium	Pr	ug/g	0	0.48	1.4	0.80	1.1
Rhenium	Re	ug/g	0	0.21	0.052	0.094	<0.05
Rhodium	Rh	ug/g	0	<0.05	<0.05	<0.05	<0.05
Rubidium	Rb	ug/g	0	45	14	22	55
Ruthenium	Ru	ug/g	0	<0.05	<0.05	<0.05	<0.05
Samarium	Sm	ug/g	0	0.80	2.2	0.77	2.1
Selenium	Se	ug/g	0	2.2	1.2	1.0	1.1
Silver	Ag	ug/g	0	0.14	0.87	0.38	0.13
Sodium	Na	ug/g	75	36000	19000	25000	10000
Strontium	Sr	ug/g	1	140	170	48	670
Sulfur	S	ug/g	25	170000	140000	91000	170000
Tantalum	Ta	ug/g	0	<0.025	<0.025	<0.025	<0.025
Terbium	Tb	ug/g	0	0.25	0.47	0.14	0.55
Tellurium	Te	ug/g	0	0.27	0.86	0.34	0.13
Thalium	Tl	ug/g	0	0.11	0.082	0.068	0.20
Thorium	Th	ug/g	-	-	-	-	-
Thulium	Tm	ug/g	0	0.14	0.16	0.060	0.17
Tin	Sn	ug/g	0	<0.20	0.74	0.53	0.26
Titanium	Ti	ug/g	1	24	58	780	50
Tungsten	W	ug/g	0	0.43	0.57	0.58	0.26
Uranium	U	ug/g	0	9.8	7.6	6.1	1.5
Vanadium	V	ug/g	0	5.9	9.4	40	3.8
Ytterbium	Yb	ug/g	0	0.88	0.98	0.43	1.0
Yttrium	Y	ug/g	0	10	13	4.7	16
Zinc	Zn	ug/g	5	3600	1500	2300	520
Zirconium	Zr	ug/g	1	<0.5	<0.5	<0.5	<0.5

	Symbol	Units	Sample name				
			Detection limit	P-PWL-Pb	P-PWL-Pc	P-WRD	P-EC-P1
Aluminium	Al	ug/g	10	6500	4400	6500	12000
Antimony	Sb	ug/g	1	8.0	2.1	4.7	3.9
Arsenic	As	ug/g	1	350	260	2200	140
Barium	Ba	ug/g	1	25	24	180	260
Beryllium	Be	ug/g	0	0.061	0.080	0.34	0.74
Boron	B	ug/g	20	20	20	<20	<20
Cadmium	Cd	ug/g	0	0.56	1.3	3.0	4.2
Calcium	Ca	ug/g	100	560	820	2000	4600
Cerium	Ce	ug/g	0	2.4	2.4	25	35
Cesium	Cs	ug/g	-	-	-	-	-
Chromium	Cr	ug/g	1	3.1	3.2	4.5	6.0
Cobalt	Co	ug/g	0	24	38	4.2	11
Copper	Cu	ug/g	2	1400	1700	240	160
Dysprosium	Dy	ug/g	0	0.13	0.20	0.81	1.7
Erbium	Er	ug/g	0	0.070	0.098	0.34	0.66
Europium	Eu	ug/g	0	0.044	0.060	0.53	0.79
Gadolinium	Gd	ug/g	0	0.16	0.23	1.5	2.6
Gallium	Ga	ug/g	1	5.6	4.6	7.0	7.8
Germanium	Ge	ug/g	5	5	5	<5.0	<5.0
Hafnium	Hf	ug/g	-	-	-	-	-
Holonium	Ho	ug/g	0	0.025	0.037	0.13	0.24
Iridium	Ir	ug/g	0	0	0	<0.1	<0.1
Iron	Fe	ug/g	20	100000	160000	260000	54000
Lanthanum	La	ug/g	0	1.2	1.2	13	17
Lead	Pb	ug/g	1	290	120	390	290
Lithium	Li	ug/g	1	2.5	2.4	3.5	7.5
Lutetium	Lu	ug/g	0	0	0	0.031	0.062
Magnesium	Mg	ug/g	20	290	490	1200	2700
Manganese	Mn	ug/g	1	100	220	710	1000
Molybdenum	Mo	ug/g	1	0.83	0.50	2.3	1.4
Neodymium	Nd	ug/g	0	1.1	1.2	11	17
Nickel	Ni	ug/g	1	12	21	3.5	6.0
Niobium	Nb	ug/g	0	0.060	0.063	0.16	0.12
Palladium	Pd	ug/g	-	-	-	-	-
Phosphorus	P	ug/g	20	110	150	4000	720
Platinum	Pt	ug/g	0	0	0	<0.05	<0.05
Potassium	K	ug/g	50	450	360	3500	1700
Praseodymium	Pr	ug/g	0	0.27	0.30	2.8	4.0
Rhenium	Re	ug/g	0	0	0	<0.05	<0.05
Rhodium	Rh	ug/g	0	0	0	<0.05	<0.05
Rubidium	Rb	ug/g	0	2.1	1.6	7.6	12
Ruthenium	Ru	ug/g	0	0	0	<0.05	<0.05
Samarium	Sm	ug/g	0	0.18	0.25	2.0	3.2
Selenium	Se	ug/g	0	2.1	1.0	2.9	1.2
Silver	Ag	ug/g	0	0.72	0.22	1.4	1.6
Sodium	Na	ug/g	75	130	140	240	180
Strontium	Sr	ug/g	1	6.3	5.7	53	76
Sulfur	S	ug/g	25	89000	120000	40000	12000
Tantalum	Ta	ug/g	0	0	0	<0.025	<0.025
Terbium	Tb	ug/g	0	0	0.032	0.18	0.32
Tellurium	Te	ug/g	0	2.1	1.2	2.7	1.0
Thalium	Tl	ug/g	0	3.2	1.8	1.4	2.1
Thorium	Th	ug/g	-	-	-	-	-
Thulium	Tm	ug/g	0	0	0	0.035	0.084
Tin	Sn	ug/g	0	17	2.8	1.6	2.2
Titanium	Ti	ug/g	1	9.5	12	33	40
Tungsten	W	ug/g	0	0.29	0.19	0.26	0.15
Uranium	U	ug/g	0	0.97	1.2	0.52	0.73
Vanadium	V	ug/g	0	11	8.7	37	20
Ytterbium	Yb	ug/g	0	0.057	0.086	0.23	0.49
Yttrium	Y	ug/g	0	0.61	0.98	3.5	7.0
Zinc	Zn	ug/g	5	42	92	160	260
Zirconium	Zr	ug/g	1	3.3	2.1	1.5	2.0

Appendix F: QAQC water

Sample blanks, field blanks, standard reference material, as well as experimental and field replicates were included for the lab QA/QC. Lab blanks show no contamination; however, field blanks demonstrate detectable levels of Al and S at Lagunas Norte and Al, Ni, Zn at Pierina. These samples may have been contaminated by the accidental incorporation of dust in the area.

Precision was determined by calculating the relative percent difference (RPD) of field or lab duplicates or triplicates. QA/QC results for metals and anions confirm that all lab duplicates are within 20% precision with the exceptions of Eu, Zr, Ti at Lagunas Norte and Pb, Cd, Fe at El Indio. Field duplicates are within 20% precision except for Ag, As, Cd, Co, Cr, Cu, Dy, Eu, Ga, K, Pb, Sb, Te, Tb, Tm, Zr, Yb at Lagunas Norte, As, Ge, Eu, Mn, Pb, Se, Zr at El Indio, and Eu Zr, Tl, Ti, Yb and Ge at Pierina. Precision may be poor due to the concentrations of these elements being close to the detection limit.

Accuracy, the measure of how close a measured quantity is to its true value, was determined by calculating the RPD of the standard reference material. Both precision and accuracy values for all samples are found in Appendix A. RPD is labelled “%Diff” in Appendix A. To evaluate accuracy of the lab measurements, the RPD of in-house standard reference material (EU-H-4) was calculated. All elements are within 10% accuracy with the exception of U, Sb, Mn, Na, Ca, and Mo, which are below 11% accuracy. Aqueous solutions are electrically neutral, the total number of cations must equal the total number of anions.

Analysis	Analytical Services Unit, Queen's University
QA/QC	Lab Blanks – Verification for contamination during laboratory analysis Experimental/Field Blanks – Verification for contamination during experiments Lab Duplicates – Verification for precision Experimental/Field Duplicates – Verification for precision Certified Reference Materials – Verification for accuracy
Calculations	Relative Standard Difference = $[(A-B)/((A+B)/2)] \times 100$, where A is the original concentration, B is duplicate concentration. Good agreement is $\pm 20\%$.

Certified Reference Material (Samples 1-27)									
	Symbol	Units	Detection limit	Control 1	Control 1 Target	Control 2	Control 2 Target	% Diff C1& C1T	% Diff C2 & C2T
Metals									
Aluminium	Al	µg/L	5	25	25	-	-	0%	-
Antimony	Sb	µg/L	2	-	-	26	25	-	4%
Arsenic	As	µg/L	2	26	25	-	-	4%	-
Barium	Ba	µg/L	0	24	25	-	-	4%	-
Beryllium	Be	µg/L	0	23	25	-	-	8%	-
Boron	B	µg/L	1000	2000	2000	-	-	0%	-
Cadmium	Cd	µg/L	0	24	25	-	-	4%	-
Calcium	Ca	µg/L	300	-	-	-	-	-	-
Cerium	Ce	µg/L	1	23	25	-	-	8%	-
Cesium	Cs	µg/L	-	-	-	-	-	-	-
Chromium	Cr	µg/L	5	24	25	-	-	4%	-
Cobalt	Co	µg/L	0	24	25	-	-	4%	-
Copper	Cu	µg/L	5	24	25	-	-	4%	-
Dysprosium	Dy	µg/L	0	22	25	-	-	13%	-
Erbium	Er	µg/L	0	23	25	-	-	8%	-
Europium	Eu	µg/L	0	23	25	-	-	8%	-
Gadolinium	Gd	µg/L	0	22	25	-	-	13%	-
Gallium	Ga	µg/L	5	26	25	-	-	4%	-
Germanium	Ge	µg/L	1	-	-	25	25	-	0%
Hafnium	Hf	µg/L	-	-	-	-	-	-	-
Holmium	Ho	µg/L	0	24	25	-	-	4%	-
Iridium	Ir	µg/L	1	-	-	-	-	-	-
Iron	Fe	µg/L	50	25	25	-	-	0%	-
Lanthanum	La	µg/L	0	23	25	-	-	8%	-
Lead	Pb	µg/L	0	23	25	-	-	8%	-
Lithium	Li	µg/L	2	-	-	-	-	-	-
Lutetium	Lu	µg/L	0	22	25	-	-	13%	-
Magnesium	Mg	µg/L	30	25	25	-	-	0%	-
Manganese	Mn	µg/L	0	24	25	-	-	4%	-
Molybdenum	Mo	µg/L	10	-	-	24	25	-	4%
Neodymium	Nd	µg/L	0	22	25	-	-	13%	-
Nickel	Ni	µg/L	1	24	25	-	-	4%	-
Niobium	Nb	µg/L	0	-	-	25	25	-	0%
Palladium	Pd	µg/L	-	-	-	-	-	-	-
Phosphorus	P	µg/L	1000	32000	30000	-	-	6%	-
Platinum	Pt	µg/L	0	-	-	-	-	-	-
Potassium	K	µg/L	200	28	25	-	-	11%	-
Praseodymium	Pr	µg/L	0	23	25	-	-	8%	-
Rhenium	Re	µg/L	0	-	-	-	-	-	-
Rhodium	Rh	µg/L	0	-	-	-	-	-	-
Rubidium	Rb	µg/L	1	23	25	-	-	8%	-
Ruthenium	Ru	µg/L	0	-	-	-	-	-	-
Samarium	Sm	µg/L	0	22	25	-	-	13%	-
Selenium	Se	µg/L	1	24	25	-	-	4%	-
Silver	Ag	µg/L	0	24	25	-	-	4%	-
Sodium	Na	µg/L	200	-	-	-	-	-	-
Strontium	Sr	µg/L	1	25	25	-	-	0%	-
Sulfur	S	µg/L	1000	31000	30000	-	-	3%	-
Tantalum	Ta	µg/L	0	-	-	25	25	-	0%
Terbium	Tb	µg/L	0	-	-	-	-	-	-
Tellurium	Te	µg/L	1	-	-	23	25	-	8%
Thallium	Tl	µg/L	0	24	25	-	-	4%	-
Thorium	Th	µg/L	-	-	-	-	-	-	-
Thulium	Tm	µg/L	0	24	25	-	-	4%	-
Tin **	Sn	µg/L	3	-	-	24	25	-	4%
Titanium	Ti	µg/L	3	-	-	26	25	-	4%
Tungsten	W	µg/L	1	-	-	23	25	-	8%
Uranium	U	µg/L	0	25	25	-	-	0%	-
Vanadium	V	µg/L	0	24	25	-	-	4%	-
Ytterbium	Yb	µg/L	0	23	25	-	-	8%	-
Yttrium	Y	µg/L	1	-	-	-	-	-	-
Zinc	Zn	µg/L	10	24	25	-	-	4%	-
Zirconium	Zr	µg/L	0	-	-	24	25	-	4%

				Certified Reference Material (Samples 1-27)		
	Symbol	Units	Detection limit	EU-H-4	EU-H-4 Target	%Diff EU-H-4 & target
Metals						
Aluminium	Al	µg/L	5	390	420	5%
Antimony	Sb	µg/L	2	540	520	4%
Arsenic	As	µg/L	2	810	780	1%
Barium	Ba	µg/L	0	1000	1100	10%
Beryllium	Be	µg/L	0	420	460	9%
Boron	B	µg/L	1000	700	710	4%
Cadmium	Cd	µg/L	0	250	270	8%
Calcium	Ca	µg/L	300	45000	41000	11%
Cerium	Ce	µg/L	1	-	-	-
Cesium	Cs	µg/L	-	-	-	-
Chromium	Cr	µg/L	5	400	400	3%
Cobalt	Co	µg/L	0	500	500	4%
Copper	Cu	µg/L	5	760	740	1%
Dysprosium	Dy	µg/L	0	-	-	-
Erbium	Er	µg/L	0	-	-	-
Europium	Eu	µg/L	0	-	-	-
Gadolinium	Gd	µg/L	0	-	-	-
Gallium	Ga	µg/L	5	-	-	-
Germanium	Ge	µg/L	1	-	-	-
Hafnium	Hf	µg/L	-	-	-	-
Holonium	Ho	µg/L	0	-	-	-
Iridium	Ir	µg/L	1	-	-	-
Iron	Fe	µg/L	50	580	580	2%
Lanthanum	La	µg/L	0	-	-	-
Lead	Pb	µg/L	0	580	610	5%
Lithium	Li	µg/L	2	-	-	-
Lutetium	Lu	µg/L	0	-	-	-
Magnesium	Mg	µg/L	30	24000	25000	0%
Manganese	Mn	µg/L	0	460	450	2%
Molybdenum	Mo	µg/L	10	700	720	13%
Neodymium	Nd	µg/L	0	-	-	-
Nickel	Ni	µg/L	1	730	740	4%
Niobium	Nb	µg/L	0	-	-	-
Palladium	Pd	µg/L	-	-	-	-
Phosphorus	P	µg/L	1000	11000	11000	0%
Platinum	Pt	µg/L	0	-	-	-
Potassium	K	µg/L	200	42000	45000	7%
Praseodymium	Pr	µg/L	0	-	-	-
Rhenium	Re	µg/L	0	-	-	-
Rhodium	Rh	µg/L	0	-	-	-
Rubidium	Rb	µg/L	1	-	-	-
Ruthenium	Ru	µg/L	0	-	-	-
Samarium	Sm	µg/L	0	-	-	-
Selenium	Se	µg/L	1	130	140	7%
Silver	Ag	µg/L	0	-	-	-
Sodium	Na	µg/L	200	46000	46000	0%
Strontium	Sr	µg/L	1	940	910	2%
Sulfur	S	µg/L	1000	-	-	-
Tantalum	Ta	µg/L	0	-	-	-
Terbium	Tb	µg/L	0	-	-	-
Tellurium	Te	µg/L	1	-	-	-
Thalium	Tl	µg/L	0	370	390	3%
Thorium	Th	µg/L	-	-	-	-
Thulium	Tm	µg/L	0	-	-	-
Tin **	Sn	µg/L	3	-	-	-
Titanium	Ti	µg/L	3	-	-	-
Tungsten	W	µg/L	1	-	-	-
Uranium	U	µg/L	0	90	99	12%
Vanadium	V	µg/L	0	810	820	5%
Ytterbium	Yb	µg/L	0	-	-	-
Yttrium	Y	µg/L	1	-	-	-
Zinc	Zn	µg/L	10	880	870	2%
Zirconium	Zr	µg/L	0	-	-	-

Certified Reference Material (Samples 28-59)									
	Symbol	Units	Detection limit	Control 1	Control 1 Target	Control 2	Control 2 Target	%Diff C1-C1T	%Diff C2-C2t
Metals									
Aluminium	Al	µg/L	5	25	25	-	-	0%	-
Antimony	Sb	µg/L	2	-	-	25	25	-	0%
Arsenic	As	µg/L	2	28	25	-	-	11%	-
Barium	Ba	µg/L	0	24	25	-	-	4%	-
Beryllium	Be	µg/L	0	24	25	-	-	4%	-
Boron	B	µg/L	1000	2100	2000	-	-	5%	-
Cadmium	Cd	µg/L	0	24	25	-	-	4%	-
Calcium	Ca	µg/L	300	-	-	-	-	-	-
Cerium	Ce	µg/L	1	24	25	-	-	4%	-
Cesium	Cs	µg/L	-	-	-	-	-	-	-
Chromium	Cr	µg/L	5	25	25	-	-	0%	-
Cobalt	Co	µg/L	0	25	25	-	-	0%	-
Copper	Cu	µg/L	5	26	25	-	-	4%	-
Dysprosium	Dy	µg/L	0	23	25	-	-	8%	-
Erbium	Er	µg/L	0	24	25	-	-	4%	-
Europium	Eu	µg/L	0	26	25	-	-	4%	-
Gadolinium	Gd	µg/L	0	23	25	-	-	8%	-
Gallium	Ga	µg/L	5	29	25	-	-	15%	-
Germanium	Ge	µg/L	1	-	-	24	25	-	4%
Hafnium	Hf	µg/L	-	-	-	-	-	-	-
Holonium	Ho	µg/L	0	24	25	-	-	4%	-
Iridium	Ir	µg/L	1	-	-	-	-	-	-
Iron	Fe	µg/L	50	26	25	-	-	4%	-
Lanthanum	La	µg/L	0	24	25	-	-	4%	-
Lead	Pb	µg/L	0	24	25	-	-	4%	-
Lithium	Li	µg/L	2	-	-	-	-	-	-
Lutetium	Lu	µg/L	0	22	25	-	-	13%	-
Magnesium	Mg	µg/L	30	25	25	-	-	0%	-
Manganese	Mn	µg/L	0	25	25	-	-	0%	-
Molybdenum	Mo	µg/L	10	-	-	26	25	-	4%
Neodymium	Nd	µg/L	0	23	25	-	-	8%	-
Nickel	Ni	µg/L	1	25	25	-	-	0%	-
Niobium	Nb	µg/L	0	-	-	26	25	-	4%
Palladium	Pd	µg/L	-	-	-	-	-	-	-
Phosphorus	P	µg/L	1000	32000	30000	-	-	6%	-
Platinum	Pt	µg/L	0	-	-	-	-	-	-
Potassium	K	µg/L	200	-	25	-	-	-	-
Praseodymium	Pr	µg/L	0	24	25	-	-	4%	-
Rhenium	Re	µg/L	0	-	-	-	-	-	-
Rhodium	Rh	µg/L	0	-	-	-	-	-	-
Rubidium	Rb	µg/L	1	25	25	-	-	0%	-
Ruthenium	Ru	µg/L	0	-	-	-	-	-	-
Samarium	Sm	µg/L	0	23	25	-	-	8%	-
Selenium	Se	µg/L	1	25	25	-	-	0%	-
Silver	Ag	µg/L	0	26	25	-	-	4%	-
Sodium	Na	µg/L	200	-	-	-	-	-	-
Strontium	Sr	µg/L	1	27	25	-	-	8%	-
Sulfur	S	µg/L	1000	31000	30000	-	-	3%	-
Tantalum	Ta	µg/L	0	-	-	25	25	-	0%
Terbium	Tb	µg/L	0	-	-	-	-	-	-
Tellurium	Te	µg/L	1	-	-	22	25	-	13%
Thallium	Tl	µg/L	0	24	25	-	-	4%	-
Thorium	Th	µg/L	-	-	-	-	-	-	-
Thulium	Tm	µg/L	0	24	25	-	-	4%	-
Tin **	Sn	µg/L	3	-	-	24	25	-	4%
Titanium	Ti	µg/L	3	-	-	25	25	-	0%
Tungsten	W	µg/L	1	-	-	25	25	-	0%
Uranium	U	µg/L	0	25	25	-	-	0%	-
Vanadium	V	µg/L	0	26	25	-	-	4%	-
Ytterbium	Yb	µg/L	0	24	25	-	-	4%	-
Yttrium	Y	µg/L	1	-	-	-	-	-	-
Zinc	Zn	µg/L	10	25	25	-	-	0%	-
Zirconium	Zr	µg/L	0	-	-	25	25	-	0%

	Symbol	Units	Detection limit	Certified Reference Material (Samples 28-59)		
				EU-H-4	EU-H-4 Target	%Diff EU-H-4 & target
Metals				390	420	7%
Aluminium	Al	µg/L	5	540	520	4%
Antimony	Sb	µg/L	2	810	780	4%
Arsenic	As	µg/L	2	1000	1100	10%
Barium	Ba	µg/L	0	420	460	9%
Beryllium	Be	µg/L	0	700	710	1%
Boron	B	µg/L	1000	250	270	8%
Cadmium	Cd	µg/L	0	45000	41000	9%
Calcium	Ca	µg/L	300	-	-	-
Cerium	Ce	µg/L	1	-	-	-
Cesium	Cs	µg/L	-	400	400	0%
Chromium	Cr	µg/L	5	500	500	0%
Cobalt	Co	µg/L	0	760	740	3%
Copper	Cu	µg/L	5	-	-	-
Dysprosium	Dy	µg/L	0	-	-	-
Erbium	Er	µg/L	0	-	-	-
Europium	Eu	µg/L	0	-	-	-
Gadolinium	Gd	µg/L	0	-	-	-
Gallium	Ga	µg/L	5	-	-	-
Germanium	Ge	µg/L	1	-	-	-
Hafnium	Hf	µg/L	-	-	-	-
Holonium	Ho	µg/L	0	-	-	-
Iridium	Ir	µg/L	1	580	580	0%
Iron	Fe	µg/L	50	-	-	-
Lanthanum	La	µg/L	0	580	610	5%
Lead	Pb	µg/L	0	-	-	-
Lithium	Li	µg/L	2	-	-	-
Lutetium	Lu	µg/L	0	24000	25000	4%
Magnesium	Mg	µg/L	30	460	450	2%
Manganese	Mn	µg/L	0	700	720	3%
Molybdenum	Mo	µg/L	10	-	-	-
Neodymium	Nd	µg/L	0	730	740	1%
Nickel	Ni	µg/L	1	-	-	-
Niobium	Nb	µg/L	0	-	-	-
Palladium	Pd	µg/L	-	11000	11000	0%
Phosphorus	P	µg/L	1000	-	-	-
Platinum	Pt	µg/L	0	42000	45000	7%
Potassium	K	µg/L	200	-	-	-
Praseodymium	Pr	µg/L	0	-	-	-
Rhenium	Re	µg/L	0	-	-	-
Rhodium	Rh	µg/L	0	-	-	-
Rubidium	Rb	µg/L	1	-	-	-
Ruthenium	Ru	µg/L	0	-	-	-
Samarium	Sm	µg/L	0	130	140	7%
Selenium	Se	µg/L	1	-	-	-
Silver	Ag	µg/L	0	46000	46000	0%
Sodium	Na	µg/L	200	940	910	3%
Strontium	Sr	µg/L	1	-	-	-
Sulfur	S	µg/L	1000	-	-	-
Tantalum	Ta	µg/L	0	-	-	-
Terbium	Tb	µg/L	0	-	-	-
Tellurium	Te	µg/L	1	370	390	5%
Thalium	Tl	µg/L	0	-	-	-
Thorium	Th	µg/L	-	-	-	-
Thulium	Tm	µg/L	0	-	-	-
Tin **	Sn	µg/L	3	-	-	-
Titanium	Ti	µg/L	3	-	-	-
Tungsten	W	µg/L	1	90	99	10%
Uranium	U	µg/L	0	810	820	1%
Vanadium	V	µg/L	0	-	-	-
Ytterbium	Yb	µg/L	0	-	-	-
Yttrium	Y	µg/L	1	880	870	1%
Zinc	Zn	µg/L	10	-	-	-
Zirconium	Zr	µg/L	0	-	-	-

Certified Reference Material (Samples 60-84)									
	Symbol	Units	Detection limit	Control 1	Control 1 Target	Control 2	Control 2 Target	%Diff C1-C1T	%Diff C2-C2t
Metals									
Aluminium	Al	µg/L	5	26	25	-	-	4%	-
Antimony	Sb	µg/L	2	-	-	24	25	-	4%
Arsenic	As	µg/L	2	25	25	-	-	0%	-
Barium	Ba	µg/L	0	24	25	-	-	4%	-
Beryllium	Be	µg/L	0	23	25	-	-	8%	-
Boron	B	µg/L	1000	1900	2000	-	-	5%	-
Cadmium	Cd	µg/L	0	23	25	-	-	8%	-
Calcium	Ca	µg/L	300	-	-	-	-	-	-
Cerium	Ce	µg/L	1	23	25	-	-	8%	-
Cesium	Cs	µg/L	-	-	-	-	-	-	-
Chromium	Cr	µg/L	5	23	25	-	-	8%	-
Cobalt	Co	µg/L	0	23	25	-	-	8%	-
Copper	Cu	µg/L	5	24	25	-	-	4%	-
Dysprosium	Dy	µg/L	0	22	25	-	-	13%	-
Erbium	Er	µg/L	0	22	25	-	-	13%	-
Europium	Eu	µg/L	0	23	25	-	-	8%	-
Gadolinium	Gd	µg/L	0	22	25	-	-	13%	-
Gallium	Ga	µg/L	5	25	25	-	-	0%	-
Germanium	Ge	µg/L	1	-	-	24	25	-	4%
Hafnium	Hf	µg/L	-	-	-	-	-	-	-
Holonium	Ho	µg/L	0	23	25	-	-	8%	-
Iridium	Ir	µg/L	1	-	-	-	-	-	-
Iron	Fe	µg/L	50	26	25	-	-	4%	-
Lanthanum	La	µg/L	0	23	25	-	-	8%	-
Lead	Pb	µg/L	0	23	25	-	-	8%	-
Lithium	Li	µg/L	2	-	-	-	-	-	-
Lutetium	Lu	µg/L	0	21	25	-	-	17%	-
Magnesium	Mg	µg/L	30	26	25	-	-	4%	-
Manganese	Mn	µg/L	0	24	25	-	-	4%	-
Molybdenum	Mo	µg/L	10	-	-	24	25	-	4%
Neodymium	Nd	µg/L	0	22	25	-	-	13%	-
Nickel	Ni	µg/L	1	23	25	-	-	8%	-
Niobium	Nb	µg/L	0	-	-	24	25	-	4%
Palladium	Pd	µg/L	-	-	-	-	-	-	-
Phosphorus	P	µg/L	1000	30000	30000	-	-	0%	-
Platinum	Pt	µg/L	0	-	-	-	-	-	-
Potassium	K	µg/L	200	24	25	-	-	4%	-
Praseodymium	Pr	µg/L	0	23	25	-	-	8%	-
Rhenium	Re	µg/L	0	-	-	-	-	-	-
Rhodium	Rh	µg/L	0	-	-	-	-	-	-
Rubidium	Rb	µg/L	1	24	25	-	-	4%	-
Ruthenium	Ru	µg/L	0	-	-	-	-	-	-
Samarium	Sm	µg/L	0	22	25	-	-	13%	-
Selenium	Se	µg/L	1	23	25	-	-	8%	-
Silver	Ag	µg/L	0	23	25	-	-	8%	-
Sodium	Na	µg/L	200	-	-	-	-	-	-
Strontium	Sr	µg/L	1	25	25	-	-	0%	-
Sulfur	S	µg/L	1000	29000	30000	-	-	3%	-
Tantalum	Ta	µg/L	0	-	-	24	25	-	4%
Terbium	Tb	µg/L	0	-	-	-	-	-	-
Tellurium	Te	µg/L	1	-	-	23	25	-	8%
Thallium	Tl	µg/L	0	23	25	-	-	8%	-
Thorium	Th	µg/L	-	-	-	-	-	-	-
Thulium	Tm	µg/L	0	23	25	-	-	8%	-
Tin **	Sn	µg/L	3	-	-	25	25	-	0%
Titanium	Ti	µg/L	3	-	-	26	25	-	4%
Tungsten	W	µg/L	1	-	-	23	25	-	8%
Uranium	U	µg/L	0	24	25	-	-	4%	-
Vanadium	V	µg/L	0	24	25	-	-	4%	-
Ytterbium	Yb	µg/L	0	22	25	-	-	13%	-
Yttrium	Y	µg/L	1	-	-	-	-	-	-
Zinc	Zn	µg/L	10	24	25	-	-	4%	-
Zirconium	Zr	µg/L	0	-	-	23	25	-	8%

	Symbol	Units	Detection limit	Certified Reference Material (Samples 60-84)		
				EU-H-4	EU-H-4 Target	%Diff EU-H-4 & target
Metals						
Aluminium	Al	µg/L	5	420	420	0%
Antimony	Sb	µg/L	2	590	520	13%
Arsenic	As	µg/L	2	850	780	9%
Barium	Ba	µg/L	0	1000	1100	10%
Beryllium	Be	µg/L	0	470	460	2%
Boron	B	µg/L	1000	720	710	1%
Cadmium	Cd	µg/L	0	270	270	0%
Calcium	Ca	µg/L	300	50000	41000	20%
Cerium	Ce	µg/L	1	-	-	-
Cesium	Cs	µg/L	-	-	-	-
Chromium	Cr	µg/L	5	410	400	2%
Cobalt	Co	µg/L	0	510	500	2%
Copper	Cu	µg/L	5	760	740	3%
Dysprosium	Dy	µg/L	0	-	-	-
Erbium	Er	µg/L	0	-	-	-
Europium	Eu	µg/L	0	-	-	-
Gadolinium	Gd	µg/L	0	-	-	-
Gallium	Ga	µg/L	5	-	-	-
Germanium	Ge	µg/L	1	-	-	-
Hafnium	Hf	µg/L	-	-	-	-
Holonium	Ho	µg/L	0	-	-	-
Iridium	Ir	µg/L	1	-	-	-
Iron	Fe	µg/L	50	650	580	11%
Lanthanum	La	µg/L	0	-	-	-
Lead	Pb	µg/L	0	650	610	6%
Lithium	Li	µg/L	2	-	-	-
Lutetium	Lu	µg/L	0	-	-	-
Magnesium	Mg	µg/L	30	28000	25000	11%
Manganese	Mn	µg/L	0	480	450	6%
Molybdenum	Mo	µg/L	10	720	720	0%
Neodymium	Nd	µg/L	0	-	-	-
Nickel	Ni	µg/L	1	750	740	1%
Niobium	Nb	µg/L	0	-	-	-
Palladium	Pd	µg/L	-	-	-	-
Phosphorus	P	µg/L	1000	11000	11000	0%
Platinum	Pt	µg/L	0	-	-	-
Potassium	K	µg/L	200	47000	45000	4%
Praseodymium	Pr	µg/L	0	-	-	-
Rhenium	Re	µg/L	0	-	-	-
Rhodium	Rh	µg/L	0	-	-	-
Rubidium	Rb	µg/L	1	-	-	-
Ruthenium	Ru	µg/L	0	-	-	-
Samarium	Sm	µg/L	0	-	-	-
Selenium	Se	µg/L	1	140	140	0%
Silver	Ag	µg/L	0	-	-	-
Sodium	Na	µg/L	200	51000	46000	10%
Strontium	Sr	µg/L	1	980	910	7%
Sulfur	S	µg/L	1000	-	-	-
Tantalum	Ta	µg/L	0	-	-	-
Terbium	Tb	µg/L	0	-	-	-
Tellurium	Te	µg/L	1	-	-	-
Thalium	Tl	µg/L	0	410	390	5%
Thorium	Th	µg/L	-	-	-	-
Thulium	Tm	µg/L	0	-	-	-
Tin **	Sn	µg/L	3	-	-	-
Titanium	Ti	µg/L	3	-	-	-
Tungsten	W	µg/L	1	-	-	-
Uranium	U	µg/L	0	110	99	11%
Vanadium	V	µg/L	0	840	820	2%
Ytterbium	Yb	µg/L	0	-	-	-
Yttrium	Y	µg/L	1	-	-	-
Zinc	Zn	µg/L	10	900	870	3%
Zirconium	Zr	µg/L	0	-	-	-

	Symbol	Units	Mine site	Lagunas Norte		El Indio		Pierina	
			Detection limit	Blank	Blank	Blank	Blank	Blank	Blank
Aluminium	Al	µg/L	5	5	5	5	5	5	5
Antimony	Sb	µg/L	2	2	2	2	2	2	2
Arsenic	As	µg/L	2	2	2	2	2	2	2
Barium	Ba	µg/L	0	0.2	0.2	0.2	0.2	0	0
Beryllium	Be	µg/L	0	0.2	0.2	0.2	0.2	0	0
Boron	B	µg/L	1000	1000	1000	1000	1000	1000	1000
Cadmium	Cd	µg/L	0	0.03	0.03	0.03	0.03	0	0
Calcium	Ca	µg/L	300	300	300	300	300	300	300
Cerium	Ce	µg/L	1	0.5	0.5	0.5	0.5	1	1
Cesium	Cs	µg/L	-	-	-	-	-	-	-
Chromium	Cr	µg/L	5	5	5	5	5	5	5
Cobalt	Co	µg/L	0	0.05	0.05	0.05	0.05	0	0
Copper	Cu	µg/L	5	5.0	5.0	5.0	5.0	5	5
Dysprosium	Dy	µg/L	0	0.1	0.1	0.1	0.1	0	0
Erbium	Er	µg/L	0	0.1	0.1	0.1	0.1	0	0
Europium	Eu	µg/L	0	0.03	0.03	0.03	0.03	0	0
Gadolinium	Gd	µg/L	0	0.1	0.1	0.1	0.1	0	0
Gallium	Ga	µg/L	5	5	5	5	5	5	5
Germanium	Ge	µg/L	1	1	1	1	1	1	1
Hafnium	Hf	µg/L	-	-	-	-	-	-	-
Holmium	Ho	µg/L	0	0.05	0.05	0.05	0.05	0	0
Iridium	Ir	µg/L	1	0.5	0.5	0.5	0.5	1	1
Iron	Fe	µg/L	50	50	50	50	50	50	50
Lanthanum	La	µg/L	0	0.4	0.4	0.4	0.4	0	0
Lead	Pb	µg/L	0	0	0	0	0	0	0
Lithium	Li	µg/L	2	2	2	2	2	2	2
Lutetium	Lu	µg/L	0	0.05	0.05	0.05	0.05	0	0
Magnesium	Mg	µg/L	30	30.000	30.000	30.000	30.000	30	30
Manganese	Mn	µg/L	0	0.3	0.3	0.3	0.3	0	0.90
Molybdenum	Mo	µg/L	10	10.0	10.0	10.0	10.0	10	10
Neodymium	Nd	µg/L	0	0.1	0.1	0.1	0.1	0	0
Nickel	Ni	µg/L	1	1	1	1	1	1	1
Niobium	Nb	µg/L	0	0.05	0.05	0.05	0.05	0	0
Palladium	Pd	µg/L	-	-	-	-	-	-	-
Phosphorus	P	µg/L	1000	1000	1000	1000	1000	1000	1000
Platinum	Pt	µg/L	0	0.05	0.05	0.05	0.05	0	0
Potassium	K	µg/L	200	200	200	200	200	200	200
Praseodymium	Pr	µg/L	0	0.1	0.1	0.1	0.1	0	0
Rhenium	Re	µg/L	0	0.2	0.2	0.2	0.2	0	0
Rhodium	Rh	µg/L	0	0.1	0.1	0.1	0.1	0	0
Rubidium	Rb	µg/L	1	1	1	1	1	1	1
Ruthenium	Ru	µg/L	0	0.1	0.1	0.1	0.1	0	0
Samarium	Sm	µg/L	0	0.1	0.1	0.1	0.1	0	0
Selenium	Se	µg/L	1	1	1	1	1	1	1
Silver	Ag	µg/L	0	0.1	0.1	0.1	0.1	0	0
Sodium	Na	µg/L	200	200	200	200	200	200	200
Strontium	Sr	µg/L	1	1	1	1	1	1	1
Sulfur	S	µg/L	1000	1000	1000	1000	1000	1000	1000
Tantalum	Ta	µg/L	0	0.05	0.05	0.05	0.05	0	0
Terbium	Tb	µg/L	0	0.050	0.050	0.050	0.050	0	0
Tellurium	Te	µg/L	1	0.5	0.5	0.5	0.5	1	1
Thalium	Tl	µg/L	0	0.1	0.1	0.1	0.1	0	0
Thorium	Th	µg/L	-	-	-	-	-	-	-
Thulium	Tm	µg/L	0	0.05	0.05	0.05	0.05	0	0
Tin **	Sn	µg/L	3	3.0	3.0	3	3	3	3
Titanium	Ti	µg/L	3	3	3	3	3	3	3
Tungsten	W	µg/L	1	0.5	0.5	0.5	0.5	1	1
Uranium	U	µg/L	0	0.02	0.02	0.02	0.02	0	0
Vanadium	V	µg/L	0	0.3	0.3	0.3	0.3	0	0
Ytterbium	Yb	µg/L	0	0.2	0.2	0.2	0.2	0	0
Yttrium	Y	µg/L	1	1.0	1.0	1.0	1.0	1	1
Zinc	Zn	µg/L	10	10.0	10.0	10.0	10.0	10	10
Zirconium	Zr	µg/L	0	0.1	0.1	0.1	0.1	0	0

			Sample name	SP3-W	SP3-W	SP3-W			
			Sample type	FA	FA	FA	%Diff 5-1	% Diff 5-6	% Diff 6-1
			Sample number	No1	No5	No6			
	Symbol	Units	Detection limit	Field Triplicate					
Sample description									
Anions									
Fluoride	F	mg/L	<0.05	<2.0	<2.0	<2.0	-	-	-
Chloride	Cl	mg/L	<0.05	<2.0	<2.0	<2.0	-	-	-
Nitrite	NO ₂ -	mg/L	<0.05	<2.0	<2.0	<2.0	-	-	-
Nitrate	NO ₃ -	mg/L	<0.05	3.8	3.8	3.8	-	-	-
Sulphate	SO ₄ 2-	mg/L	<0.10	690.0	690.0	690.0	-	-	-
pH		-		2.9	2.9	2.9	-	-	-
Metals									
Aluminium	Al	µg/L	5	47000	48000	47000	2%	2%	0%
Antimony	Sb	µg/L	2	2	2	2	0%	0%	0%
Arsenic	As	µg/L	2	9.1	11	10	19%	10%	9%
Barium	Ba	µg/L	0	54	52	52	4%	0%	4%
Beryllium	Be	µg/L	0	7.3	7.3	7.3	0%	0%	0%
Boron	B	µg/L	1000	1000	1000	1000	0%	0%	0%
Cadmium	Cd	µg/L	0	34	33	33	3%	0%	3%
Calcium	Ca	µg/L	300	120000	120000	120000	0%	0%	0%
Cerium	Ce	µg/L	1	62	61	61	2%	0%	2%
Cesium	Cs	µg/L	-	-	-	-	-	-	-
Chromium	Cr	µg/L	5	13	17	13	27%	27%	0%
Cobalt	Co	µg/L	0	150	150	150	0%	0%	0%
Copper	Cu	µg/L	5	9600	9700	9500	1%	2%	1%
Dysprosium	Dy	µg/L	0	7.6	7.4	7.4	3%	0%	3%
Erbium	Er	µg/L	0	3.7	3.6	3.6	3%	0%	3%
Europium	Eu	µg/L	0	2.9	2.5	2.5	15%	0%	15%
Gadolinium	Gd	µg/L	0	9.6	9.7	9.5	1%	2%	1%
Gallium	Ga	µg/L	5	8.5	7.7	8.4	10%	9%	1%
Germanium	Ge	µg/L	1	3.3	3.0	3.1	10%	3%	6%
Hafnium	Hf	µg/L	-	-	-	-	-	-	-
Holonium	Ho	µg/L	0	1.4	1.4	1.4	0%	0%	0%
Iridium	Ir	µg/L	1	1	1	1	0%	0%	0%
Iron	Fe	µg/L	50	49000	48000	48000	2%	0%	2%
Lanthanum	La	µg/L	0	29	28	29	4%	4%	0%
Lead	Pb	µg/L	0	30	30	30	0%	0%	0%
Lithium	Li	µg/L	2	16	16	16	0%	0%	0%
Lutetium	Lu	µg/L	0	0.38	0.38	0.38	0%	0%	0%
Magnesium	Mg	µg/L	30	17000	17000	17000	0%	0%	0%
Manganese	Mn	µg/L	0	5600	5800	5800	4%	0%	4%
Molybdenum	Mo	µg/L	10	10	10	10	0%	0%	0%
Neodymium	Nd	µg/L	0	36	36	36	0%	0%	0%
Nickel	Ni	µg/L	1	140	140	140	0%	0%	0%
Niobium	Nb	µg/L	0	0	0	0	0%	0%	0%
Palladium	Pd	µg/L	-	-	-	-	-	-	-
Phosphorus	P	µg/L	1000	1000	1000	1000	0%	0%	0%
Platinum	Pt	µg/L	0	0	0	0	0%	0%	0%
Potassium	K	µg/L	200	2400	2500	2300	4%	8%	4%
Praseodymium	Pr	µg/L	0	8.6	8.5	8.8	1%	3%	2%
Rhenium	Re	µg/L	0	0	0	0	0%	0%	0%
Rhodium	Rh	µg/L	0	0	0	0	0%	0%	0%
Rubidium	Rb	µg/L	1	4.6	4.4	4.4	4%	0%	4%
Ruthenium	Ru	µg/L	0	0	0	0	0%	0%	0%
Samarium	Sm	µg/L	0	8.5	8.6	8.3	1%	4%	2%
Selenium	Se	µg/L	1	6.3	6.0	6.0	5%	0%	5%
Silver	Ag	µg/L	0	0	0	0	0%	0%	0%
Sodium	Na	µg/L	200	12000	12000	12000	0%	0%	0%
Strontium	Sr	µg/L	1	630	610	620	3%	2%	2%
Sulfur	S	µg/L	1000	270000	270000	270000	0%	0%	0%
Tantalum	Ta	µg/L	0	0	0	0	0%	0%	0%
Terbium	Tb	µg/L	0	1.4	1.4	1.4	0%	0%	0%
Tellurium	Te	µg/L	1	1	0.75	0.66	40%	13%	28%
Thalium	Tl	µg/L	0	0.65	0.59	0.58	10%	2%	11%
Thorium	Th	µg/L	-	-	-	-	-	-	-
Thulium	Tm	µg/L	0	0.49	0.46	0.44	6%	4%	11%
Tin **	Sn	µg/L	3	3.0	3.0	3.0	0%	0%	0%
Titanium	Ti	µg/L	3	3	3	3	0%	0%	0%
Tungsten	W	µg/L	1	1	1	1	0%	0%	0%
Uranium	U	µg/L	0	3.0	3.0	3.0	0%	0%	0%
Vanadium	V	µg/L	0	0	0	0	0%	0%	0%
Ytterbium	Yb	µg/L	0	2.8	2.7	2.8	4%	4%	0%
Yttrium	Y	µg/L	1	42	43	42	2%	2%	0%
Zinc	Zn	µg/L	10	2000	2100	2100	5%	0%	5%
Zirconium	Zr	µg/L	0	0.13	0.13	0.13	0%	0%	0%

Sample description	Sample name			SP3-W	SP3-W	SP3-W	%Diff 32-33
	Sample type			FFA	UA	UA	
	Sample number			No23	No32	No33	
	Symbol	Units	Detection limit	Field Duplicate			
Anions							
Fluoride	F	mg/L	<0.05	<2.0	0.0	<2.0	-
Chloride	Cl	mg/L	<0.05	<2.0	<2.0	<2.0	-
Nitrite	NO ₂ ⁻	mg/L	<0.05	<2.0	<2.0	<2.0	-
Nitrate	NO ₃ ⁻	mg/L	<0.05	3.8	3.8	3.8	-
Sulphate	SO ₄ ²⁻	mg/L	<0.10	690.0	690.0	690.0	-
pH	-	-	-	2.9	2.9	2.9	-
Metals							
Aluminium	Al	µg/L	5	45000	47000	45000	4%
Antimony	Sb	µg/L	2	2	7.9	7.3	8%
Arsenic	As	µg/L	2	18	99	93	6%
Barium	Ba	µg/L	0	50	72	72	0%
Beryllium	Be	µg/L	0	6.7	8.1	8.1	0%
Boron	B	µg/L	1000	1000	<1000	<1000	0%
Cadmium	Cd	µg/L	0	31	39	39	0%
Calcium	Ca	µg/L	300	120000	130000	130000	0%
Cerium	Ce	µg/L	1	58	76	75	1%
Cesium	Cs	µg/L	-	-	-	-	-
Chromium	Cr	µg/L	5	13	16	16	0%
Cobalt	Co	µg/L	0	150	170	170	0%
Copper	Cu	µg/L	5	9000	11000	11000	0%
Dysprosium	Dy	µg/L	0	7.3	9.1	9.2	1%
Erbium	Er	µg/L	0	3.6	4.6	4.6	0%
Europium	Eu	µg/L	0	2.5	3.3	3.1	6%
Gadolinium	Gd	µg/L	0	8.7	12	11	9%
Gallium	Ga	µg/L	5	8.0	8.9	11	21%
Germanium	Ge	µg/L	1	3.3	3.6	3.4	6%
Hafnium	Hf	µg/L	-	-	-	-	-
Holonium	Ho	µg/L	0	1.4	1.7	1.7	0%
Iridium	Ir	µg/L	1	1	<0.5	<0.5	0%
Iron	Fe	µg/L	50	47000	69000	68000	1%
Lanthanum	La	µg/L	0	27	36	35	3%
Lead	Pb	µg/L	0	29	41	40	2%
Lithium	Li	µg/L	2	14	19	19	0%
Lutetium	Lu	µg/L	0	0.36	0.44	0.44	0%
Magnesium	Mg	µg/L	30	16000	18000	18000	0%
Manganese	Mn	µg/L	0	5500	5800	5600	4%
Molybdenum	Mo	µg/L	10	10	<10	<10	0%
Neodymium	Nd	µg/L	0	34	45	45	0%
Nickel	Ni	µg/L	1	140	160	160	0%
Niobium	Nb	µg/L	0	0	<0.05	<0.05	0%
Palladium	Pd	µg/L	-	-	-	-	-
Phosphorus	P	µg/L	1000	1000	<1000	<1000	0%
Platinum	Pt	µg/L	0	0	<0.05	<0.05	0%
Potassium	K	µg/L	200	2300	2700	2700	0%
Praseodymium	Pr	µg/L	0	8.2	10	10	0%
Rhenium	Re	µg/L	0	0	<0.2	<0.2	0%
Rhodium	Rh	µg/L	0	0	<0.1	<0.1	0%
Rubidium	Rb	µg/L	1	4.3	5.7	5.6	2%
Ruthenium	Ru	µg/L	0	0	<0.1	<0.1	0%
Samarium	Sm	µg/L	0	8.0	10	11	10%
Selenium	Se	µg/L	1	4.9	7.3	7.4	1%
Silver	Ag	µg/L	0	0	<0.1	0.17	52%
Sodium	Na	µg/L	200	12000	14000	13000	7%
Strontium	Sr	µg/L	1	590	720	710	1%
Sulfur	S	µg/L	1000	250000	270000	270000	0%
Tantalum	Ta	µg/L	0	0	<0.05	<0.05	0%
Terbium	Tb	µg/L	0	1.4	1.8	1.7	6%
Tellurium	Te	µg/L	1	1.4	0.91	1.2	27%
Thalium	Tl	µg/L	0	0.60	0.48	0.49	2%
Thorium	Th	µg/L	-	-	-	-	-
Thulium	Tm	µg/L	0	0.46	0.55	0.56	2%
Tin **	Sn	µg/L	3	3.0	<3.0	<3.0	0%
Titanium	Ti	µg/L	3	3	7.5	4.7	46%
Tungsten	W	µg/L	1	1	<0.5	<0.5	0%
Uranium	U	µg/L	0	2.7	3.7	3.7	0%
Vanadium	V	µg/L	0	0	2.3	2.3	0%
Ytterbium	Yb	µg/L	0	2.5	3.4	3.4	0%
Yttrium	Y	µg/L	1	42	51	49	4%
Zinc	Zn	µg/L	10	1900	2000	1900	5%
Zirconium	Zr	µg/L	0	0.25	0.31	0.37	18%

Sample description	Sample name			DW-B-11-W	DW-B-11-W	DW-B-11-W	%Diff 30-31
	Sample type			FFA	UA	UA	
	Sample number			No21	No30	No31	
	Symbol	Units	Detection limit	Field Duplicate			
Anions							
Fluoride	F	mg/L	<0.05	<2.0	<2.0	<2.0	-
Chloride	Cl	mg/L	<0.05	<2.0	<2.0	<2.0	-
Nitrite	NO ₂ -	mg/L	<0.05	<2.0	<2.0	<2.0	-
Nitrate	NO ₃ -	mg/L	<0.05	<2.0	<2.0	<2.0	-
Sulphate	SO ₄ 2-	mg/L	<0.10	845.0	845.0	845.0	-
pH	-	-		2.8	2.8	2.8	-
Metals							
Aluminium	Al	µg/L	5	26000	28000	26000	7%
Antimony	Sb	µg/L	2	210	240	240	0%
Arsenic	As	µg/L	2	1100	1300	1200	8%
Barium	Ba	µg/L	0	15	18	18	0%
Beryllium	Be	µg/L	0	1.8	1.9	1.8	5%
Boron	B	µg/L	1000	1000	<1000	<1000	0%
Cadmium	Cd	µg/L	0	170	210	200	5%
Calcium	Ca	µg/L	300	78000	91000	89000	2%
Cerium	Ce	µg/L	1	14	17	16	6%
Cesium	Cs	µg/L	-	-	-	-	-
Chromium	Cr	µg/L	5	24	29	28	4%
Cobalt	Co	µg/L	0	220	260	260	0%
Copper	Cu	µg/L	5	100000	140000	140000	0%
Dysprosium	Dy	µg/L	0	1.8	2.2	2.1	5%
Erbium	Er	µg/L	0	1.0	1.2	1.1	9%
Europium	Eu	µg/L	0	0.63	0.68	0.84	21%
Gadolinium	Gd	µg/L	0	2.3	2.8	2.7	4%
Gallium	Ga	µg/L	5	14	17	13	27%
Germanium	Ge	µg/L	1	3.2	3.6	3.6	0%
Hafnium	Hf	µg/L	-	-	-	-	-
Holonium	Ho	µg/L	0	0.36	0.42	0.42	0%
Iridium	Ir	µg/L	1	1	<0.5	<0.5	0%
Iron	Fe	µg/L	50	170000	190000	190000	0%
Lanthanum	La	µg/L	0	6.2	7.8	7.4	5%
Lead	Pb	µg/L	0	280	360	350	3%
Lithium	Li	µg/L	2	14	19	18	5%
Lutetium	Lu	µg/L	0	0.12	0.15	0.14	7%
Magnesium	Mg	µg/L	30	4100	4700	4600	2%
Manganese	Mn	µg/L	0	2000	2300	2100	9%
Molybdenum	Mo	µg/L	10	10	11	12	9%
Neodymium	Nd	µg/L	0	9.3	12	11	9%
Nickel	Ni	µg/L	1	160	190	180	5%
Niobium	Nb	µg/L	0	0	<0.05	<0.05	0%
Palladium	Pd	µg/L	-	-	-	-	-
Phosphorus	P	µg/L	1000	1000	<1000	<1000	0%
Platinum	Pt	µg/L	0	0	<0.05	<0.05	0%
Potassium	K	µg/L	200	1200	1200	1300	8%
Praseodymium	Pr	µg/L	0	2.1	2.5	2.5	0%
Rhenium	Re	µg/L	0	0	<0.2	<0.2	0%
Rhodium	Rh	µg/L	0	0	<0.1	<0.1	0%
Rubidium	Rb	µg/L	1	5.4	6.8	6.5	5%
Ruthenium	Ru	µg/L	0	0	<0.1	<0.1	0%
Samarium	Sm	µg/L	0	2.0	2.6	2.6	0%
Selenium	Se	µg/L	1	3.1	4.2	3.8	10%
Silver	Ag	µg/L	0	0	<0.1	<0.1	0%
Sodium	Na	µg/L	200	15000	17000	16000	6%
Strontium	Sr	µg/L	1	350	410	410	0%
Sulfur	S	µg/L	1000	320000	330000	320000	3%
Tantalum	Ta	µg/L	0	0	<0.05	<0.05	0%
Terbium	Tb	µg/L	0	0.33	0.42	0.41	2%
Tellurium	Te	µg/L	1	20	40	42	5%
Thallium	Tl	µg/L	0	9.7	12	11	9%
Thorium	Th	µg/L	-	-	-	-	-
Thulium	Tm	µg/L	0	0.12	0.16	0.15	6%
Tin **	Sn	µg/L	3	3.0	<3.0	<3.0	0%
Titanium	Ti	µg/L	3	3	<3.0	<3.0	0%
Tungsten	W	µg/L	1	1	<0.5	<0.5	0%
Uranium	U	µg/L	0	3.8	4.7	4.5	4%
Vanadium	V	µg/L	0	8.3	11	10	10%
Ytterbium	Yb	µg/L	0	0.81	1.1	0.96	14%
Yttrium	Y	µg/L	1	11	12	12	0%
Zinc	Zn	µg/L	10	4600	4800	4500	6%
Zirconium	Zr	µg/L	0	0.23	0.19	<0.1	62%

Sample description	Sample name			DW-B-11-W	DW-B-11-W	DW-B-11-W	% Diff 2-3	%Diff 3-4	% Diff 2-4
	Sample type			FA	FA	FA			
	Sample number			No2	No3	No4			
	Symbol	Units	Detection limit	Field TriPLICATE					
Anions									
Fluoride	F	mg/L	<0.05	<2.0	<2.0	<2.0	-	-	-
Chloride	Cl	mg/L	<0.05	<2.0	<2.0	<2.0	-	-	-
Nitrite	NO ₂ ⁻	mg/L	<0.05	<2.0	<2.0	<2.0	-	-	-
Nitrate	NO ₃ ⁻	mg/L	<0.05	<2.0	<2.0	<2.0	-	-	-
Sulphate	SO ₄ ²⁻	mg/L	<0.10	845.0	845.0	845.0	-	-	-
pH	-	-		2.8	2.8	2.8	-	-	-
Metals									
Aluminium	Al	µg/L	5	27000	29000	28000	7%	4%	4%
Antimony	Sb	µg/L	2	210	210	210	0%	0%	0%
Arsenic	As	µg/L	2	1300	1400	1300	7%	7%	0%
Barium	Ba	µg/L	0	15	15	15	0%	0%	0%
Beryllium	Be	µg/L	0	1.8	1.8	1.8	0%	0%	0%
Boron	B	µg/L	1000	1000	1000	1000	0%	0%	0%
Cadmium	Cd	µg/L	0	170	170	170	0%	0%	0%
Calcium	Ca	µg/L	300	78000	80000	76000	3%	5%	3%
Cerium	Ce	µg/L	1	13	13	13	0%	0%	0%
Cesium	Cs	µg/L	-	-	-	-	-	-	-
Chromium	Cr	µg/L	5	23	24	23	4%	4%	0%
Cobalt	Co	µg/L	0	210	220	210	5%	5%	0%
Copper	Cu	µg/L	5	110000	110000	110000	0%	0%	0%
Dysprosium	Dy	µg/L	0	1.8	1.7	1.8	6%	6%	0%
Erbium	Er	µg/L	0	0.94	0.91	0.89	3%	2%	5%
Europium	Eu	µg/L	0	0.58	0.66	0.74	13%	11%	24%
Gadolinium	Gd	µg/L	0	2.3	2.2	2.2	4%	0%	4%
Gallium	Ga	µg/L	5	12	13	13	8%	0%	8%
Germanium	Ge	µg/L	1	3.6	3.3	3.5	9%	6%	3%
Hafnium	Hf	µg/L	-	-	-	-	-	-	-
Holonium	Ho	µg/L	0	0.33	0.35	0.34	6%	3%	3%
Iridium	Ir	µg/L	1	1	1	1	0%	0%	0%
Iron	Fe	µg/L	50	170000	170000	170000	0%	0%	0%
Lanthanum	La	µg/L	0	6.0	5.9	6.0	2%	2%	0%
Lead	Pb	µg/L	0	290	280	290	4%	4%	0%
Lithium	Li	µg/L	2	15	15	15	0%	0%	0%
Lutetium	Lu	µg/L	0	0.12	0.11	0.12	9%	9%	0%
Magnesium	Mg	µg/L	30	3900	4100	4000	5%	2%	3%
Manganese	Mn	µg/L	0	2200	2300	2200	4%	4%	0%
Molybdenum	Mo	µg/L	10	10	10	10	0%	0%	0%
Neodymium	Nd	µg/L	0	8.8	8.9	8.7	1%	2%	1%
Nickel	Ni	µg/L	1	150	150	150	0%	0%	0%
Niobium	Nb	µg/L	0	0	0	0	0%	0%	0%
Palladium	Pd	µg/L	-	-	-	-	-	-	-
Phosphorus	P	µg/L	1000	1000	1100	1000	10%	10%	0%
Platinum	Pt	µg/L	0	0	0	0	0%	0%	0%
Potassium	K	µg/L	200	1100	1200	1100	9%	9%	0%
Praseodymium	Pr	µg/L	0	2.0	2.0	2.0	0%	0%	0%
Rhenium	Re	µg/L	0	0	0	0	0%	0%	0%
Rhodium	Rh	µg/L	0	0	0	0	0%	0%	0%
Rubidium	Rb	µg/L	1	5.4	5.3	5.4	2%	2%	0%
Ruthenium	Ru	µg/L	0	0	0	0	0%	0%	0%
Samarium	Sm	µg/L	0	2.0	1.9	1.8	5%	5%	11%
Selenium	Se	µg/L	1	2.9	2.6	2.6	11%	0%	11%
Silver	Ag	µg/L	0	0	0	0	0%	0%	0%
Sodium	Na	µg/L	200	14000	15000	15000	7%	0%	7%
Strontium	Sr	µg/L	1	350	340	350	3%	3%	0%
Sulfur	S	µg/L	1000	320000	330000	320000	3%	3%	0%
Tantalum	Ta	µg/L	0	0	0	0	0%	0%	0%
Terbium	Tb	µg/L	0	0.34	0.34	0.31	0%	9%	9%
Tellurium	Te	µg/L	1	37	38	38	3%	0%	3%
Thallium	Tl	µg/L	0	9.6	9.6	9.5	0%	1%	1%
Thorium	Th	µg/L	-	-	-	-	-	-	-
Thulium	Tm	µg/L	0	0.12	0.11	0.11	9%	0%	9%
Tin **	Sn	µg/L	3	3.0	3.0	3.0	0%	0%	0%
Titanium	Ti	µg/L	3	3	3	3	0%	0%	0%
Tungsten	W	µg/L	1	1	1	1	0%	0%	0%
Uranium	U	µg/L	0	3.7	3.7	3.7	0%	0%	0%
Vanadium	V	µg/L	0	8.2	7.7	7.5	6%	3%	9%
Ytterbium	Yb	µg/L	0	0.74	0.75	0.76	1%	1%	3%
Yttrium	Y	µg/L	1	10	10	11	0%	10%	10%
Zinc	Zn	µg/L	10	4900	5100	5100	4%	0%	4%
Zirconium	Zr	µg/L	0	0	0	0	0%	0%	0%

Sample description	Symbol	Units	Sample name	SP3-W2	SP3-W2	SP3-W2	SP3-W3	%Diff 18-19
			Sample type	FA	FA	FFA	UA	
			Sample number	No18	No19	No26	No35	
			Detection limit	Field Duplicate				
Anions								
Fluoride	F	mg/L	<0.05	<2.0	<2.0	<2.0	<2.0	-
Chloride	Cl	mg/L	<0.05	<2.0	<2.0	<2.0	<2.0	-
Nitrite	NO ₂ -	mg/L	<0.05	<2.0	<2.0	<2.0	<2.0	-
Nitrate	NO ₃ -	mg/L	<0.05	4.0	4.0	4.0	4.0	-
Sulphate	SO ₄ 2--	mg/L	<0.10	750.0	750.0	750.0	750.0	-
pH		-		2.9	2.9	2.9	2.9	-
Metals								
Aluminium	Al	µg/L	5	49000	50000	46000	49000	2%
Antimony	Sb	µg/L	2	2	2	2	11	0%
Arsenic	As	µg/L	2	13	15	16	130	14%
Barium	Ba	µg/L	0	56	58	51	80	4%
Beryllium	Be	µg/L	0	7.6	7.7	6.6	8.7	1%
Boron	B	µg/L	1000	1000	1000	1000	<1000	0%
Cadmium	Cd	µg/L	0	37	38	32	42	3%
Calcium	Ca	µg/L	300	130000	130000	120000	140000	0%
Cerium	Ce	µg/L	1	69	70	60	83	1%
Cesium	Cs	µg/L	-	-	-	-	-	-
Chromium	Cr	µg/L	5	15	16	13	17	6%
Cobalt	Co	µg/L	0	170	180	150	180	6%
Copper	Cu	µg/L	5	9900	10000	9500	12000	1%
Dysprosium	Dy	µg/L	0	8.6	8.6	7.4	10	0%
Erbium	Er	µg/L	0	4.1	4.4	3.7	4.9	7%
Europium	Eu	µg/L	0	3.0	3.1	2.7	3.5	3%
Gadolinium	Gd	µg/L	0	11	11	9.3	13	0%
Gallium	Ga	µg/L	5	8.0	9.3	8.0	9.9	15%
Germanium	Ge	µg/L	1	3.3	3.4	2.9	3.9	3%
Hafnium	Hf	µg/L	-	-	-	-	-	-
Holonium	Ho	µg/L	0	1.6	1.5	1.4	1.9	6%
Iridium	Ir	µg/L	1	1	1	1	<0.5	0%
Iron	Fe	µg/L	50	56000	56000	49000	79000	0%
Lanthanum	La	µg/L	0	32	32	28	39	0%
Lead	Pb	µg/L	0	33	34	29	45	3%
Lithium	Li	µg/L	2	17	17	14	21	0%
Lutetium	Lu	µg/L	0	0.43	0.42	0.37	0.51	2%
Magnesium	Mg	µg/L	30	19000	19000	17000	20000	0%
Manganese	Mn	µg/L	0	6100	6100	5700	6200	0%
Molybdenum	Mo	µg/L	10	10	10	10	<10	0%
Neodymium	Nd	µg/L	0	40	41	35	49	2%
Nickel	Ni	µg/L	1	170	170	150	170	0%
Niobium	Nb	µg/L	0	0	0	0	<0.05	0%
Palladium	Pd	µg/L	-	-	-	-	-	-
Phosphorus	P	µg/L	1000	1000	1000	1000	<1000	0%
Platinum	Pt	µg/L	0	0	0	0	<0.05	0%
Potassium	K	µg/L	200	2700	2700	3100	2800	0%
Praseodymium	Pr	µg/L	0	9.7	9.9	8.5	11	2%
Rhenium	Re	µg/L	0	0	0	0	<0.2	0%
Rhodium	Rh	µg/L	0	0	0	0	<0.1	0%
Rubidium	Rb	µg/L	1	4.6	4.8	5.7	6.0	4%
Ruthenium	Ru	µg/L	0	0	0	0	<0.1	0%
Samarium	Sm	µg/L	0	9.5	9.9	8.0	11	4%
Selenium	Se	µg/L	1	6.9	7.8	6.8	8.8	12%
Silver	Ag	µg/L	0	0.83	0.90	0.78	0.12	8%
Sodium	Na	µg/L	200	15000	15000	14000	14000	0%
Strontium	Sr	µg/L	1	680	680	610	760	0%
Sulfur	S	µg/L	1000	3800000	4100000	3800000	270000	8%
Tantalum	Ta	µg/L	0	0	0	0	<0.05	0%
Terbium	Tb	µg/L	0	1.6	1.6	1.4	1.9	0%
Tellurium	Te	µg/L	1	0.65	0.62	0.81	1.2	5%
Thallium	Tl	µg/L	0	0.69	0.64	0.62	0.59	8%
Thorium	Th	µg/L	-	-	-	-	-	-
Thulium	Tm	µg/L	0	0.52	0.54	0.46	0.63	4%
Tin **	Sn	µg/L	3	3.0	3.0	3.0	<3.0	0%
Titanium	Ti	µg/L	3	3	3	3	12	0%
Tungsten	W	µg/L	1	1	1	1	<0.5	0%
Uranium	U	µg/L	0	3.3	3.4	2.9	4.0	3%
Vanadium	V	µg/L	0	0	0	0	3.5	0%
Ytterbium	Yb	µg/L	0	3.1	3.2	2.7	3.7	3%
Yttrium	Y	µg/L	1	50	49	44	52	2%
Zinc	Zn	µg/L	10	2100	2100	2000	2000	0%
Zirconium	Zr	µg/L	0	0.29	0.44	0.27	0.38	41%

Sample description	Sample name			DAR-1-W	DAR-1-W	*DAR-1-W	%Diff 8-9	% Diff 9-10	%Diff 10-8
	Symbol	Units	Sample type	FA	FA	FA			
			Sample number	No8	No9	No10			
			Detection limit	Field Triplicate					
Anions									
Fluoride	F	mg/L	<0.05	<5.0	<5.0	<5.0	-	-	-
Chloride	Cl	mg/L	<0.05	<5.0	<5.0	<5.0	-	-	-
Nitrite	NO ₂ -	mg/L	<0.05	<5.0	<5.0	<5.0	-	-	-
Nitrate	NO ₃ -	mg/L	<0.05	9.5	9.5	9.5	-	-	-
Sulphate	SO ₄ 2-	mg/L	<0.10	5400.0	5400.0	5400.0	-	-	-
pH	-	-	-	2.6	2.6	2.6	-	-	-
Metals									
Aluminium	Al	µg/L	5	380000	380000	390000	0%	3%	3%
Antimony	Sb	µg/L	2	3.1	3.2	4.0	3%	22%	25%
Arsenic	As	µg/L	2	920	950	890	3%	7%	3%
Barium	Ba	µg/L	0	8.4	8.3	12	1%	36%	35%
Beryllium	Be	µg/L	0	46	47	52	2%	10%	12%
Boron	B	µg/L	1000	1000	1000	1000	0%	0%	0%
Cadmium	Cd	µg/L	0	180	180	200	0%	11%	11%
Calcium	Ca	µg/L	300	400000	400000	460000	0%	14%	14%
Cerium	Ce	µg/L	1	520	540	610	4%	12%	16%
Cesium	Cs	µg/L	-	-	-	-	-	-	-
Chromium	Cr	µg/L	5	74	76	88	3%	15%	17%
Cobalt	Co	µg/L	0	890	910	1000	2%	9%	12%
Copper	Cu	µg/L	5	17000	18000	17000	6%	6%	0%
Dysprosium	Dy	µg/L	0	65	67	75	3%	11%	14%
Erbium	Er	µg/L	0	33	34	38	3%	11%	14%
Europium	Eu	µg/L	0	23	23	27	0%	16%	16%
Gadolinium	Gd	µg/L	0	80	83	93	4%	11%	15%
Gallium	Ga	µg/L	5	58	58	69	0%	17%	17%
Germanium	Ge	µg/L	1	27	28	33	4%	16%	20%
Hafnium	Hf	µg/L	-	-	-	-	-	-	-
Holonium	Ho	µg/L	0	12	13	15	8%	14%	22%
Iridium	Ir	µg/L	1	1	1	1	0%	0%	0%
Iron	Fe	µg/L	50	640000	630000	650000	2%	3%	2%
Lanthanum	La	µg/L	0	240	250	280	4%	11%	15%
Lead	Pb	µg/L	0	2.9	2.8	4.7	4%	51%	47%
Lithium	Li	µg/L	2	110	110	120	0%	9%	9%
Lutetium	Lu	µg/L	0	3.2	3.3	3.7	3%	11%	14%
Magnesium	Mg	µg/L	30	130000	130000	150000	0%	14%	14%
Manganese	Mn	µg/L	0	40000	42000	40000	5%	5%	0%
Molybdenum	Mo	µg/L	10	10	10	10	0%	0%	0%
Neodymium	Nd	µg/L	0	300	310	350	3%	12%	15%
Nickel	Ni	µg/L	1	820	830	960	1%	15%	16%
Niobium	Nb	µg/L	0	0.19	0.20	0.23	5%	14%	19%
Palladium	Pd	µg/L	-	-	-	-	-	-	-
Phosphorus	P	µg/L	1000	6800	6600	6800	3%	3%	0%
Platinum	Pt	µg/L	0	0	0	0	0%	0%	0%
Potassium	K	µg/L	200	1200	1300	1400	8%	7%	15%
Praseodymium	Pr	µg/L	0	71	73	82	3%	12%	14%
Rhenium	Re	µg/L	0	0	0	0	0%	0%	0%
Rhodium	Rh	µg/L	0	0	0	0	0%	0%	0%
Rubidium	Rb	µg/L	1	8.6	8.6	9.9	0%	14%	14%
Ruthenium	Ru	µg/L	0	0	0	0	0%	0%	0%
Samarium	Sm	µg/L	0	71	73	83	3%	13%	16%
Selenium	Se	µg/L	1	20	21	24	5%	13%	18%
Silver	Ag	µg/L	0	0	0	0	0%	0%	0%
Sodium	Na	µg/L	200	27000	27000	31000	0%	14%	14%
Strontium	Sr	µg/L	1	2100	2000	2100	5%	5%	0%
Sulfur	S	µg/L	1000	1700000	1900000	1800000	11%	5%	6%
Tantalum	Ta	µg/L	0	0	0.051	0.060	2%	16%	18%
Terbium	Tb	µg/L	0	12	12	14	0%	15%	15%
Tellurium	Te	µg/L	1	1.8	2.1	2.6	15%	21%	36%
Thalium	Tl	µg/L	0	0.28	0.30	0.33	7%	10%	16%
Thorium	Th	µg/L	-	-	-	-	-	-	-
Thulium	Tm	µg/L	0	4.1	4.2	4.7	2%	11%	14%
Tin **	Sn	µg/L	3	3.0	3.0	3.0	0%	0%	0%
Titanium	Ti	µg/L	3	26	22	28	17%	24%	7%
Tungsten	W	µg/L	1	1	1	1	0%	0%	0%
Uranium	U	µg/L	0	21	22	25	5%	13%	17%
Vanadium	V	µg/L	0	24	23	27	4%	16%	12%
Ytterbium	Yb	µg/L	0	24	24	28	0%	15%	15%
Yttrium	Y	µg/L	1	350	370	420	6%	13%	18%
Zinc	Zn	µg/L	10	14000	14000	14000	0%	0%	0%
Zirconium	Zr	µg/L	0	1.7	1.8	2.3	6%	24%	30%

Sample description	Sample name			DAR-1-W	DAR-1-W	DAR-1-W	% Diff 28-29
	Sample type			FFA	UA	UA	
	Sample number			No24	No28	No29 *	
	Symbol	Units	Detection limit	Field Duplicate			
Anions							
Fluoride	F	mg/L	<0.05	<5.0	<5.0	<5.0	-
Chloride	Cl	mg/L	<0.05	<5.0	<5.0	<5.0	-
Nitrite	NO ₂ -	mg/L	<0.05	<5.0	<5.0	<5.0	-
Nitrate	NO ₃ -	mg/L	<0.05	9.5	9.5	9.5	-
Sulphate	SO ₄ 2-	mg/L	<0.10	5400.0	5400.0	5400.0	-
pH	-	-		2.6	2.6	2.6	-
Metals							
Aluminium	Al	µg/L	5	370000	370000	360000	3%
Antimony	Sb	µg/L	2	3.6	4.5	3.5	25%
Arsenic	As	µg/L	2	960	850	910	7%
Barium	Ba	µg/L	0	8.8	11	9.6	14%
Beryllium	Be	µg/L	0	45	62	53	16%
Boron	B	µg/L	1000	1000	<1000	<1000	0%
Cadmium	Cd	µg/L	0	180	230	200	14%
Calcium	Ca	µg/L	300	400000	420000	440000	5%
Cerium	Ce	µg/L	1	530	680	580	16%
Cesium	Cs	µg/L	-	-	-	-	-
Chromium	Cr	µg/L	5	77	100	84	17%
Cobalt	Co	µg/L	0	930	1200	1000	18%
Copper	Cu	µg/L	5	16000	23000	20000	14%
Dysprosium	Dy	µg/L	0	65	86	74	15%
Erbium	Er	µg/L	0	33	43	36	18%
Europium	Eu	µg/L	0	23	31	26	18%
Gadolinium	Gd	µg/L	0	80	110	92	18%
Gallium	Ga	µg/L	5	59	90	72	22%
Germanium	Ge	µg/L	1	28	35	28	22%
Hafnium	Hf	µg/L	-	-	-	-	-
Holonium	Ho	µg/L	0	13	16	14	13%
Iridium	Ir	µg/L	1	1	<0.5	<0.5	0%
Iron	Fe	µg/L	50	620000	670000	660000	2%
Lanthanum	La	µg/L	0	240	310	270	14%
Lead	Pb	µg/L	0	3.3	3.9	4.1	5%
Lithium	Li	µg/L	2	100	150	130	14%
Lutetium	Lu	µg/L	0	3.3	4.2	3.5	18%
Magnesium	Mg	µg/L	30	130000	160000	140000	13%
Manganese	Mn	µg/L	0	40000	44000	47000	7%
Molybdenum	Mo	µg/L	10	10	<10	<10	0%
Neodymium	Nd	µg/L	0	300	400	350	13%
Nickel	Ni	µg/L	1	850	1100	920	18%
Niobium	Nb	µg/L	0	0.20	0.25	0.22	13%
Palladium	Pd	µg/L	-	-	-	-	-
Phosphorus	P	µg/L	1000	6600	6400	6300	2%
Platinum	Pt	µg/L	0	0	<0.05	<0.05	0%
Potassium	K	µg/L	200	1300	1500	1400	7%
Praseodymium	Pr	µg/L	0	71	97	80	19%
Rhenium	Re	µg/L	0	0	<0.2	<0.2	0%
Rhodium	Rh	µg/L	0	0	<0.1	<0.1	0%
Rubidium	Rb	µg/L	1	8.4	11	9.7	13%
Ruthenium	Ru	µg/L	0	0	<0.1	<0.1	0%
Samarium	Sm	µg/L	0	72	97	82	17%
Selenium	Se	µg/L	1	19	26	24	8%
Silver	Ag	µg/L	0	0	<0.1	<0.1	0%
Sodium	Na	µg/L	200	28000	33000	28000	16%
Strontium	Sr	µg/L	1	2000	2000	2000	0%
Sulfur	S	µg/L	1000	1700000	1800000	1800000	0%
Tantalum	Ta	µg/L	0	0.052	0.077	0.068	12%
Terbium	Tb	µg/L	0	12	16	14	13%
Tellurium	Te	µg/L	1	1.9	2.2	2.2	0%
Thallium	Tl	µg/L	0	0.30	0.22	<0.1	75%
Thorium	Th	µg/L	-	-	-	-	-
Thulium	Tm	µg/L	0	4.1	5.3	4.5	16%
Tin **	Sn	µg/L	3	3.0	<3.0	<3.0	0%
Titanium	Ti	µg/L	3	20	27	25	8%
Tungsten	W	µg/L	1	1	<0.5	<0.5	0%
Uranium	U	µg/L	0	21	28	24	15%
Vanadium	V	µg/L	0	24	31	26	18%
Ytterbium	Yb	µg/L	0	24	31	26	18%
Yttrium	Y	µg/L	1	370	480	400	18%
Zinc	Zn	µg/L	10	14000	13000	13000	0%
Zirconium	Zr	µg/L	0	1.9	3.3	2.4	32%

Sample description	Symbol	Units	Sample name	LN-BP-W	LN-BP-W	%Diff 11-12
			Sample type	FA	FA	
			Sample number	No11*	No12	
			Detection limit	Field Duplicate		
Anions						
Fluoride	F	mg/L	<0.05	<0.25	<0.25	-
Chloride	Cl	mg/L	<0.05	0.7	0.7	-
Nitrite	NO ₂ -	mg/L	<0.05	<0.25	<0.25	-
Nitrate	NO ₃ -	mg/L	<0.05	7.8	7.8	-
Sulphate	SO ₄ 2-	mg/L	<0.10	190.0	190.0	-
pH	-	-	-	3.0	3.0	-
Metals						
Aluminium	Al	µg/L	5	6200	6300	2%
Antimony	Sb	µg/L	2	2	2	0%
Arsenic	As	µg/L	2	3.6	2.6	32%
Barium	Ba	µg/L	0	42	35	18%
Beryllium	Be	µg/L	0	0.26	0	26%
Boron	B	µg/L	1000	1000	1000	0%
Cadmium	Cd	µg/L	0	7.4	6.0	21%
Calcium	Ca	µg/L	300	34000	28000	19%
Cerium	Ce	µg/L	1	12	9.3	25%
Cesium	Cs	µg/L	-	-	-	-
Chromium	Cr	µg/L	5	5	5	0%
Cobalt	Co	µg/L	0	94	78	19%
Copper	Cu	µg/L	5	3800	3800	0%
Dysprosium	Dy	µg/L	0	1.2	0.93	25%
Erbium	Er	µg/L	0	0.61	0.53	14%
Europium	Eu	µg/L	0	0.51	0.36	34%
Gadolinium	Gd	µg/L	0	1.6	1.3	21%
Gallium	Ga	µg/L	5	5	5	0%
Germanium	Ge	µg/L	1	1	1	0%
Hafnium	Hf	µg/L	-	-	-	-
Holonium	Ho	µg/L	0	0.22	0.19	15%
Iridium	Ir	µg/L	1	1	1	0%
Iron	Fe	µg/L	50	16000	13000	21%
Lanthanum	La	µg/L	0	5.0	4.1	20%
Lead	Pb	µg/L	0	50	41	20%
Lithium	Li	µg/L	2	4.3	3.5	21%
Lutetium	Lu	µg/L	0	0.060	0.053	12%
Magnesium	Mg	µg/L	30	3100	2500	21%
Manganese	Mn	µg/L	0	1000	930	7%
Molybdenum	Mo	µg/L	10	10	10	0%
Neodymium	Nd	µg/L	0	7.0	5.6	22%
Nickel	Ni	µg/L	1	86	71	19%
Niobium	Nb	µg/L	0	0	0	0%
Palladium	Pd	µg/L	-	-	-	-
Phosphorus	P	µg/L	1000	1000	1000	0%
Platinum	Pt	µg/L	0	0	0	0%
Potassium	K	µg/L	200	1900	1500	24%
Praseodymium	Pr	µg/L	0	1.6	1.3	21%
Rhenium	Re	µg/L	0	0	0	0%
Rhodium	Rh	µg/L	0	0	0	0%
Rubidium	Rb	µg/L	1	4.8	4.0	18%
Ruthenium	Ru	µg/L	0	0	0	0%
Samarium	Sm	µg/L	0	1.4	1.2	15%
Selenium	Se	µg/L	1	26	21	21%
Silver	Ag	µg/L	0	2.0	1.5	29%
Sodium	Na	µg/L	200	18000	14000	25%
Strontium	Sr	µg/L	1	110	90	20%
Sulfur	S	µg/L	1000	4600000	4100000	11%
Tantalum	Ta	µg/L	0	0	0	0%
Terbium	Tb	µg/L	0	0.22	0.17	26%
Tellurium	Te	µg/L	1	1	1	0%
Thalium	Tl	µg/L	0	2.2	1.9	15%
Thorium	Th	µg/L	-	-	-	-
Thulium	Tm	µg/L	0	0.079	0.057	32%
Tin **	Sn	µg/L	3	3.0	3.0	0%
Titanium	Ti	µg/L	3	3	3	0%
Tungsten	W	µg/L	1	1	1	0%
Uranium	U	µg/L	0	0.41	0.34	19%
Vanadium	V	µg/L	0	0	0	0%
Ytterbium	Yb	µg/L	0	0.42	0.35	18%
Yttrium	Y	µg/L	1	7.0	6.2	12%
Zinc	Zn	µg/L	10	120	94	24%
Zirconium	Zr	µg/L	0	0.16	0	46%

Sample description	Sample name			LN-BP-W	LN-BP-W	LN-BP-W	%Diff 37-38
	Symbol	Units	Sample type	FFA	UA	UA	
			Sample number	No25	No37	No38	
			Detection limit	Field Duplicate			
Anions							
Fluoride	F	mg/L	<0.05	<0.25	<0.25	<0.25	-
Chloride	Cl	mg/L	<0.05	0.7	0.7	0.7	-
Nitrite	NO ₂ ⁻	mg/L	<0.05	<0.25	<0.25	<0.25	-
Nitrate	NO ₃ ⁻	mg/L	<0.05	7.8	7.8	7.8	-
Sulphate	SO ₄ ²⁻	mg/L	<0.10	190.0	190.0	190.0	-
pH	-	-	-	3.0	3.0	3.0	-
Metals							
Aluminium	Al	µg/L	5	5800	6200	6100	2%
Antimony	Sb	µg/L	2	2	<2.0	<2.0	0%
Arsenic	As	µg/L	2	5.9	3.1	2.2	34%
Barium	Ba	µg/L	0	35	37	36	3%
Beryllium	Be	µg/L	0	0	<0.2	<0.2	0%
Boron	B	µg/L	1000	1000	<1000	<1000	0%
Cadmium	Cd	µg/L	0	5.8	6.7	6.5	3%
Calcium	Ca	µg/L	300	27000	26000	25000	4%
Cerium	Ce	µg/L	1	9.1	11	11	0%
Cesium	Cs	µg/L	-	-	-	-	-
Chromium	Cr	µg/L	5	5	<5.0	<5.0	0%
Cobalt	Co	µg/L	0	77	76	75	1%
Copper	Cu	µg/L	5	3600	4200	4000	5%
Dysprosium	Dy	µg/L	0	0.87	1.0	1.0	0%
Erbium	Er	µg/L	0	0.45	0.59	0.57	3%
Europium	Eu	µg/L	0	0.40	0.45	0.40	12%
Gadolinium	Gd	µg/L	0	1.2	1.5	1.4	7%
Gallium	Ga	µg/L	5	5	<5.0	<5.0	0%
Germanium	Ge	µg/L	1	1	<1.0	<1.0	0%
Hafnium	Hf	µg/L	-	-	-	-	-
Holmium	Ho	µg/L	0	0.18	0.21	0.20	5%
Iridium	Ir	µg/L	1	1	<0.5	<0.5	0%
Iron	Fe	µg/L	50	13000	13000	12000	8%
Lanthanum	La	µg/L	0	4.0	4.7	4.5	4%
Lead	Pb	µg/L	0	40	49	49	0%
Lithium	Li	µg/L	2	3.4	3.9	3.8	3%
Lutetium	Lu	µg/L	0	0	0.064	0.054	17%
Magnesium	Mg	µg/L	30	2500	2500	2300	8%
Manganese	Mn	µg/L	0	910	980	930	5%
Molybdenum	Mo	µg/L	10	10	<10	<10	0%
Neodymium	Nd	µg/L	0	5.4	6.6	6.4	3%
Nickel	Ni	µg/L	1	69	69	67	3%
Niobium	Nb	µg/L	0	0	<0.05	<0.05	0%
Palladium	Pd	µg/L	-	-	-	-	-
Phosphorus	P	µg/L	1000	1000	<1000	<1000	0%
Platinum	Pt	µg/L	0	0	<0.05	<0.05	0%
Potassium	K	µg/L	200	1600	1400	1300	7%
Praseodymium	Pr	µg/L	0	1.3	1.5	1.5	0%
Rhenium	Re	µg/L	0	0	<0.2	<0.2	0%
Rhodium	Rh	µg/L	0	0	<0.1	<0.1	0%
Rubidium	Rb	µg/L	1	3.8	4.4	4.4	0%
Ruthenium	Ru	µg/L	0	0	<0.1	<0.1	0%
Samarium	Sm	µg/L	0	1.1	1.3	1.3	0%
Selenium	Se	µg/L	1	20	26	25	4%
Silver	Ag	µg/L	0	1.5	2.1	1.9	10%
Sodium	Na	µg/L	200	14000	14000	13000	7%
Strontium	Sr	µg/L	1	86	93	89	4%
Sulfur	S	µg/L	1000	4200000	6300000	5600000	12%
Tantalum	Ta	µg/L	0	0	<0.05	<0.05	0%
Terbium	Tb	µg/L	0	0.17	0.21	0.22	5%
Tellurium	Te	µg/L	1	1	<0.5	<0.5	0%
Thalium	Tl	µg/L	0	1.8	1.9	1.9	0%
Thorium	Th	µg/L	-	-	-	-	-
Thulium	Tm	µg/L	0	0.056	0.076	0.076	0%
Tin **	Sn	µg/L	3	3.0	<3.0	<3.0	0%
Titanium	Ti	µg/L	3	3	<3.0	<3.0	0%
Tungsten	W	µg/L	1	1	<0.5	<0.5	0%
Uranium	U	µg/L	0	0.37	0.39	0.37	5%
Vanadium	V	µg/L	0	0	<0.3	<0.3	0%
Ytterbium	Yb	µg/L	0	0.34	0.51	0.40	24%
Yttrium	Y	µg/L	1	5.7	6.3	5.8	8%
Zinc	Zn	µg/L	10	96	91	83	9%
Zirconium	Zr	µg/L	0	0.24	0.23	0.15	42%

			Sample name	LN-PW2-W	LN-PW2-W	LN-PW2-W	%Diff 13-14	%Diff 14-15	% Diff 13-15
			Sample type	FA	FA	FA			
			Sample number	No13	No14	No15			
Symbol	Units	Detection limit	Field Triplicate						
Sample description									
Anions									
Fluoride	F	mg/L	<0.05	<2.0	<2.0	<2.0	-	-	-
Chloride	Cl	mg/L	<0.05	6.4	6.4	6.4	-	-	-
Nitrite	NO ₂ -	mg/L	<0.05	<2.0	<2.0	<2.0	-	-	-
Nitrate	NO ₃ -	mg/L	<0.05	<2.0	<2.0	<2.0	-	-	-
Sulphate	SO ₄ 2--	mg/L	<0.10	310.0	310.0	310.0	-	-	-
pH	-	-	-	6.2	6.2	6.2	-	-	-
Metals									
Aluminium	Al	µg/L	5	59	59	63	0%	7%	7%
Antimony	Sb	µg/L	2	5.7	6.2	6.9	8%	11%	19%
Arsenic	As	µg/L	2	8.9	9.4	9.0	5%	4%	1%
Barium	Ba	µg/L	0	25	25	27	0%	8%	8%
Beryllium	Be	µg/L	0	0	0	0	0%	0%	0%
Boron	B	µg/L	1000	1000	1000	1000	0%	0%	0%
Cadmium	Cd	µg/L	0	0.17	0.12	0.18	34%	40%	6%
Calcium	Ca	µg/L	300	150000	150000	160000	0%	6%	6%
Cerium	Ce	µg/L	1	1	1	1	0%	0%	0%
Cesium	Cs	µg/L	-	-	-	-	-	-	-
Chromium	Cr	µg/L	5	5	5	5	0%	0%	0%
Cobalt	Co	µg/L	0	0.41	0.53	0.51	26%	4%	22%
Copper	Cu	µg/L	5	10	7.5	6.9	29%	8%	37%
Dysprosium	Dy	µg/L	0	0	0	0	0%	0%	0%
Erbium	Er	µg/L	0	0	0	0	0%	0%	0%
Europium	Eu	µg/L	0	0	0	0	0%	0%	0%
Gadolinium	Gd	µg/L	0	0	0	0	0%	0%	0%
Gallium	Ga	µg/L	5	5	5	5	0%	0%	0%
Germanium	Ge	µg/L	1	1	1	1	0%	0%	0%
Hafnium	Hf	µg/L	-	-	-	-	-	-	-
Holonium	Ho	µg/L	0	0	0	0	0%	0%	0%
Iridium	Ir	µg/L	1	1	1	1	0%	0%	0%
Iron	Fe	µg/L	50	50	50	50	0%	0%	0%
Lanthanum	La	µg/L	0	0	0	0	0%	0%	0%
Lead	Pb	µg/L	0	0.24	0.25	0.21	4%	17%	13%
Lithium	Li	µg/L	2	10	11	11	10%	0%	10%
Lutetium	Lu	µg/L	0	0	0	0	0%	0%	0%
Magnesium	Mg	µg/L	30	3800	3800	4100	0%	8%	8%
Manganese	Mn	µg/L	0	6.0	5.2	6.5	14%	22%	8%
Molybdenum	Mo	µg/L	10	36	35	37	3%	6%	3%
Neodymium	Nd	µg/L	0	0	0	0	0%	0%	0%
Nickel	Ni	µg/L	1	1.8	1	1	57%	0%	57%
Niobium	Nb	µg/L	0	0	0	0	0%	0%	0%
Palladium	Pd	µg/L	-	-	-	-	-	-	-
Phosphorus	P	µg/L	1000	1000	1000	1000	0%	0%	0%
Platinum	Pt	µg/L	0	0	0	0	0%	0%	0%
Potassium	K	µg/L	200	360	330	440	9%	29%	20%
Praseodymium	Pr	µg/L	0	0	0	0	0%	0%	0%
Rhenium	Re	µg/L	0	0	0	0	0%	0%	0%
Rhodium	Rh	µg/L	0	0	0	0	0%	0%	0%
Rubidium	Rb	µg/L	1	1	1	1	0%	0%	0%
Ruthenium	Ru	µg/L	0	0	0	0	0%	0%	0%
Samarium	Sm	µg/L	0	0	0	0	0%	0%	0%
Selenium	Se	µg/L	1	4.7	4.3	5.3	9%	21%	12%
Silver	Ag	µg/L	0	0.99	0.85	0.96	15%	12%	3%
Sodium	Na	µg/L	200	27000	27000	29000	0%	7%	7%
Strontium	Sr	µg/L	1	1000	1000	1100	0%	10%	10%
Sulfur	S	µg/L	1000	4000000	4700000	4600000	16%	2%	14%
Tantalum	Ta	µg/L	0	0	0	0	0%	0%	0%
Terbium	Tb	µg/L	0	0	0	0	0%	0%	0%
Tellurium	Te	µg/L	1	1	1	1	0%	0%	0%
Thalium	Tl	µg/L	0	0	0	0	0%	0%	0%
Thorium	Th	µg/L	-	-	-	-	-	-	-
Thulium	Tm	µg/L	0	0	0	0	0%	0%	0%
Tin **	Sn	µg/L	3	3.0	3.0	3.0	0%	0%	0%
Titanium	Ti	µg/L	3	3	3	3	0%	0%	0%
Tungsten	W	µg/L	1	1	1	1	0%	0%	0%
Uranium	U	µg/L	0	1.2	1.1	1.2	9%	9%	0%
Vanadium	V	µg/L	0	0.66	0.66	0.70	0%	6%	6%
Ytterbium	Yb	µg/L	0	0	0	0	0%	0%	0%
Yttrium	Y	µg/L	1	1	1	1	0%	0%	0%
Zinc	Zn	µg/L	10	10	10	10	0%	0%	0%
Zirconium	Zr	µg/L	0	0.11	0.19	0.13	53%	38%	17%

Sample description	Sample name			LN-PW2-W	LN-PW2-W	LN-PW2-W	%Diff 39-40
	Symbol	Units	Sample type	FFA	UA	UA	
			Sample number	No22	No39	No40	
			Detection limit	Field Duplicate			
Anions							
Fluoride	F	mg/L	<0.05	<2.0	<2.0	<2.0	-
Chloride	Cl	mg/L	<0.05	6.4	6.4	6.4	-
Nitrite	NO ₂ ⁻	mg/L	<0.05	<2.0	<2.0	<2.0	-
Nitrate	NO ₃ ⁻	mg/L	<0.05	<2.0	<2.0	<2.0	-
Sulphate	SO ₄ ²⁻	mg/L	<0.10	310.0	310.0	310.0	-
pH	-	-	-	6.2	6.2	6.2	-
Metals							
Aluminium	Al	µg/L	5	60	130	120	8%
Antimony	Sb	µg/L	2	5.7	7.2	6.2	15%
Arsenic	As	µg/L	2	12	13	10	26%
Barium	Ba	µg/L	0	23	32	29	10%
Beryllium	Be	µg/L	0	0	<0.2	<0.2	0%
Boron	B	µg/L	1000	1000	<1000	<1000	0%
Cadmium	Cd	µg/L	0	0.12	0.16	0.19	17%
Calcium	Ca	µg/L	300	140000	170000	150000	13%
Cerium	Ce	µg/L	1	1	<0.5	<0.5	0%
Cesium	Cs	µg/L	-	-	-	-	-
Chromium	Cr	µg/L	5	5	<5.0	<5.0	0%
Cobalt	Co	µg/L	0	0.39	0.51	0.44	15%
Copper	Cu	µg/L	5	16	9.4	6.7	34%
Dysprosium	Dy	µg/L	0	0	<0.1	<0.1	0%
Erbium	Er	µg/L	0	0	<0.1	<0.1	0%
Europium	Eu	µg/L	0	0	<0.03	<0.03	0%
Gadolinium	Gd	µg/L	0	0	<0.1	<0.1	0%
Gallium	Ga	µg/L	5	5	<5.0	<5.0	0%
Germanium	Ge	µg/L	1	1	<1.0	<1.0	0%
Hafnium	Hf	µg/L	-	-	-	-	-
Holonium	Ho	µg/L	0	0	<0.05	<0.05	0%
Iridium	Ir	µg/L	1	1	<0.5	<0.5	0%
Iron	Fe	µg/L	50	72	190	190	0%
Lanthanum	La	µg/L	0	0	<0.4	<0.4	0%
Lead	Pb	µg/L	0	0.45	2.7	2.6	4%
Lithium	Li	µg/L	2	9.8	13	13	0%
Lutetium	Lu	µg/L	0	0	<0.05	<0.05	0%
Magnesium	Mg	µg/L	30	3600	4300	3900	10%
Manganese	Mn	µg/L	0	8.3	<0.3	<0.3	0%
Molybdenum	Mo	µg/L	10	34	43	41	5%
Neodymium	Nd	µg/L	0	0	<0.1	<0.1	0%
Nickel	Ni	µg/L	1	1.4	<1.0	<1.0	0%
Niobium	Nb	µg/L	0	0	<0.05	<0.05	0%
Palladium	Pd	µg/L	-	-	-	-	-
Phosphorus	P	µg/L	1000	1000	<1000	<1000	0%
Platinum	Pt	µg/L	0	0	<0.05	<0.05	0%
Potassium	K	µg/L	200	350	340	300	13%
Praseodymium	Pr	µg/L	0	0	<0.1	<0.1	0%
Rhenium	Re	µg/L	0	0	<0.2	<0.2	0%
Rhodium	Rh	µg/L	0	0	<0.1	<0.1	0%
Rubidium	Rb	µg/L	1	1	<1.0	<1.0	0%
Ruthenium	Ru	µg/L	0	0	<0.1	<0.1	0%
Samarium	Sm	µg/L	0	0	<0.1	<0.1	0%
Selenium	Se	µg/L	1	3.7	4.3	3.9	10%
Silver	Ag	µg/L	0	0.70	<0.1	<0.1	0%
Sodium	Na	µg/L	200	26000	29000	27000	7%
Strontium	Sr	µg/L	1	990	1000	1200	18%
Sulfur	S	µg/L	1000	3600000	130000	120000	8%
Tantalum	Ta	µg/L	0	0	<0.05	<0.05	0%
Terbium	Tb	µg/L	0	0	<0.05	<0.05	0%
Tellurium	Te	µg/L	1	1	<0.5	<0.5	0%
Thalium	Tl	µg/L	0	0.15	<0.1	<0.1	0%
Thorium	Th	µg/L	-	-	-	-	-
Thulium	Tm	µg/L	0	0	<0.05	<0.05	0%
Tin **	Sn	µg/L	3	3.0	<3.0	<3.0	0%
Titanium	Ti	µg/L	3	3	<3.0	<3.0	0%
Tungsten	W	µg/L	1	1	<0.5	<0.5	0%
Uranium	U	µg/L	0	0.99	1.5	1.4	7%
Vanadium	V	µg/L	0	0.44	0.88	0.89	1%
Ytterbium	Yb	µg/L	0	0	<0.2	<0.2	0%
Yttrium	Y	µg/L	1	1	<1.0	<1.0	0%
Zinc	Zn	µg/L	10	10	<10	<10	0%
Zirconium	Zr	µg/L	0	0.14	<0.1	<0.1	0%

Sample description	Symbol	Units	Sample name	LN-VWD-W	LN-VWD-W	%Diff 16-17
			Sample type	FA	FA	
			Sample number	No16	No17	
			Detection limit	Field Duplicate		
Anions						
Fluoride	F	mg/L	<0.05	<5.0	<5.0	-
Chloride	Cl	mg/L	<0.05	<5.0	<5.0	-
Nitrite	NO ₂ -	mg/L	<0.05	<5.0	<5.0	-
Nitrate	NO ₃ -	mg/L	<0.05	20.2	20.2	-
Sulphate	SO ₄ 2-	mg/L	<0.10	3600.0	3600.0	-
pH	-	-	-	2.6	2.6	-
Metals						
Aluminium	Al	µg/L	5	200000	200000	0%
Antimony	Sb	µg/L	2	2	2	0%
Arsenic	As	µg/L	2	330	340	3%
Barium	Ba	µg/L	0	11	11	0%
Beryllium	Be	µg/L	0	47	47	0%
Boron	B	µg/L	1000	1000	1000	0%
Cadmium	Cd	µg/L	0	130	130	0%
Calcium	Ca	µg/L	300	490000	510000	4%
Cerium	Ce	µg/L	1	330	330	0%
Cesium	Cs	µg/L	-	-	-	-
Chromium	Cr	µg/L	5	110	120	9%
Cobalt	Co	µg/L	0	900	920	2%
Copper	Cu	µg/L	5	21000	23000	9%
Dysprosium	Dy	µg/L	0	36	35	3%
Erbium	Er	µg/L	0	18	18	0%
Europium	Eu	µg/L	0	12	13	8%
Gadolinium	Gd	µg/L	0	44	44	0%
Gallium	Ga	µg/L	5	36	39	8%
Germanium	Ge	µg/L	1	16	16	0%
Hafnium	Hf	µg/L	-	-	-	-
Holonium	Ho	µg/L	0	6.6	6.7	2%
Iridium	Ir	µg/L	1	1	1	0%
Iron	Fe	µg/L	50	490000	500000	2%
Lanthanum	La	µg/L	0	150	150	0%
Lead	Pb	µg/L	0	6.8	6.8	0%
Lithium	Li	µg/L	2	82	82	0%
Lutetium	Lu	µg/L	0	2.0	2.1	5%
Magnesium	Mg	µg/L	30	73000	75000	3%
Manganese	Mn	µg/L	0	31000	34000	9%
Molybdenum	Mo	µg/L	10	10	10	0%
Neodymium	Nd	µg/L	0	170	170	0%
Nickel	Ni	µg/L	1	960	990	3%
Niobium	Nb	µg/L	0	0.078	0.083	6%
Palladium	Pd	µg/L	-	-	-	-
Phosphorus	P	µg/L	1000	1700	1600	6%
Platinum	Pt	µg/L	0	0	0	0%
Potassium	K	µg/L	200	920	990	7%
Praseodymium	Pr	µg/L	0	41	40	2%
Rhenium	Re	µg/L	0	0	0	0%
Rhodium	Rh	µg/L	0	0	0	0%
Rubidium	Rb	µg/L	1	12	12	0%
Ruthenium	Ru	µg/L	0	0	0	0%
Samarium	Sm	µg/L	0	40	40	0%
Selenium	Se	µg/L	1	24	24	0%
Silver	Ag	µg/L	0	0.88	0.79	11%
Sodium	Na	µg/L	200	49000	50000	2%
Strontium	Sr	µg/L	1	3000	2900	3%
Sulfur	S	µg/L	1000	4900000	5200000	6%
Tantalum	Ta	µg/L	0	0	0	0%
Terbium	Tb	µg/L	0	6.6	6.5	2%
Tellurium	Te	µg/L	1	2.9	2.4	19%
Thalium	Tl	µg/L	0	0.58	0.62	7%
Thorium	Th	µg/L	-	-	-	-
Thulium	Tm	µg/L	0	2.3	2.3	0%
Tin **	Sn	µg/L	3	3.0	3.0	0%
Titanium	Ti	µg/L	3	9.8	6.9	35%
Tungsten	W	µg/L	1	1	1	0%
Uranium	U	µg/L	0	21	21	0%
Vanadium	V	µg/L	0	26	27	4%
Ytterbium	Yb	µg/L	0	14	14	0%
Yttrium	Y	µg/L	1	190	190	0%
Zinc	Zn	µg/L	10	7300	6700	9%
Zirconium	Zr	µg/L	0	2.2	2.4	9%

			Sample name	LN-VWD-W	LN-VWD-W	LN-PW-W
			Sample type	FFA	UA	UA
			Sample number	No27 *	No41	No36
Symbol	Units	Detection limit				
Sample description						
Anions						
Fluoride	F	mg/L	<0.05	<5.0	<5.0	-
Chloride	Cl	mg/L	<0.05	<5.0	<5.0	-
Nitrite	NO ₂ -	mg/L	<0.05	<5.0	<5.0	-
Nitrate	NO ₃ -	mg/L	<0.05	20.2	20.2	-
Sulphate	SO ₄ 2-	mg/L	<0.10	3600.0	3600.0	-
pH	-	-	-	2.6	2.6	-
Metals						
Aluminium	Al	µg/L	5	190000	200000	2600
Antimony	Sb	µg/L	2	2	<2.0	2.1
Arsenic	As	µg/L	2	320	270	8.0
Barium	Ba	µg/L	0	9.6	11	18
Beryllium	Be	µg/L	0	41	45	0.21
Boron	B	µg/L	1000	1000	<1000	<1000
Cadmium	Cd	µg/L	0	110	120	5.7
Calcium	Ca	µg/L	300	460000	420000	440000
Cerium	Ce	µg/L	1	290	320	9.1
Cesium	Cs	µg/L	-	-	-	-
Chromium	Cr	µg/L	5	110	100	<5.0
Cobalt	Co	µg/L	0	820	770	24
Copper	Cu	µg/L	5	22000	21000	240
Dysprosium	Dy	µg/L	0	30	35	0.96
Erbium	Er	µg/L	0	16	18	0.49
Europium	Eu	µg/L	0	10	10	0.36
Gadolinium	Gd	µg/L	0	38	44	1.1
Gallium	Ga	µg/L	5	34	35	<5.0
Germanium	Ge	µg/L	1	15	13	<1.0
Hafnium	Hf	µg/L	-	-	-	-
Holonium	Ho	µg/L	0	6.0	6.8	0.20
Iridium	Ir	µg/L	1	1	<0.5	<0.5
Iron	Fe	µg/L	50	450000	410000	13000
Lanthanum	La	µg/L	0	130	140	4.6
Lead	Pb	µg/L	0	7.0	7.1	12
Lithium	Li	µg/L	2	70	83	8.3
Lutetium	Lu	µg/L	0	1.8	2.1	<0.05
Magnesium	Mg	µg/L	30	66000	61000	20000
Manganese	Mn	µg/L	0	33000	38000	3600
Molybdenum	Mo	µg/L	10	10	<10	28
Neodymium	Nd	µg/L	0	150	170	4.7
Nickel	Ni	µg/L	1	900	830	16
Niobium	Nb	µg/L	0	0.12	0.078	<0.05
Palladium	Pd	µg/L	-	-	-	-
Phosphorus	P	µg/L	1000	1600	1500	<1000
Platinum	Pt	µg/L	0	0	<0.05	<0.05
Potassium	K	µg/L	200	980	720	2000
Praseodymium	Pr	µg/L	0	36	40	1.2
Rhenium	Re	µg/L	0	0	<0.2	<0.2
Rhodium	Rh	µg/L	0	0	<0.1	<0.1
Rubidium	Rb	µg/L	1	11	12	15
Ruthenium	Ru	µg/L	0	0	<0.1	<0.1
Samarium	Sm	µg/L	0	34	41	1.0
Selenium	Se	µg/L	1	22	25	5.2
Silver	Ag	µg/L	0	0.88	0.83	0.47
Sodium	Na	µg/L	200	45000	40000	35000
Strontium	Sr	µg/L	1	2800	2900	2200
Sulfur	S	µg/L	1000	5200000	7000000	360000
Tantalum	Ta	µg/L	0	0	<0.05	<0.05
Terbium	Tb	µg/L	0	5.6	6.6	0.17
Tellurium	Te	µg/L	1	4.2	2.8	<0.5
Thalium	Tl	µg/L	0	0.50	0.35	0.12
Thorium	Th	µg/L	-	-	-	-
Thulium	Tm	µg/L	0	2.0	2.4	0.059
Tin **	Sn	µg/L	3	3.0	<3.0	<3.0
Titanium	Ti	µg/L	3	8.0	3.9	<3.0
Tungsten	W	µg/L	1	1	<0.5	<0.5
Uranium	U	µg/L	0	18	22	0.75
Vanadium	V	µg/L	0	22	23	1.4
Ytterbium	Yb	µg/L	0	13	15	0.38
Yttrium	Y	µg/L	1	180	160	5.1
Zinc	Zn	µg/L	10	6500	6800	210
Zirconium	Zr	µg/L	0	2.0	2.1	0.10

Sample description	Sample name			IN23-W	IN23-W	IN23-W	%Diff 43-44	%Diff 44-45	%Diff 43-45
	Symbol	Units	Sample type	UA	FA	FA			
			Sample number	No43	No44	No45			
			Detection limit	Field Triplicate					
Anions									
Fluoride	F	mg/L	<0.05	<2.0	<2.0	<2.0	-	-	-
Chloride	Cl	mg/L	<0.05	16.0	16.0	16.0	-	-	-
Nitrite	NO ₂ ⁻	mg/L	<0.05	<2.0	<2.0	<2.0	-	-	-
Nitrate	NO ₃ ⁻	mg/L	<0.05	6.5	6.5	6.5	-	-	-
Sulphate	SO ₄ ²⁻	mg/L	<0.10	870.0	870.0	870.0	-	-	-
pH		-		6.7	6.7	6.7	-	-	-
Metals									
Aluminium	Al	µg/L	5	<5.0	<5.0	<5.0	0%	0%	0%
Antimony	Sb	µg/L	2	<2.0	<2.0	<2.0	0%	0%	0%
Arsenic	As	µg/L	2	3.0	3.5	2.1	15%	50%	35%
Barium	Ba	µg/L	0	21	25	25	17%	0%	17%
Beryllium	Be	µg/L	0	<0.2	<0.2	<0.2	0%	0%	0%
Boron	B	µg/L	1000	<1000	<1000	<1000	0%	0%	0%
Cadmium	Cd	µg/L	0	<0.03	<0.03	<0.03	0%	0%	0%
Calcium	Ca	µg/L	300	71000	84000	86000	17%	2%	19%
Cerium	Ce	µg/L	1	<0.5	<0.5	<0.5	0%	0%	0%
Cesium	Cs	µg/L	-	-	-	-	-	-	-
Chromium	Cr	µg/L	5	<5.0	<5.0	<5.0	0%	0%	0%
Cobalt	Co	µg/L	0	<0.05	<0.05	<0.05	0%	0%	0%
Copper	Cu	µg/L	5	<5.0	<5.0	<5.0	0%	0%	0%
Dysprosium	Dy	µg/L	0	<0.1	<0.1	<0.1	0%	0%	0%
Erbium	Er	µg/L	0	<0.1	<0.1	<0.1	0%	0%	0%
Europium	Eu	µg/L	0	<0.03	<0.03	<0.03	0%	0%	0%
Gadolinium	Gd	µg/L	0	<0.1	<0.1	<0.1	0%	0%	0%
Gallium	Ga	µg/L	5	<5.0	<5.0	<5.0	0%	0%	0%
Germanium	Ge	µg/L	1	<1.0	<1.0	<1.0	0%	0%	0%
Hafnium	Hf	µg/L	-	-	-	-	-	-	-
Holonium	Ho	µg/L	0	<0.05	<0.05	<0.05	0%	0%	0%
Iridium	Ir	µg/L	1	<0.5	<0.5	<0.5	0%	0%	0%
Iron	Fe	µg/L	50	<50	<50	<50	0%	0%	0%
Lanthanum	La	µg/L	0	<0.4	<0.4	<0.4	0%	0%	0%
Lead	Pb	µg/L	0	<0.2	<0.2	<0.2	0%	0%	0%
Lithium	Li	µg/L	2	2.0	2.4	2.4	18%	0%	18%
Lutetium	Lu	µg/L	0	<0.05	<0.05	<0.05	0%	0%	0%
Magnesium	Mg	µg/L	30	10000	12000	13000	18%	8%	26%
Manganese	Mn	µg/L	0	<0.3	1.5	1.5	133%	0%	133%
Molybdenum	Mo	µg/L	10	<10	<10	<10	0%	0%	0%
Neodymium	Nd	µg/L	0	<0.1	<0.1	<0.1	0%	0%	0%
Nickel	Ni	µg/L	1	<1.0	<1.0	<1.0	0%	0%	0%
Niobium	Nb	µg/L	0	<0.05	<0.05	<0.05	0%	0%	0%
Palladium	Pd	µg/L	-	-	-	-	-	-	-
Phosphorus	P	µg/L	1000	<1000	<1000	<1000	0%	0%	0%
Platinum	Pt	µg/L	0	<0.05	<0.05	<0.05	0%	0%	0%
Potassium	K	µg/L	200	1100	1100	1200	0%	9%	9%
Praseodymium	Pr	µg/L	0	<0.1	<0.1	<0.1	0%	0%	0%
Rhenium	Re	µg/L	0	<0.2	<0.2	<0.2	0%	0%	0%
Rhodium	Rh	µg/L	0	<0.1	<0.1	<0.1	0%	0%	0%
Rubidium	Rb	µg/L	1	1.3	1.5	1.6	14%	6%	21%
Ruthenium	Ru	µg/L	0	<0.1	<0.1	<0.1	0%	0%	0%
Samarium	Sm	µg/L	0	<0.1	<0.1	<0.1	0%	0%	0%
Selenium	Se	µg/L	1	1.1	<1.0	1.4	10%	33%	24%
Silver	Ag	µg/L	0	<0.1	<0.1	<0.1	0%	0%	0%
Sodium	Na	µg/L	200	16000	19000	20000	17%	5%	22%
Strontium	Sr	µg/L	1	720	840	860	15%	2%	18%
Sulfur	S	µg/L	1000	64000	63000	59000	2%	7%	8%
Tantalum	Ta	µg/L	0	<0.05	<0.05	<0.05	0%	0%	0%
Terbium	Tb	µg/L	0	<0.05	<0.05	<0.05	0%	0%	0%
Tellurium	Te	µg/L	1	<0.5	<0.5	<0.5	0%	0%	0%
Thallium	Tl	µg/L	0	<0.1	<0.1	<0.1	0%	0%	0%
Thorium	Th	µg/L	-	-	-	-	-	-	-
Thulium	Tm	µg/L	0	<0.05	<0.05	<0.05	0%	0%	0%
Tin **	Sn	µg/L	3	<3.0	<3.0	<3.0	0%	0%	0%
Titanium	Ti	µg/L	3	<3.0	<3.0	<3.0	0%	0%	0%
Tungsten	W	µg/L	1	<0.5	<0.5	<0.5	0%	0%	0%
Uranium	U	µg/L	0	1.2	1.3	1.4	8%	7%	15%
Vanadium	V	µg/L	0	0.32	0.34	0.34	6%	0%	6%
Ytterbium	Yb	µg/L	0	<0.2	<0.2	<0.2	0%	0%	0%
Yttrium	Y	µg/L	1	<1.0	<1.0	<1.0	0%	0%	0%
Zinc	Zn	µg/L	10	<10	<10	<10	0%	0%	0%
Zirconium	Zr	µg/L	0	<0.1	<0.1	<0.1	0%	0%	0%

Sample description	Symbol	Units	Sample name	IN28-W	IN28-W	IN28-W	%Diff 46-47	%Diff 48-47	%Diff 48-46
			Sample type	FA	FA	FA			
			Sample number	No46 *	No47	No48			
Detection limit	Field Triplicate								
Anions									
Fluoride	F	mg/L	<0.05	2.7	2.7	2.7	-	-	-
Chloride	Cl	mg/L	<0.05	8.9	8.9	8.9	-	-	-
Nitrite	NO ₂ -	mg/L	<0.05	<2.0	<2.0	<2.0	-	-	-
Nitrate	NO ₃ -	mg/L	<0.05	<2.0	<2.0	<2.0	-	-	-
Sulphate	SO ₄ 2--	mg/L	<0.10	670.0	670.0	670.0	-	-	-
pH	-	-	-	4.4	4.4	4.4	-	-	-
Metals									
Aluminium	Al	µg/L	5	15000	14000	15000	13%	6.90%	0.00%
Antimony	Sb	µg/L	2	<2.0	<2.0	<2.0	0%	0.00%	0.00%
Arsenic	As	µg/L	2	110	110	110	0%	0.00%	0.00%
Barium	Ba	µg/L	0	8.4	8.5	8.4	1%	1.18%	0.00%
Beryllium	Be	µg/L	0	1.8	1.8	1.8	0%	0.00%	0.00%
Boron	B	µg/L	1000	1800	1700	1800	11%	5.71%	0.00%
Cadmium	Cd	µg/L	0	9.0	9.1	9.2	0%	1.09%	2.20%
Calcium	Ca	µg/L	300	160000	160000	170000	0%	6.06%	6.06%
Cerium	Ce	µg/L	1	2.6	2.7	2.7	-	0.00%	3.77%
Cesium	Cs	µg/L	-	-	-	-	-	-	-
Chromium	Cr	µg/L	5	<5.0	<5.0	<5.0	0%	0.00%	0.00%
Cobalt	Co	µg/L	0	55	56	57	0%	1.77%	3.57%
Copper	Cu	µg/L	5	28000	28000	29000	0%	3.51%	3.51%
Dysprosium	Dy	µg/L	0	1.6	1.7	1.7	3%	0.00%	6.06%
Erbium	Er	µg/L	0	0.62	0.72	0.67	5%	7.19%	7.75%
Europium	Eu	µg/L	0	0.42	0.51	0.48	1%	6.06%	13.33%
Gadolinium	Gd	µg/L	0	2.0	2.1	2.1	2%	0.00%	4.88%
Gallium	Ga	µg/L	5	<5.0	<5.0	<5.0	0%	0.00%	0.00%
Germanium	Ge	µg/L	1	1.4	1.4	<1.0	-	33.33%	33.33%
Hafnium	Hf	µg/L	-	-	-	-	-	-	-
Holonium	Ho	µg/L	0	0.28	0.27	0.27	3%	0.00%	3.64%
Iridium	Ir	µg/L	1	<0.5	<0.5	<0.5	0%	0.00%	0.00%
Iron	Fe	µg/L	50	23000	23000	24000	0%	4.26%	4.26%
Lanthanum	La	µg/L	0	0.90	0.91	0.91	0%	0.00%	1.10%
Lead	Pb	µg/L	0	0.54	0.52	0.55	0%	5.61%	1.83%
Lithium	Li	µg/L	2	440	450	460	5%	2.20%	4.44%
Lutetium	Lu	µg/L	0	0.053	0.066	0.055	0%	18.18%	3.70%
Magnesium	Mg	µg/L	30	28000	28000	29000	0%	3.51%	3.51%
Manganese	Mn	µg/L	0	3200	3000	3200	12%	6.45%	0.00%
Molybdenum	Mo	µg/L	10	<10	<10	<10	0%	0.00%	0.00%
Neodymium	Nd	µg/L	0	2.2	2.3	2.5	0%	8.33%	12.77%
Nickel	Ni	µg/L	1	38	40	40	11%	0.00%	5.13%
Niobium	Nb	µg/L	0	<0.05	<0.05	<0.05	-	0.00%	0.00%
Palladium	Pd	µg/L	-	-	-	-	-	-	-
Phosphorus	P	µg/L	1000	<1000	<1000	<1000	0%	0.00%	0.00%
Platinum	Pt	µg/L	0	<0.05	<0.05	<0.05	0%	0.00%	0.00%
Potassium	K	µg/L	200	12000	12000	13000	0%	8.00%	8.00%
Praseodymium	Pr	µg/L	0	0.44	0.44	0.44	0%	0.00%	0.00%
Rhenium	Re	µg/L	0	<0.2	<0.2	<0.2	0%	0.00%	0.00%
Rhodium	Rh	µg/L	0	<0.1	<0.1	<0.1	0%	0.00%	0.00%
Rubidium	Rb	µg/L	1	120	120	120	0%	0.00%	0.00%
Ruthenium	Ru	µg/L	0	<0.1	<0.1	<0.1	0%	0.00%	0.00%
Samarium	Sm	µg/L	0	1.1	1.1	1.1	0%	0.00%	0.00%
Selenium	Se	µg/L	1	<1.0	<1.0	<1.0	0%	0.00%	0.00%
Silver	Ag	µg/L	0	<0.1	<0.1	<0.1	0%	0.00%	0.00%
Sodium	Na	µg/L	200	68000	68000	71000	0%	4.32%	4.32%
Strontium	Sr	µg/L	1	1000	960	1000	0%	4.08%	0.00%
Sulfur	S	µg/L	1000	270000	270000	270000	0%	0.00%	0.00%
Tantalum	Ta	µg/L	0	<0.05	<0.05	<0.05	0%	0.00%	0.00%
Terbium	Tb	µg/L	0	0.32	0.32	0.33	0%	3.08%	3.08%
Tellurium	Te	µg/L	1	<0.5	<0.5	<0.5	0%	0.00%	0.00%
Thalium	Tl	µg/L	0	0.28	0.26	0.29	-	10.91%	3.51%
Thorium	Th	µg/L	-	-	-	-	-	-	-
Thulium	Tm	µg/L	0	0.076	0.088	0.085	1%	3.47%	11.18%
Tin **	Sn	µg/L	3	<3.0	<3.0	<3.0	0%	0.00%	0.00%
Titanium	Ti	µg/L	3	<3.0	<3.0	<3.0	0%	0.00%	0.00%
Tungsten	W	µg/L	1	<0.5	<0.5	<0.5	0%	0.00%	0.00%
Uranium	U	µg/L	0	2.9	2.8	2.9	3%	3.51%	0.00%
Vanadium	V	µg/L	0	<0.3	<0.3	<0.3	0%	0.00%	0.00%
Ytterbium	Yb	µg/L	0	0.44	0.45	0.47	0%	4.35%	6.59%
Yttrium	Y	µg/L	1	7.0	7.2	6.9	0%	4.26%	1.44%
Zinc	Zn	µg/L	10	2000	1900	2000	10%	5.13%	0.00%
Zirconium	Zr	µg/L	0	<0.1	<0.1	42	0%	199.05%	199.05%

Sample description	Symbol	Units	Sample name	IN-RMATR-W	IN-RMATR-W	IN-RMATR-W	%Diff 49-50	%Diff 49-51	%Diff 50-51
			Sample type	FA	FA	FA			
			Sample number	No49	No50	No51			
			Detection limit		Field TriPLICATE				
Anions									
Fluoride	F	mg/L	<0.05	3.8	3.8	3.8	-	-	-
Chloride	Cl	mg/L	<0.05	14.0	14.0	14.0	-	-	-
Nitrite	NO ₂ ⁻	mg/L	<0.05	<2.0	<2.0	<2.0	-	-	-
Nitrate	NO ₃ ⁻	mg/L	<0.05	<2.0	<2.0	<2.0	-	-	-
Sulphate	SO ₄ ²⁻	mg/L	<0.10	860.0	860.0	860.0	-	-	-
pH	-	-	-	3.5	3.5	3.5	-	-	-
Metals									
Aluminium	Al	µg/L	5	30000	31000	31000	3.28%	3.28%	0.00%
Antimony	Sb	µg/L	2	<2.0	<2.0	<2.0	0.00%	0.00%	0.00%
Arsenic	As	µg/L	2	74	78	79	5.26%	6.54%	1.27%
Barium	Ba	µg/L	0	6.9	6.9	7.1	0.00%	2.86%	2.86%
Beryllium	Be	µg/L	0	2.8	2.8	2.9	0.00%	3.51%	3.51%
Boron	B	µg/L	1000	1600	1600	1600	0.00%	0.00%	0.00%
Cadmium	Cd	µg/L	0	17	16	17	6.06%	0.00%	6.06%
Calcium	Ca	µg/L	300	180000	170000	180000	5.71%	0.00%	5.71%
Cerium	Ce	µg/L	1	6.6	6.7	7.0	1.50%	5.88%	4.38%
Cesium	Cs	µg/L	-	-	-	-	-	-	-
Chromium	Cr	µg/L	5	<5.0	<5.0	<5.0	0.00%	0.00%	0.00%
Cobalt	Co	µg/L	0	87	87	89	0.00%	2.27%	2.27%
Copper	Cu	µg/L	5	20000	20000	20000	0.00%	0.00%	0.00%
Dysprosium	Dy	µg/L	0	3.3	3.2	3.3	3.08%	0.00%	3.08%
Erbium	Er	µg/L	0	1.6	1.7	1.7	6.06%	6.06%	0.00%
Europium	Eu	µg/L	0	0.74	0.77	0.80	3.97%	7.79%	3.82%
Gadolinium	Gd	µg/L	0	3.5	3.3	3.6	5.88%	2.82%	8.70%
Gallium	Ga	µg/L	5	<5.0	<5.0	<5.0	0.00%	0.00%	0.00%
Germanium	Ge	µg/L	1	1.3	1.0	1.3	26.09%	0.00%	26.09%
Hafnium	Hf	µg/L	-	-	-	-	-	-	-
Holonium	Ho	µg/L	0	0.64	0.60	0.65	6.45%	1.55%	8.00%
Iridium	Ir	µg/L	1	<0.5	<0.5	<0.5	0.00%	0.00%	0.00%
Iron	Fe	µg/L	50	23000	22000	23000	4.44%	0.00%	4.44%
Lanthanum	La	µg/L	0	1.9	1.9	2.0	0.00%	5.13%	5.13%
Lead	Pb	µg/L	0	0.82	1.1	0.80	29.17%	2.47%	31.58%
Lithium	Li	µg/L	2	460	460	470	0.00%	2.15%	2.15%
Lutetium	Lu	µg/L	0	0.15	0.16	0.17	6.45%	12.50%	6.06%
Magnesium	Mg	µg/L	30	41000	41000	42000	0.00%	2.41%	2.41%
Manganese	Mn	µg/L	0	5800	6000	6000	3.39%	3.39%	0.00%
Molybdenum	Mo	µg/L	10	<10	<10	<10	0.00%	0.00%	0.00%
Neodymium	Nd	µg/L	0	5.9	6.1	5.8	3.33%	1.71%	5.04%
Nickel	Ni	µg/L	1	59	57	60	3.45%	1.68%	5.13%
Niobium	Nb	µg/L	0	<0.05	<0.05	<0.05	0.00%	0.00%	0.00%
Palladium	Pd	µg/L	-	-	-	-	-	-	-
Phosphorus	P	µg/L	1000	<1000	<1000	<1000	0.00%	0.00%	0.00%
Platinum	Pt	µg/L	0	<0.05	<0.05	<0.05	0.00%	0.00%	0.00%
Potassium	K	µg/L	200	12000	11000	12000	8.70%	0.00%	8.70%
Praseodymium	Pr	µg/L	0	1.1	1.0	1.1	9.52%	0.00%	9.52%
Rhenium	Re	µg/L	0	<0.2	<0.2	<0.2	0.00%	0.00%	0.00%
Rhodium	Rh	µg/L	0	<0.1	<0.1	<0.1	0.00%	0.00%	0.00%
Rubidium	Rb	µg/L	1	120	110	120	8.70%	0.00%	8.70%
Ruthenium	Ru	µg/L	0	<0.1	<0.1	<0.1	0.00%	0.00%	0.00%
Samarium	Sm	µg/L	0	2.4	2.3	2.0	4.26%	18.18%	13.95%
Selenium	Se	µg/L	1	<1.0	<1.0	<1.0	0.00%	0.00%	0.00%
Silver	Ag	µg/L	0	<0.1	<0.1	<0.1	0.00%	0.00%	0.00%
Sodium	Na	µg/L	200	66000	66000	68000	0.00%	2.99%	2.99%
Strontium	Sr	µg/L	1	890	890	900	0.00%	1.12%	1.12%
Sulfur	S	µg/L	1000	310000	330000	320000	6.25%	3.17%	3.08%
Tantalum	Ta	µg/L	0	<0.05	<0.05	<0.05	0.00%	0.00%	0.00%
Terbium	Tb	µg/L	0	0.60	0.60	0.60	0.00%	0.00%	0.00%
Tellurium	Te	µg/L	1	<0.5	<0.5	<0.5	0.00%	0.00%	0.00%
Thallium	Tl	µg/L	0	0.52	0.54	0.58	3.77%	10.91%	7.14%
Thorium	Th	µg/L	-	-	-	-	-	-	-
Thulium	Tm	µg/L	0	0.21	0.19	0.19	10.00%	10.00%	0.00%
Tin **	Sn	µg/L	3	<3.0	<3.0	<3.0	0.00%	0.00%	0.00%
Titanium	Ti	µg/L	3	<3.0	<3.0	<3.0	0.00%	0.00%	0.00%
Tungsten	W	µg/L	1	<0.5	<0.5	<0.5	0.00%	0.00%	0.00%
Uranium	U	µg/L	0	7.2	7.1	7.4	1.40%	2.74%	4.14%
Vanadium	V	µg/L	0	<0.3	<0.3	<0.3	0.00%	0.00%	0.00%
Ytterbium	Yb	µg/L	0	1.2	1.2	1.1	0.00%	8.70%	8.70%
Yttrium	Y	µg/L	1	17	17	17	0.00%	0.00%	0.00%
Zinc	Zn	µg/L	10	3700	3800	3800	2.67%	2.67%	0.00%
Zirconium	Zr	µg/L	0	3.1	1.2	0.77	88.37%	120.41%	43.65%

Sample description	Symbol	Units	Sample name	IN2-W	IN2-W	IN2-W	%Diff 52-53	%Diff 54-52	%Diff 53-54
			Sample type	FA	FA	FA			
			Sample number	No52	No53	No54			
			Detection limit	Field Triplicate					
Anions									
Fluoride	F	mg/L	<0.05	2.4	2.4	2.4	-	-	-
Chloride	Cl	mg/L	<0.05	12.5	12.5	12.5	-	-	-
Nitrite	NO ₂ ⁻	mg/L	<0.05	<2.0	<2.0	<2.0	-	-	-
Nitrate	NO ₃ ⁻	mg/L	<0.05	<2.0	<2.0	<2.0	-	-	-
Sulphate	SO ₄ ²⁻	mg/L	<0.10	1050.0	1050.0	1050.0	-	-	-
pH		-		3.4	3.4	3.4	-	-	-
Metals									
Aluminium	Al	µg/L	5	46000	48000	46000	4.26%	0.00%	4.26%
Antimony	Sb	µg/L	2	<2.0	<2.0	<2.0	0.00%	0.00%	0.00%
Arsenic	As	µg/L	2	2.3	2.4	2.7	4.26%	16.00%	11.76%
Barium	Ba	µg/L	0	8.0	8.0	8.7	0.00%	8.38%	8.38%
Beryllium	Be	µg/L	0	3.1	3.1	3.4	0.00%	9.23%	9.23%
Boron	B	µg/L	1000	1400	1500	1400	6.90%	0.00%	6.90%
Cadmium	Cd	µg/L	0	19	19	21	0.00%	10.00%	10.00%
Calcium	Ca	µg/L	300	200000	200000	220000	0.00%	9.52%	9.52%
Cerium	Ce	µg/L	1	11	12	12	8.70%	8.70%	0.00%
Cesium	Cs	µg/L	-	-	-	-	-	-	-
Chromium	Cr	µg/L	5	<5.0	<5.0	<5.0	0.00%	0.00%	0.00%
Cobalt	Co	µg/L	0	110	110	120	0.00%	8.70%	8.70%
Copper	Cu	µg/L	5	16000	16000	17000	0.00%	6.06%	6.06%
Dysprosium	Dy	µg/L	0	4.6	4.8	5.2	4.26%	12.24%	8.00%
Erbium	Er	µg/L	0	2.4	2.4	2.7	0.00%	11.76%	11.76%
Europium	Eu	µg/L	0	1.1	1.1	1.1	0.00%	0.00%	0.00%
Gadolinium	Gd	µg/L	0	4.7	4.7	5.4	0.00%	13.86%	13.86%
Gallium	Ga	µg/L	5	<5.0	<5.0	<5.0	0.00%	0.00%	0.00%
Germanium	Ge	µg/L	1	1.1	<1.0	<1.0	9.52%	9.52%	0.00%
Hafnium	Hf	µg/L	-	-	-	-	-	-	-
Holonium	Ho	µg/L	0	0.93	0.95	0.98	2.13%	5.24%	3.11%
Iridium	Ir	µg/L	1	<0.5	<0.5	<0.5	0.00%	0.00%	0.00%
Iron	Fe	µg/L	50	13000	13000	15000	0.00%	14.29%	14.29%
Lanthanum	La	µg/L	0	3.5	3.6	3.9	2.82%	10.81%	8.00%
Lead	Pb	µg/L	0	0.86	0.92	1.0	6.74%	15.05%	8.33%
Lithium	Li	µg/L	2	410	420	460	2.41%	11.49%	9.09%
Lutetium	Lu	µg/L	0	0.22	0.25	0.26	12.77%	16.67%	3.92%
Magnesium	Mg	µg/L	30	51000	51000	56000	0.00%	9.35%	9.35%
Manganese	Mn	µg/L	0	7500	7600	7400	1.32%	1.34%	2.67%
Molybdenum	Mo	µg/L	10	<10	<10	<10	0.00%	0.00%	0.00%
Neodymium	Nd	µg/L	0	9.8	9.6	10	2.06%	2.02%	4.08%
Nickel	Ni	µg/L	1	74	75	83	1.34%	11.46%	10.13%
Niobium	Nb	µg/L	0	<0.05	<0.05	<0.05	0.00%	0.00%	0.00%
Palladium	Pd	µg/L	-	-	-	-	-	-	-
Phosphorus	P	µg/L	1000	<1000	<1000	<1000	0.00%	0.00%	0.00%
Platinum	Pt	µg/L	0	<0.05	<0.05	<0.05	0.00%	0.00%	0.00%
Potassium	K	µg/L	200	10000	10000	11000	0.00%	9.52%	9.52%
Praseodymium	Pr	µg/L	0	1.8	1.9	1.9	5.41%	5.41%	0.00%
Rhenium	Re	µg/L	0	0.23	<0.2	<0.2	13.95%	13.95%	0.00%
Rhodium	Rh	µg/L	0	<0.1	<0.1	<0.1	0.00%	0.00%	0.00%
Rubidium	Rb	µg/L	1	95	96	100	1.05%	5.13%	4.08%
Ruthenium	Ru	µg/L	0	<0.1	<0.1	<0.1	0.00%	0.00%	0.00%
Samarium	Sm	µg/L	0	3.3	3.2	3.5	3.08%	5.88%	8.96%
Selenium	Se	µg/L	1	<1.0	<1.0	1.2	0.00%	18.18%	18.18%
Silver	Ag	µg/L	0	<0.1	<0.1	<0.1	0.00%	0.00%	0.00%
Sodium	Na	µg/L	200	62000	63000	69000	1.60%	10.69%	9.09%
Strontium	Sr	µg/L	1	810	830	890	2.44%	9.41%	6.98%
Sulfur	S	µg/L	1000	420000	370000	360000	12.66%	15.38%	2.74%
Tantalum	Ta	µg/L	0	<0.05	<0.05	<0.05	0.00%	0.00%	0.00%
Terbium	Tb	µg/L	0	0.81	0.84	0.91	3.64%	11.63%	8.00%
Tellurium	Te	µg/L	1	<0.5	<0.5	<0.5	0.00%	0.00%	0.00%
Thallium	Tl	µg/L	0	0.43	0.49	0.51	13.04%	17.02%	4.00%
Thorium	Th	µg/L	-	-	-	-	-	-	-
Thulium	Tm	µg/L	0	0.29	0.31	0.33	6.67%	12.90%	6.25%
Tin **	Sn	µg/L	3	<3.0	<3.0	<3.0	0.00%	0.00%	0.00%
Titanium	Ti	µg/L	3	<3.0	<3.0	<3.0	0.00%	0.00%	0.00%
Tungsten	W	µg/L	1	<0.5	<0.5	<0.5	0.00%	0.00%	0.00%
Uranium	U	µg/L	0	10	11	11	9.52%	9.52%	0.00%
Vanadium	V	µg/L	0	<0.3	<0.3	<0.3	0.00%	0.00%	0.00%
Ytterbium	Yb	µg/L	0	1.8	1.8	2.1	0.00%	15.38%	15.38%
Yttrium	Y	µg/L	1	25	25	28	0.00%	11.32%	11.32%
Zinc	Zn	µg/L	10	4100	4200	4000	2.41%	2.47%	4.88%
Zirconium	Zr	µg/L	0	0.54	0.42	0.37	25.00%	37.36%	12.66%

Sample description	Symbol	Units	Sample name	IN13-W	IN13-W	IN13-W	%Diff 55-57	%Diff 55-56	%Diff 56-57
			Sample type	FA	FA	FA			
			Sample number	No55	No56	No57			
			Detection limit	Field Triplicate					
Anions									
Fluoride	F	mg/L	<0.05	2.2	2.2	2.2	-	-	-
Chloride	Cl	mg/L	<0.05	140.0	140.0	140.0	-	-	-
Nitrite	NO ₂ ⁻	mg/L	<0.05	<2.0	<2.0	<2.0	-	-	-
Nitrate	NO ₃ ⁻	mg/L	<0.05	<2.0	<2.0	<2.0	-	-	-
Sulphate	SO ₄ ²⁻	mg/L	<0.10	995.0	995.0	995.0	-	-	-
pH		-		4.3	4.3	4.3	-	-	-
Metals									
Aluminium	Al	µg/L	5	24000	23000	24000	0.00%	4.26%	4.26%
Antimony	Sb	µg/L	2	<2.0	<2.0	<2.0	0.00%	0.00%	0.00%
Arsenic	As	µg/L	2	61	64	62	1.63%	4.80%	3.17%
Barium	Ba	µg/L	0	14	13	13	7.41%	7.41%	0.00%
Beryllium	Be	µg/L	0	1.9	1.9	1.9	0.00%	0.00%	0.00%
Boron	B	µg/L	1000	5500	5400	5600	1.80%	1.83%	3.64%
Cadmium	Cd	µg/L	0	11	11	11	0.00%	0.00%	0.00%
Calcium	Ca	µg/L	300	250000	250000	250000	0.00%	0.00%	0.00%
Cerium	Ce	µg/L	1	9.2	9.2	8.9	3.31%	0.00%	3.31%
Cesium	Cs	µg/L	-	-	-	-	-	-	-
Chromium	Cr	µg/L	5	<5.0	<5.0	<5.0	0.00%	0.00%	0.00%
Cobalt	Co	µg/L	0	75	75	73	2.70%	0.00%	2.70%
Copper	Cu	µg/L	5	8600	8500	8300	3.55%	1.17%	2.38%
Dysprosium	Dy	µg/L	0	3.5	3.4	3.2	8.96%	2.90%	6.06%
Erbium	Er	µg/L	0	1.7	1.7	1.6	6.06%	0.00%	6.06%
Europium	Eu	µg/L	0	0.91	0.68	0.66	31.85%	28.93%	2.99%
Gadolinium	Gd	µg/L	0	3.6	3.6	3.5	2.82%	0.00%	2.82%
Gallium	Ga	µg/L	5	<5.0	<5.0	<5.0	0.00%	0.00%	0.00%
Germanium	Ge	µg/L	1	1.8	1.3	1.6	11.76%	32.26%	20.69%
Hafnium	Hf	µg/L	-	-	-	-	-	-	-
Holonium	Ho	µg/L	0	0.67	0.64	0.63	6.15%	4.58%	1.57%
Iridium	Ir	µg/L	1	<0.5	<0.5	<0.5	0.00%	0.00%	0.00%
Iron	Fe	µg/L	50	3600	3600	3500	2.82%	0.00%	2.82%
Lanthanum	La	µg/L	0	3.2	3.2	3.2	0.00%	0.00%	0.00%
Lead	Pb	µg/L	0	0.31	0.34	0.33	6.25%	9.23%	2.99%
Lithium	Li	µg/L	2	1300	1300	1300	0.00%	0.00%	0.00%
Lutetium	Lu	µg/L	0	0.16	0.17	0.17	6.06%	6.06%	0.00%
Magnesium	Mg	µg/L	30	63000	62000	61000	3.23%	1.60%	1.63%
Manganese	Mn	µg/L	0	5100	5000	5400	5.71%	1.98%	7.69%
Molybdenum	Mo	µg/L	10	<10	<10	<10	0.00%	0.00%	0.00%
Neodymium	Nd	µg/L	0	7.7	7.7	7.4	3.97%	0.00%	3.97%
Nickel	Ni	µg/L	1	51	50	50	1.98%	1.98%	0.00%
Niobium	Nb	µg/L	0	<0.05	<0.05	<0.05	0.00%	0.00%	0.00%
Palladium	Pd	µg/L	-	-	-	-	-	-	-
Phosphorus	P	µg/L	1000	<1000	<1000	<1000	0.00%	0.00%	0.00%
Platinum	Pt	µg/L	0	<0.05	<0.05	<0.05	0.00%	0.00%	0.00%
Potassium	K	µg/L	200	15000	15000	15000	0.00%	0.00%	0.00%
Praseodymium	Pr	µg/L	0	1.5	1.5	1.4	6.90%	0.00%	6.90%
Rhenium	Re	µg/L	0	0.21	<0.2	0.24	13.33%	4.88%	18.18%
Rhodium	Rh	µg/L	0	<0.1	<0.1	<0.1	0.00%	0.00%	0.00%
Rubidium	Rb	µg/L	1	140	140	140	0.00%	0.00%	0.00%
Ruthenium	Ru	µg/L	0	<0.1	<0.1	<0.1	0.00%	0.00%	0.00%
Samarium	Sm	µg/L	0	2.4	2.4	2.5	4.08%	0.00%	4.08%
Selenium	Se	µg/L	1	1.7	2.1	2.1	21.05%	21.05%	0.00%
Silver	Ag	µg/L	0	<0.1	<0.1	<0.1	0.00%	0.00%	0.00%
Sodium	Na	µg/L	200	180000	180000	180000	0.00%	0.00%	0.00%
Strontium	Sr	µg/L	1	1100	1100	1100	0.00%	0.00%	0.00%
Sulfur	S	µg/L	1000	350000	350000	360000	2.82%	0.00%	2.82%
Tantalum	Ta	µg/L	0	<0.05	<0.05	<0.05	0.00%	0.00%	0.00%
Terbium	Tb	µg/L	0	0.61	0.61	0.57	6.78%	0.00%	6.78%
Tellurium	Te	µg/L	1	<0.5	<0.5	<0.5	0.00%	0.00%	0.00%
Thallium	Tl	µg/L	0	0.48	0.44	0.45	6.45%	8.70%	2.25%
Thorium	Th	µg/L	-	-	-	-	-	-	-
Thulium	Tm	µg/L	0	0.21	0.22	0.21	0.00%	4.65%	4.65%
Tin **	Sn	µg/L	3	<3.0	<3.0	<3.0	0.00%	0.00%	0.00%
Titanium	Ti	µg/L	3	<3.0	<3.0	<3.0	0.00%	0.00%	0.00%
Tungsten	W	µg/L	1	<0.5	<0.5	<0.5	0.00%	0.00%	0.00%
Uranium	U	µg/L	0	6.0	5.8	5.7	5.13%	3.39%	1.74%
Vanadium	V	µg/L	0	<0.3	<0.3	<0.3	0.00%	0.00%	0.00%
Ytterbium	Yb	µg/L	0	1.4	1.2	1.1	24.00%	15.38%	8.70%
Yttrium	Y	µg/L	1	19	19	19	0.00%	0.00%	0.00%
Zinc	Zn	µg/L	10	2400	2300	2400	0.00%	4.26%	4.26%
Zirconium	Zr	µg/L	0	0.33	0.28	0.27	20.00%	16.39%	3.64%

Sample description	Symbol	Units	Sample name	P-ARD-17-W	P-ARD-17-W	%Diff 73-74
			Sample type	FA	FA	
			Sample number	No73	No74	
			Detection limit	Field Duplicate		
Anions						
Fluoride	F	mg/L	<0.05	<0.10	<0.10	-
Chloride	Cl	mg/L	<0.05	0.5	0.5	-
Nitrite	NO ₂ -	mg/L	<0.05	<0.10	<0.10	-
Nitrate	NO ₃ -	mg/L	<0.05	<0.10	<0.10	-
Sulphate	SO ₄ 2-	mg/L	<0.10	54.0	54.0	-
pH		-		3.1	3.1	-
Metals						
Aluminium	Al	µg/L	5	2300	2400	4%
Antimony	Sb	µg/L	2	4.5	4.7	4%
Arsenic	As	µg/L	2	33	33	0%
Barium	Ba	µg/L	0	23	22	4%
Beryllium	Be	µg/L	0	<0.2	<0.2	0%
Boron	B	µg/L	1000	<1000	<1000	0%
Cadmium	Cd	µg/L	0	2.2	1.9	15%
Calcium	Ca	µg/L	300	2300	2600	12%
Cerium	Ce	µg/L	1	1.0	0.96	4%
Cesium	Cs	µg/L	-	-	-	
Chromium	Cr	µg/L	5	<5.0	<5.0	0%
Cobalt	Co	µg/L	0	3.3	3.5	6%
Copper	Cu	µg/L	5	600	620	3%
Dysprosium	Dy	µg/L	0	0.25	0.22	13%
Erbium	Er	µg/L	0	0.15	0.13	14%
Europium	Eu	µg/L	0	0.033	0.082	85%
Gadolinium	Gd	µg/L	0	0.25	0.21	17%
Gallium	Ga	µg/L	5	<5.0	<5.0	0%
Germanium	Ge	µg/L	1	<1.0	<1.0	0%
Hafnium	Hf	µg/L	-	-	-	
Holonium	Ho	µg/L	0	0.052	0.050	4%
Iridium	Ir	µg/L	1	<0.5	<0.5	0%
Iron	Fe	µg/L	50	5000	5100	2%
Lanthanum	La	µg/L	0	0.45	0.44	2%
Lead	Pb	µg/L	0	5.2	4.7	10%
Lithium	Li	µg/L	2	<2.0	<2.0	0%
Lutetium	Lu	µg/L	0	<0.05	<0.05	0%
Magnesium	Mg	µg/L	30	710	730	3%
Manganese	Mn	µg/L	0	1600	1600	0%
Molybdenum	Mo	µg/L	10	<10	<10	0%
Neodymium	Nd	µg/L	0	0.70	0.68	3%
Nickel	Ni	µg/L	1	2.4	2.4	0%
Niobium	Nb	µg/L	0	<0.05	<0.05	0%
Palladium	Pd	µg/L	-	-	-	
Phosphorus	P	µg/L	1000	<1000	<1000	0%
Platinum	Pt	µg/L	0	<0.05	<0.05	0%
Potassium	K	µg/L	200	1300	1300	0%
Praseodymium	Pr	µg/L	0	0.15	0.15	0%
Rhenium	Re	µg/L	0	<0.2	<0.2	0%
Rhodium	Rh	µg/L	0	<0.1	<0.1	0%
Rubidium	Rb	µg/L	1	6.6	6.2	6%
Ruthenium	Ru	µg/L	0	<0.1	<0.1	0%
Samarium	Sm	µg/L	0	0.21	0.19	10%
Selenium	Se	µg/L	1	<1.0	1.0	0%
Silver	Ag	µg/L	0	<0.1	<0.1	0%
Sodium	Na	µg/L	200	1100	1100	0%
Strontium	Sr	µg/L	1	8.7	9.3	7%
Sulfur	S	µg/L	1000	20000	20000	0%
Tantalum	Ta	µg/L	0	<0.05	<0.05	0%
Terbium	Tb	µg/L	0	<0.05	<0.05	0%
Tellurium	Te	µg/L	1	<0.5	<0.5	0%
Thalium	Tl	µg/L	0	<0.1	<0.1	0%
Thorium	Th	µg/L	-	-	-	
Thulium	Tm	µg/L	0	<0.05	<0.05	0%
Tin **	Sn	µg/L	3	<3.0	<3.0	0%
Titanium	Ti	µg/L	3	<3.0	<3.0	0%
Tungsten	W	µg/L	1	<0.5	<0.5	0%
Uranium	U	µg/L	0	0.20	0.20	0%
Vanadium	V	µg/L	0	<0.3	<0.3	0%
Ytterbium	Yb	µg/L	0	<0.2	<0.2	0%
Yttrium	Y	µg/L	1	1.3	1.5	14%
Zinc	Zn	µg/L	10	1800	1800	0%
Zirconium	Zr	µg/L	0	<0.1	<0.1	0%

Sample description	Sample name			P-ARD17- W	P-ARD17- W	%Diff 65-66
	Symbol	Units	Sample type	UA	UA	
			Sample number	No66	No65 *	
			Detection limit	Field Duplicate		
Anions						
Fluoride	F	mg/L	<0.05	<0.10	<0.10	-
Chloride	Cl	mg/L	<0.05	0.5	0.5	-
Nitrite	NO ₂ -	mg/L	<0.05	<0.10	<0.10	-
Nitrate	NO ₃ -	mg/L	<0.05	<0.10	<0.10	-
Sulphate	SO ₄ 2--	mg/L	<0.10	54.0	54.0	-
pH		-		3.1	3.1	-
Metals						
Aluminium	Al	µg/L	5	2200	2200	0%
Antimony	Sb	µg/L	2	4.7	4.7	0%
Arsenic	As	µg/L	2	35	34	3%
Barium	Ba	µg/L	0	21	21	0%
Beryllium	Be	µg/L	0	<0.2	<0.2	0%
Boron	B	µg/L	1000	<1000	<1000	0%
Cadmium	Cd	µg/L	0	2.0	2.0	0%
Calcium	Ca	µg/L	300	2200	2400	9%
Cerium	Ce	µg/L	1	0.94	0.96	2%
Cesium	Cs	µg/L	-	-	-	-
Chromium	Cr	µg/L	5	<5.0	<5.0	0%
Cobalt	Co	µg/L	0	3.4	3.4	0%
Copper	Cu	µg/L	5	600	600	0%
Dysprosium	Dy	µg/L	0	0.23	0.22	4%
Erbium	Er	µg/L	0	0.13	0.12	8%
Europium	Eu	µg/L	0	0.084	0.057	38%
Gadolinium	Gd	µg/L	0	0.23	0.21	9%
Gallium	Ga	µg/L	5	<5.0	<5.0	0%
Germanium	Ge	µg/L	1	<1.0	<1.0	0%
Hafnium	Hf	µg/L	-	-	-	-
Holonium	Ho	µg/L	0	<0.05	<0.05	0%
Iridium	Ir	µg/L	1	<0.5	<0.5	0%
Iron	Fe	µg/L	50	5000	5000	0%
Lanthanum	La	µg/L	0	<0.4	0.41	2%
Lead	Pb	µg/L	0	4.8	4.9	2%
Lithium	Li	µg/L	2	<2.0	<2.0	0%
Lutetium	Lu	µg/L	0	<0.05	<0.05	0%
Magnesium	Mg	µg/L	30	690	700	1%
Manganese	Mn	µg/L	0	1500	1500	0%
Molybdenum	Mo	µg/L	10	<10	<10	0%
Neodymium	Nd	µg/L	0	0.71	0.68	4%
Nickel	Ni	µg/L	1	3.5	3.6	3%
Niobium	Nb	µg/L	0	<0.05	<0.05	0%
Palladium	Pd	µg/L	-	-	-	-
Phosphorus	P	µg/L	1000	<1000	<1000	0%
Platinum	Pt	µg/L	0	<0.05	<0.05	0%
Potassium	K	µg/L	200	1200	1200	0%
Praseodymium	Pr	µg/L	0	0.14	0.14	0%
Rhenium	Re	µg/L	0	<0.2	<0.2	0%
Rhodium	Rh	µg/L	0	<0.1	<0.1	0%
Rubidium	Rb	µg/L	1	6.0	6.2	3%
Ruthenium	Ru	µg/L	0	<0.1	<0.1	0%
Samarium	Sm	µg/L	0	0.20	0.18	11%
Selenium	Se	µg/L	1	1.1	1.1	0%
Silver	Ag	µg/L	0	<0.1	<0.1	0%
Sodium	Na	µg/L	200	1100	1100	0%
Strontium	Sr	µg/L	1	8.4	9.8	15%
Sulfur	S	µg/L	1000	19000	19000	0%
Tantalum	Ta	µg/L	0	<0.05	<0.05	0%
Terbium	Tb	µg/L	0	<0.05	<0.05	0%
Tellurium	Te	µg/L	1	<0.5	<0.5	0%
Thalium	Tl	µg/L	0	<0.1	<0.1	0%
Thorium	Th	µg/L	-	-	-	-
Thulium	Tm	µg/L	0	<0.05	<0.05	0%
Tin **	Sn	µg/L	3	<3.0	<3.0	0%
Titanium	Ti	µg/L	3	<3.0	<3.0	0%
Tungsten	W	µg/L	1	<0.5	<0.5	0%
Uranium	U	µg/L	0	0.18	0.18	0%
Vanadium	V	µg/L	0	<0.3	<0.3	0%
Ytterbium	Yb	µg/L	0	<0.2	<0.2	0%
Yttrium	Y	µg/L	1	1.4	1.4	0%
Zinc	Zn	µg/L	10	1700	1700	0%
Zirconium	Zr	µg/L	0	<0.1	0.80	156%

Sample description	Symbol	Units	Sample name	P-WRD-W	P-WRD-W	P-WRD-W	%Diff 62-67	%Diff 62-68	%Diff 67-68
			Sample type	UA	UA	UA			
			Sample number	No62	No67	No68			
			Detection limit	Field Triplicate					
Anions									
Fluoride	F	mg/L	<0.05	<5.0	<5.0	<5.0	-	-	-
Chloride	Cl	mg/L	<0.05	<5.0	<5.0	<5.0	-	-	-
Nitrite	NO ₂ -	mg/L	<0.05	<5.0	<5.0	<5.0	-	-	-
Nitrate	NO ₃ -	mg/L	<0.05	<5.0	<5.0	<5.0	-	-	-
Sulphate	SO ₄ 2--	mg/L	<0.10	2750.0	2750.0	2750.0	-	-	-
pH	-	-	-	2.6	2.6	2.6	-	-	-
Metals									
Aluminium	Al	µg/L	5	100000	75000	76000	29%	27%	1%
Antimony	Sb	µg/L	2	<2.0	<2.0	<2.0	0%	0%	0%
Arsenic	As	µg/L	2	850	630	630	30%	30%	0%
Barium	Ba	µg/L	0	8.5	6.1	6.2	33%	31%	2%
Beryllium	Be	µg/L	0	30	21	21	35%	35%	0%
Boron	B	µg/L	1000	<1000	<1000	<1000	0%	0%	0%
Cadmium	Cd	µg/L	0	730	520	520	34%	34%	0%
Calcium	Ca	µg/L	300	360000	260000	250000	32%	36%	4%
Cerium	Ce	µg/L	1	280	200	200	33%	33%	0%
Cesium	Cs	µg/L	-	-	-	-	-	-	-
Chromium	Cr	µg/L	5	17	12	11	34%	43%	9%
Cobalt	Co	µg/L	0	720	510	500	34%	36%	2%
Copper	Cu	µg/L	5	35000	25000	25000	33%	33%	0%
Dysprosium	Dy	µg/L	0	37	26	25	35%	39%	4%
Erbium	Er	µg/L	0	18	13	13	32%	32%	0%
Europium	Eu	µg/L	0	15	10	10	40%	40%	0%
Gadolinium	Gd	µg/L	0	49	33	33	39%	39%	0%
Gallium	Ga	µg/L	5	30	19	20	45%	40%	5%
Germanium	Ge	µg/L	1	16	10	11	46%	37%	10%
Hafnium	Hf	µg/L	-	-	-	-	-	-	-
Holonium	Ho	µg/L	0	7.1	5.0	5.0	35%	35%	0%
Iridium	Ir	µg/L	1	<0.5	<0.5	<0.5	0%	0%	0%
Iron	Fe	µg/L	50	450000	310000	310000	37%	37%	0%
Lanthanum	La	µg/L	0	130	89	89	37%	37%	0%
Lead	Pb	µg/L	0	16	12	11	29%	37%	9%
Lithium	Li	µg/L	2	79	59	60	29%	27%	2%
Lutetium	Lu	µg/L	0	1.9	1.3	1.3	38%	38%	0%
Magnesium	Mg	µg/L	30	44000	31000	31000	35%	35%	0%
Manganese	Mn	µg/L	0	110000	80000	79000	32%	33%	1%
Molybdenum	Mo	µg/L	10	<10	<10	<10	0%	0%	0%
Neodymium	Nd	µg/L	0	170	110	120	43%	34%	9%
Nickel	Ni	µg/L	1	200	140	140	35%	35%	0%
Niobium	Nb	µg/L	0	0.076	<0.05	<0.05	41%	41%	0%
Palladium	Pd	µg/L	-	-	-	-	-	-	-
Phosphorus	P	µg/L	1000	3200	2500	2600	25%	21%	4%
Platinum	Pt	µg/L	0	<0.05	<0.05	<0.05	0%	0%	0%
Potassium	K	µg/L	200	1300	900	910	36%	35%	1%
Praseodymium	Pr	µg/L	0	38	26	26	38%	38%	0%
Rhenium	Re	µg/L	0	<0.2	<0.2	<0.2	0%	0%	0%
Rhodium	Rh	µg/L	0	<0.1	<0.1	<0.1	0%	0%	0%
Rubidium	Rb	µg/L	1	7.2	5.6	5.5	25%	27%	2%
Ruthenium	Ru	µg/L	0	<0.1	<0.1	<0.1	0%	0%	0%
Samarium	Sm	µg/L	0	41	28	29	38%	34%	4%
Selenium	Se	µg/L	1	8.2	6.0	6.4	31%	25%	6%
Silver	Ag	µg/L	0	<0.1	<0.1	<0.1	0%	0%	0%
Sodium	Na	µg/L	200	11000	9000	9000	20%	20%	0%
Strontium	Sr	µg/L	1	1000	800	800	22%	22%	0%
Sulfur	S	µg/L	1000	820000	630000	620000	26%	28%	2%
Tantalum	Ta	µg/L	0	<0.05	<0.05	<0.05	0%	0%	0%
Terbium	Tb	µg/L	0	7.1	4.9	4.9	37%	37%	0%
Tellurium	Te	µg/L	1	3.1	1.9	1.5	48%	70%	24%
Thalium	Tl	µg/L	0	1.6	0.95	0.94	51%	52%	1%
Thorium	Th	µg/L	-	-	-	-	-	-	-
Thulium	Tm	µg/L	0	2.3	1.6	1.6	36%	36%	0%
Tin **	Sn	µg/L	3	<3.0	<3.0	<3.0	0%	0%	0%
Titanium	Ti	µg/L	3	5.2	<3.0	<3.0	54%	54%	0%
Tungsten	W	µg/L	1	<0.5	<0.5	<0.5	0%	0%	0%
Uranium	U	µg/L	0	34	24	24	34%	34%	0%
Vanadium	V	µg/L	0	11	8.3	7.9	28%	33%	5%
Ytterbium	Yb	µg/L	0	14	9.8	9.7	35%	36%	1%
Yttrium	Y	µg/L	1	220	150	150	38%	38%	0%
Zinc	Zn	µg/L	10	28000	20000	19000	33%	38%	5%
Zirconium	Zr	µg/L	0	0.25	0.56	0.32	77%	25%	55%

Sample description	Symbol	Units	Sample name	P-WRD-W	P-WRD-W	P-WRD-W	%Diff 76-77	%Diff 77-78	%Diff 76-78
			Sample type	FA	FA	FA			
			Sample number	No76	No77	No78			
Detection limit	Field Triplicate								
Anions									
Fluoride	F	mg/L	<0.05	<5.0	<5.0	<5.0	-	-	-
Chloride	Cl	mg/L	<0.05	<5.0	<5.0	<5.0	-	-	-
Nitrite	NO ₂ -	mg/L	<0.05	<5.0	<5.0	<5.0	-	-	-
Nitrate	NO ₃ -	mg/L	<0.05	<5.0	<5.0	<5.0	-	-	-
Sulphate	SO ₄ 2-	mg/L	<0.10	2750.0	2750.0	2750.0	-	-	-
pH	-	-	-	2.6	2.6	2.6	-	-	-
Metals									
Aluminium	Al	µg/L	5	120000	120000	110000	0%	9%	9%
Antimony	Sb	µg/L	2	<2.0	<2.0	<2.0	0%	0%	0%
Arsenic	As	µg/L	2	910	890	890	2%	0%	2%
Barium	Ba	µg/L	0	9.3	9.1	9.0	2%	1%	3%
Beryllium	Be	µg/L	0	32	31	31	3%	0%	3%
Boron	B	µg/L	1000	<1000	<1000	<1000	0%	0%	0%
Cadmium	Cd	µg/L	0	790	770	760	3%	1%	4%
Calcium	Ca	µg/L	300	390000	380000	380000	3%	0%	3%
Cerium	Ce	µg/L	1	310	310	300	0%	3%	3%
Cesium	Cs	µg/L	-	-	-	-	-	-	-
Chromium	Cr	µg/L	5	18	17	18	6%	6%	0%
Cobalt	Co	µg/L	0	770	760	760	1%	0%	1%
Copper	Cu	µg/L	5	37000	37000	37000	0%	0%	0%
Dysprosium	Dy	µg/L	0	41	40	39	2%	3%	5%
Erbium	Er	µg/L	0	20	20	19	0%	5%	5%
Europium	Eu	µg/L	0	16	16	16	0%	0%	0%
Gadolinium	Gd	µg/L	0	52	51	50	2%	2%	4%
Gallium	Ga	µg/L	5	30	31	30	3%	3%	0%
Germanium	Ge	µg/L	1	18	16	16	12%	0%	12%
Hafnium	Hf	µg/L	-	-	-	-	-	-	-
Holonium	Ho	µg/L	0	7.9	7.7	7.5	3%	3%	5%
Iridium	Ir	µg/L	1	<0.5	<0.5	<0.5	0%	0%	0%
Iron	Fe	µg/L	50	480000	470000	470000	2%	0%	2%
Lanthanum	La	µg/L	0	140	140	140	0%	0%	0%
Lead	Pb	µg/L	0	16	16	16	0%	0%	0%
Lithium	Li	µg/L	2	84	84	82	0%	2%	2%
Lutetium	Lu	µg/L	0	2.0	2.0	2.0	0%	0%	0%
Magnesium	Mg	µg/L	30	47000	47000	47000	0%	0%	0%
Manganese	Mn	µg/L	0	140000	160000	140000	13%	13%	0%
Molybdenum	Mo	µg/L	10	<10	<10	<10	0%	0%	0%
Neodymium	Nd	µg/L	0	180	180	170	0%	6%	6%
Nickel	Ni	µg/L	1	210	200	200	5%	0%	5%
Niobium	Nb	µg/L	0	<0.05	<0.05	<0.05	0%	0%	0%
Palladium	Pd	µg/L	-	-	-	-	-	-	-
Phosphorus	P	µg/L	1000	3700	3700	3500	0%	6%	6%
Platinum	Pt	µg/L	0	<0.05	<0.05	<0.05	0%	0%	0%
Potassium	K	µg/L	200	1200	1300	1300	8%	0%	8%
Praseodymium	Pr	µg/L	0	41	40	40	2%	0%	2%
Rhenium	Re	µg/L	0	<0.2	<0.2	<0.2	0%	0%	0%
Rhodium	Rh	µg/L	0	<0.1	<0.1	<0.1	0%	0%	0%
Rubidium	Rb	µg/L	1	7.5	7.6	7.2	1%	5%	4%
Ruthenium	Ru	µg/L	0	<0.1	<0.1	<0.1	0%	0%	0%
Samarium	Sm	µg/L	0	46	44	44	4%	0%	4%
Selenium	Se	µg/L	1	9.0	7.9	8.1	13%	2%	11%
Silver	Ag	µg/L	0	<0.1	<0.1	<0.1	0%	0%	0%
Sodium	Na	µg/L	200	12000	12000	12000	0%	0%	0%
Strontium	Sr	µg/L	1	1300	1300	1200	0%	8%	8%
Sulfur	S	µg/L	1000	890000	1000000	900000	12%	11%	1%
Tantalum	Ta	µg/L	0	<0.05	<0.05	<0.05	0%	0%	0%
Terbium	Tb	µg/L	0	7.6	7.5	7.5	1%	0%	1%
Tellurium	Te	µg/L	1	2.4	2.2	2.7	9%	20%	12%
Thalium	Tl	µg/L	0	1.4	1.4	1.4	0%	0%	0%
Thorium	Th	µg/L	-	-	-	-	-	-	-
Thulium	Tm	µg/L	0	2.5	2.5	2.4	0%	4%	4%
Tin **	Sn	µg/L	3	<3.0	<3.0	<3.0	0%	0%	0%
Titanium	Ti	µg/L	3	3.2	5.2	<3.0	48%	54%	6%
Tungsten	W	µg/L	1	<0.5	<0.5	<0.5	0%	0%	0%
Uranium	U	µg/L	0	36	35	35	3%	0%	3%
Vanadium	V	µg/L	0	12	11	11	9%	0%	9%
Ytterbium	Yb	µg/L	0	15	15	15	0%	0%	0%
Yttrium	Y	µg/L	1	240	230	230	4%	0%	4%
Zinc	Zn	µg/L	10	34000	41000	35000	19%	16%	3%
Zirconium	Zr	µg/L	0	0.38	0.34	0.36	11%	6%	5%

Sample description	Symbol	Units	Sample name	P-EC-W	P-EC-W	P-EC-W	%Diff 61-69	%Diff 61-70	%Diff 69-70
			Sample type	UA	UA	UA			
			Sample number	No61	No69	No70			
			Detection limit	Field Triplicate					
Anions									
Fluoride	F	mg/L	<0.05	<5.0	<5.0	<5.0	-	-	-
Chloride	Cl	mg/L	<0.05	<5.0	<5.0	<5.0	-	-	-
Nitrite	NO ₂ -	mg/L	<0.05	<5.0	<5.0	<5.0	-	-	-
Nitrate	NO ₃ -	mg/L	<0.05	<5.0	<5.0	<5.0	-	-	-
Sulphate	SO ₄ 2--	mg/L	<0.10	1200.0	1200.0	1200.0	-	-	-
pH	-	-	-	2.8	2.8	2.8	-	-	-
Metals									
Aluminium	Al	µg/L	5	38000	38000	39000	0%	3%	1%
Antimony	Sb	µg/L	2	<2.0	<2.0	<2.0	0%	0%	0%
Arsenic	As	µg/L	2	25	8.1	8.0	102%	103%	0%
Barium	Ba	µg/L	0	32	34	34	6%	6%	0%
Beryllium	Be	µg/L	0	7.5	7.8	7.6	4%	1%	1%
Boron	B	µg/L	1000	<1000	<1000	<1000	0%	0%	0%
Cadmium	Cd	µg/L	0	1000	1100	1100	10%	10%	0%
Calcium	Ca	µg/L	300	360000	360000	370000	0%	3%	1%
Cerium	Ce	µg/L	1	62	66	65	6%	5%	0%
Cesium	Cs	µg/L	-	-	-	-	-	-	-
Chromium	Cr	µg/L	5	<5.0	<5.0	<5.0	0%	0%	0%
Cobalt	Co	µg/L	0	350	360	370	3%	6%	1%
Copper	Cu	µg/L	5	5100	5300	5400	4%	6%	0%
Dysprosium	Dy	µg/L	0	11	11	11	0%	0%	0%
Erbium	Er	µg/L	0	5.0	5.5	5.5	10%	10%	0%
Europium	Eu	µg/L	0	3.9	3.9	3.8	0%	3%	1%
Gadolinium	Gd	µg/L	0	13	14	13	7%	0%	2%
Gallium	Ga	µg/L	5	8.8	8.9	8.8	1%	0%	0%
Germanium	Ge	µg/L	1	3.1	3.0	3.3	3%	6%	2%
Hafnium	Hf	µg/L	-	-	-	-	-	-	-
Holonium	Ho	µg/L	0	1.9	2.1	2.1	10%	10%	0%
Iridium	Ir	µg/L	1	<0.5	<0.5	<0.5	0%	0%	0%
Iron	Fe	µg/L	50	33000	36000	36000	9%	9%	0%
Lanthanum	La	µg/L	0	30	31	31	3%	3%	0%
Lead	Pb	µg/L	0	120	130	130	8%	8%	0%
Lithium	Li	µg/L	2	32	34	33	6%	3%	1%
Lutetium	Lu	µg/L	0	0.51	0.50	0.49	2%	4%	1%
Magnesium	Mg	µg/L	30	16000	16000	16000	0%	0%	0%
Manganese	Mn	µg/L	0	27000	28000	31000	4%	14%	3%
Molybdenum	Mo	µg/L	10	<10	<10	<10	0%	0%	0%
Neodymium	Nd	µg/L	0	40	42	42	5%	5%	0%
Nickel	Ni	µg/L	1	100	100	110	0%	10%	2%
Niobium	Nb	µg/L	0	<0.05	<0.05	<0.05	0%	0%	0%
Palladium	Pd	µg/L	-	-	-	-	-	-	-
Phosphorus	P	µg/L	1000	<1000	<1000	<1000	0%	0%	0%
Platinum	Pt	µg/L	0	<0.05	<0.05	<0.05	0%	0%	0%
Potassium	K	µg/L	200	4700	4800	4800	2%	2%	0%
Praseodymium	Pr	µg/L	0	8.9	9.4	9.3	5%	4%	0%
Rhenium	Re	µg/L	0	<0.2	<0.2	<0.2	0%	0%	0%
Rhodium	Rh	µg/L	0	<0.1	<0.1	<0.1	0%	0%	0%
Rubidium	Rb	µg/L	1	13	14	14	7%	7%	0%
Ruthenium	Ru	µg/L	0	<0.1	<0.1	<0.1	0%	0%	0%
Samarium	Sm	µg/L	0	10	11	11	10%	10%	0%
Selenium	Se	µg/L	1	3.3	4.0	3.6	19%	9%	3%
Silver	Ag	µg/L	0	<0.1	<0.1	<0.1	0%	0%	0%
Sodium	Na	µg/L	200	12000	12000	13000	0%	8%	2%
Strontium	Sr	µg/L	1	860	880	880	2%	2%	0%
Sulfur	S	µg/L	1000	310000	320000	350000	3%	12%	2%
Tantalum	Ta	µg/L	0	<0.05	<0.05	<0.05	0%	0%	0%
Terbium	Tb	µg/L	0	1.9	2.0	2.1	5%	10%	1%
Tellurium	Te	µg/L	1	0.84	0.78	0.75	7%	11%	1%
Thalium	Tl	µg/L	0	10	12	11	18%	10%	2%
Thorium	Th	µg/L	-	-	-	-	-	-	-
Thulium	Tm	µg/L	0	0.65	0.69	0.68	6%	5%	0%
Tin **	Sn	µg/L	3	<3.0	<3.0	<3.0	0%	0%	0%
Titanium	Ti	µg/L	3	<3.0	<3.0	<3.0	0%	0%	0%
Tungsten	W	µg/L	1	<0.5	<0.5	<0.5	0%	0%	0%
Uranium	U	µg/L	0	8.4	8.6	8.4	2%	0%	1%
Vanadium	V	µg/L	0	<0.3	<0.3	<0.3	0%	0%	0%
Ytterbium	Yb	µg/L	0	4.0	4.0	4.0	0%	0%	0%
Yttrium	Y	µg/L	1	63	64	65	2%	3%	0%
Zinc	Zn	µg/L	10	18000	18000	20000	0%	11%	3%
Zirconium	Zr	µg/L	0	0.12	<0.1	<0.1	18%	18%	0%

Sample description	Symbol	Units	Sample name	P-EC-W	P-EC-W	P-EC-W	%Diff 82-83	%Diff 83-84	%Diff 82-84
			Sample type	FA	FA	FA			
			Sample number	No 82	No 83	No84 *			
			Detection limit	Field Triplicate					
Anions									
Fluoride	F	mg/L	<0.05	<5.0	<5.0	<5.0	-	-	-
Chloride	Cl	mg/L	<0.05	<5.0	<5.0	<5.0	-	-	-
Nitrite	NO ₂ -	mg/L	<0.05	<5.0	<5.0	<5.0	-	-	-
Nitrate	NO ₃ -	mg/L	<0.05	<5.0	<5.0	<5.0	-	-	-
Sulphate	SO ₄ 2-	mg/L	<0.10	1200.0	1200.0	1200.0	-	-	-
pH	-	-	-	2.8	2.8	2.8	-	-	-
Metals									
Aluminium	Al	µg/L	5	42000	39000	38000	2%	1%	3%
Antimony	Sb	µg/L	2	<2.0	<2.0	<2.0	0%	0%	0%
Arsenic	As	µg/L	2	5.2	4.9	4.3	1%	3%	5%
Barium	Ba	µg/L	0	33	33	32	0%	1%	1%
Beryllium	Be	µg/L	0	7.5	7.2	7.0	1%	1%	2%
Boron	B	µg/L	1000	<1000	<1000	<1000	0%	0%	0%
Cadmium	Cd	µg/L	0	1200	1100	1100	2%	0%	2%
Calcium	Ca	µg/L	300	360000	360000	360000	0%	0%	0%
Cerium	Ce	µg/L	1	65	64	62	0%	1%	1%
Cesium	Cs	µg/L	-	-	-	-	-	-	-
Chromium	Cr	µg/L	5	<5.0	<5.0	5.1	0%	0%	0%
Cobalt	Co	µg/L	0	360	370	360	1%	1%	0%
Copper	Cu	µg/L	5	5300	5400	5400	0%	0%	0%
Dysprosium	Dy	µg/L	0	11	11	10	0%	2%	2%
Erbium	Er	µg/L	0	5.3	5.2	5.1	0%	0%	1%
Europium	Eu	µg/L	0	3.9	4.0	4.1	1%	1%	1%
Gadolinium	Gd	µg/L	0	13	13	13	0%	0%	0%
Gallium	Ga	µg/L	5	10	8.5	9.4	4%	3%	2%
Germanium	Ge	µg/L	1	3.0	3.8	3.6	6%	1%	5%
Hafnium	Hf	µg/L	-	-	-	-	-	-	-
Holonium	Ho	µg/L	0	2.1	2.0	2.0	1%	0%	1%
Iridium	Ir	µg/L	1	<0.5	<0.5	<0.5	0%	0%	0%
Iron	Fe	µg/L	50	34000	35000	35000	1%	0%	1%
Lanthanum	La	µg/L	0	31	30	30	1%	0%	1%
Lead	Pb	µg/L	0	120	120	120	0%	0%	0%
Lithium	Li	µg/L	2	33	32	32	1%	0%	1%
Lutetium	Lu	µg/L	0	0.50	0.51	0.50	0%	0%	0%
Magnesium	Mg	µg/L	30	16000	16000	16000	0%	0%	0%
Manganese	Mn	µg/L	0	31000	35000	36000	3%	1%	4%
Molybdenum	Mo	µg/L	10	<10	<10	<10	0%	0%	0%
Neodymium	Nd	µg/L	0	42	42	40	0%	1%	1%
Nickel	Ni	µg/L	1	100	110	100	2%	2%	0%
Niobium	Nb	µg/L	0	<0.05	<0.05	<0.05	0%	0%	0%
Palladium	Pd	µg/L	-	-	-	-	-	-	-
Phosphorus	P	µg/L	1000	<1000	<1000	<1000	0%	0%	0%
Platinum	Pt	µg/L	0	<0.05	<0.05	<0.05	0%	0%	0%
Potassium	K	µg/L	200	4700	4900	4800	1%	1%	1%
Praseodymium	Pr	µg/L	0	9.3	9.2	9.0	0%	1%	1%
Rhenium	Re	µg/L	0	<0.2	<0.2	<0.2	0%	0%	0%
Rhodium	Rh	µg/L	0	<0.1	<0.1	<0.1	0%	0%	0%
Rubidium	Rb	µg/L	1	14	13	13	2%	0%	2%
Ruthenium	Ru	µg/L	0	<0.1	<0.1	<0.1	0%	0%	0%
Samarium	Sm	µg/L	0	11	11	11	0%	0%	0%
Selenium	Se	µg/L	1	3.5	3.9	3.6	3%	2%	1%
Silver	Ag	µg/L	0	<0.1	<0.1	<0.1	0%	0%	0%
Sodium	Na	µg/L	200	13000	13000	13000	0%	0%	0%
Strontium	Sr	µg/L	1	890	910	900	1%	0%	0%
Sulfur	S	µg/L	1000	340000	380000	420000	3%	3%	5%
Tantalum	Ta	µg/L	0	<0.05	<0.05	<0.05	0%	0%	0%
Terbium	Tb	µg/L	0	2.0	2.0	1.9	0%	1%	1%
Tellurium	Te	µg/L	1	0.61	0.71	0.66	4%	2%	2%
Thalium	Tl	µg/L	0	11	10	10	2%	0%	2%
Thorium	Th	µg/L	-	-	-	-	-	-	-
Thulium	Tm	µg/L	0	0.66	0.66	0.66	0%	0%	0%
Tin **	Sn	µg/L	3	<3.0	<3.0	<3.0	0%	0%	0%
Titanium	Ti	µg/L	3	<3.0	<3.0	<3.0	0%	0%	0%
Tungsten	W	µg/L	1	<0.5	<0.5	<0.5	0%	0%	0%
Uranium	U	µg/L	0	8.3	8.3	8.1	0%	1%	1%
Vanadium	V	µg/L	0	<0.3	<0.3	<0.3	0%	0%	0%
Ytterbium	Yb	µg/L	0	4.1	4.0	3.9	1%	1%	1%
Yttrium	Y	µg/L	1	65	66	66	0%	0%	0%
Zinc	Zn	µg/L	10	21000	23000	24000	2%	1%	3%
Zirconium	Zr	µg/L	0	<0.1	<0.1	<0.1	0%	0%	0%

Sample description	Symbol	Units	Sample name	P-PD-W	P-PD-W	P-PD-W	%Diff 63-71	%Diff 63-72	%Diff 71-72
			Sample type	UA	UA	UA			
			Sample number	No71	No72	No63			
			Detection limit	Field Triplicate					
Anions									
Fluoride	F	mg/L	<0.05	<2.0	<2.0	<2.0	-	-	-
Chloride	Cl	mg/L	<0.05	<2.0	<2.0	<2.0	-	-	-
Nitrite	NO ₂ -	mg/L	<0.05	<2.0	<2.0	<2.0	-	-	-
Nitrate	NO ₃ -	mg/L	<0.05	3.8	3.8	3.8	-	-	-
Sulphate	SO ₄ 2-	mg/L	<0.10	880.0	880.0	880.0	-	-	-
pH	-	-	-	2.7	2.7	2.7	-	-	-
Metals									
Aluminium	Al	µg/L	5	45000	44000	40000	12%	10%	2%
Antimony	Sb	µg/L	2	<2.0	<2.0	<2.0	0%	0%	0%
Arsenic	As	µg/L	2	1800	1700	1400	25%	19%	6%
Barium	Ba	µg/L	0	24	26	22	9%	17%	8%
Beryllium	Be	µg/L	0	2.2	2.4	2.0	10%	18%	9%
Boron	B	µg/L	1000	<1000	<1000	<1000	0%	0%	0%
Cadmium	Cd	µg/L	0	2100	2100	1900	10%	10%	0%
Calcium	Ca	µg/L	300	33000	34000	32000	3%	6%	3%
Cerium	Ce	µg/L	1	5.7	6.2	5.2	9%	18%	8%
Cesium	Cs	µg/L	-	-	-	-	-	-	-
Chromium	Cr	µg/L	5	12	11	11	9%	0%	9%
Cobalt	Co	µg/L	0	530	520	510	4%	2%	2%
Copper	Cu	µg/L	5	24	23	26	8%	12%	4%
Dysprosium	Dy	µg/L	0	2.5	2.7	2.3	8%	16%	8%
Erbium	Er	µg/L	0	1.4	1.5	1.2	15%	22%	7%
Europium	Eu	µg/L	0	0.70	0.66	0.61	14%	8%	6%
Gadolinium	Gd	µg/L	0	2.7	2.8	2.4	12%	15%	4%
Gallium	Ga	µg/L	5	40	39	37	8%	5%	3%
Germanium	Ge	µg/L	1	3.9	5.0	4.1	5%	20%	25%
Hafnium	Hf	µg/L	-	-	-	-	-	-	-
Holonium	Ho	µg/L	0	0.54	0.54	0.49	10%	10%	0%
Iridium	Ir	µg/L	1	<0.5	<0.5	<0.5	0%	0%	0%
Iron	Fe	µg/L	50	230000	230000	220000	4%	4%	0%
Lanthanum	La	µg/L	0	1.9	2.1	1.8	5%	15%	10%
Lead	Pb	µg/L	0	720	770	640	12%	18%	7%
Lithium	Li	µg/L	2	14	15	13	7%	14%	7%
Lutetium	Lu	µg/L	0	0.12	0.12	0.10	18%	18%	0%
Magnesium	Mg	µg/L	30	5300	5300	5200	2%	2%	0%
Manganese	Mn	µg/L	0	15000	15000	13000	14%	14%	0%
Molybdenum	Mo	µg/L	10	<10	<10	<10	0%	0%	0%
Neodymium	Nd	µg/L	0	6.0	6.2	5.4	11%	14%	3%
Nickel	Ni	µg/L	1	170	170	160	6%	6%	0%
Niobium	Nb	µg/L	0	<0.05	<0.05	<0.05	0%	0%	0%
Palladium	Pd	µg/L	-	-	-	-	-	-	-
Phosphorus	P	µg/L	1000	<1000	<1000	<1000	0%	0%	0%
Platinum	Pt	µg/L	0	<0.05	<0.05	<0.05	0%	0%	0%
Potassium	K	µg/L	200	1300	1300	1300	0%	0%	0%
Praseodymium	Pr	µg/L	0	1.1	1.1	0.96	14%	14%	0%
Rhenium	Re	µg/L	0	<0.2	<0.2	<0.2	0%	0%	0%
Rhodium	Rh	µg/L	0	<0.1	<0.1	<0.1	0%	0%	0%
Rubidium	Rb	µg/L	1	4.6	4.9	4.0	14%	20%	6%
Ruthenium	Ru	µg/L	0	<0.1	<0.1	<0.1	0%	0%	0%
Samarium	Sm	µg/L	0	1.8	1.8	1.7	6%	6%	0%
Selenium	Se	µg/L	1	1.5	1.4	1.6	6%	13%	7%
Silver	Ag	µg/L	0	<0.1	<0.1	<0.1	0%	0%	0%
Sodium	Na	µg/L	200	3300	3400	3200	3%	6%	3%
Strontium	Sr	µg/L	1	37	38	35	6%	8%	3%
Sulfur	S	µg/L	1000	200000	190000	190000	5%	0%	5%
Tantalum	Ta	µg/L	0	<0.05	<0.05	<0.05	0%	0%	0%
Terbium	Tb	µg/L	0	0.43	0.47	0.40	7%	16%	9%
Tellurium	Te	µg/L	1	0.66	0.94	0.90	31%	4%	35%
Thalium	Tl	µg/L	0	65	69	58	11%	17%	6%
Thorium	Th	µg/L	-	-	-	-	-	-	-
Thulium	Tm	µg/L	0	0.19	0.21	0.17	11%	21%	10%
Tin **	Sn	µg/L	3	<3.0	<3.0	<3.0	0%	0%	0%
Titanium	Ti	µg/L	3	<3.0	<3.0	<3.0	0%	0%	0%
Tungsten	W	µg/L	1	<0.5	<0.5	<0.5	0%	0%	0%
Uranium	U	µg/L	0	4.5	4.8	4.0	12%	18%	6%
Vanadium	V	µg/L	0	34	34	32	6%	6%	0%
Ytterbium	Yb	µg/L	0	1.2	1.3	1.0	18%	26%	8%
Yttrium	Y	µg/L	1	17	16	16	6%	0%	6%
Zinc	Zn	µg/L	10	36000	35000	34000	6%	3%	3%
Zirconium	Zr	µg/L	0	<0.1	<0.1	<0.1	0%	0%	0%

Sample description	Symbol	Units	Sample type	FA	FA	FA	%Diff 79-80	%Diff 79-81	%Diff 80-81
			Sample number	No79	No 80	No 81			
			Detection limit	Field Triplicate					
Anions									
Fluoride	F	mg/L	<0.05	<2.0	<2.0	<2.0	-	-	-
Chloride	Cl	mg/L	<0.05	<2.0	<2.0	<2.0	-	-	-
Nitrite	NO ₂ -	mg/L	<0.05	<2.0	<2.0	<2.0	-	-	-
Nitrate	NO ₃ -	mg/L	<0.05	3.8	3.8	3.8	-	-	-
Sulphate	SO ₄ 2-	mg/L	<0.10	880.0	880.0	880.0	-	-	-
pH	-	-	-	2.7	2.7	2.7	-	-	-
Metals									
Aluminium	Al	µg/L	5	42000	46000	45000	9%	7%	2%
Antimony	Sb	µg/L	2	<2.0	<2.0	<2.0	0%	0%	0%
Arsenic	As	µg/L	2	1700	1900	1800	11%	6%	5%
Barium	Ba	µg/L	0	24	24	24	0%	0%	0%
Beryllium	Be	µg/L	0	2.2	2.2	2.1	0%	5%	5%
Boron	B	µg/L	1000	<1000	<1000	<1000	0%	0%	0%
Cadmium	Cd	µg/L	0	2100	2300	2200	9%	5%	4%
Calcium	Ca	µg/L	300	33000	34000	36000	3%	9%	6%
Cerium	Ce	µg/L	1	5.8	5.6	5.8	4%	0%	4%
Cesium	Cs	µg/L	-	-	-	-	-	-	-
Chromium	Cr	µg/L	5	12	12	12	0%	0%	0%
Cobalt	Co	µg/L	0	530	530	540	0%	2%	2%
Copper	Cu	µg/L	5	22	21	22	5%	0%	5%
Dysprosium	Dy	µg/L	0	2.5	2.5	2.5	0%	0%	0%
Erbium	Er	µg/L	0	1.4	1.4	1.4	0%	0%	0%
Europium	Eu	µg/L	0	0.70	0.74	0.79	6%	12%	7%
Gadolinium	Gd	µg/L	0	2.6	2.6	2.7	0%	4%	4%
Gallium	Ga	µg/L	5	40	39	38	3%	5%	3%
Germanium	Ge	µg/L	1	4.2	4.2	4.8	0%	13%	13%
Hafnium	Hf	µg/L	-	-	-	-	-	-	-
Holonium	Ho	µg/L	0	0.54	0.52	0.52	4%	4%	0%
Iridium	Ir	µg/L	1	<0.5	<0.5	<0.5	0%	0%	0%
Iron	Fe	µg/L	50	230000	230000	240000	0%	4%	4%
Lanthanum	La	µg/L	0	1.9	1.9	2.0	0%	5%	5%
Lead	Pb	µg/L	0	730	730	730	0%	0%	0%
Lithium	Li	µg/L	2	14	14	14	0%	0%	0%
Lutetium	Lu	µg/L	0	0.11	0.12	0.12	9%	9%	0%
Magnesium	Mg	µg/L	30	5300	5300	5400	0%	2%	2%
Manganese	Mn	µg/L	0	15000	16000	16000	6%	6%	0%
Molybdenum	Mo	µg/L	10	<10	<10	<10	0%	0%	0%
Neodymium	Nd	µg/L	0	5.8	5.8	6.0	0%	3%	3%
Nickel	Ni	µg/L	1	170	170	170	0%	0%	0%
Niobium	Nb	µg/L	0	<0.05	<0.05	<0.05	0%	0%	0%
Palladium	Pd	µg/L	-	-	-	-	-	-	-
Phosphorus	P	µg/L	1000	<1000	<1000	<1000	0%	0%	0%
Platinum	Pt	µg/L	0	<0.05	<0.05	<0.05	0%	0%	0%
Potassium	K	µg/L	200	1300	1400	1300	7%	0%	7%
Praseodymium	Pr	µg/L	0	1.0	1.0	1.1	0%	10%	10%
Rhenium	Re	µg/L	0	<0.2	<0.2	<0.2	0%	0%	0%
Rhodium	Rh	µg/L	0	<0.1	<0.1	<0.1	0%	0%	0%
Rubidium	Rb	µg/L	1	4.5	4.4	4.7	2%	4%	7%
Ruthenium	Ru	µg/L	0	<0.1	<0.1	<0.1	0%	0%	0%
Samarium	Sm	µg/L	0	1.8	1.8	1.9	0%	5%	5%
Selenium	Se	µg/L	1	1.3	<1.0	1.4	26%	7%	33%
Silver	Ag	µg/L	0	<0.1	<0.1	<0.1	0%	0%	0%
Sodium	Na	µg/L	200	3300	3300	3400	0%	3%	3%
Strontium	Sr	µg/L	1	36	37	39	3%	8%	5%
Sulfur	S	µg/L	1000	190000	190000	210000	0%	10%	10%
Tantalum	Ta	µg/L	0	<0.05	<0.05	<0.05	0%	0%	0%
Terbium	Tb	µg/L	0	0.45	0.42	0.43	7%	5%	2%
Tellurium	Te	µg/L	1	0.82	0.76	0.70	8%	16%	8%
Thalium	Tl	µg/L	0	65	64	64	2%	2%	0%
Thorium	Th	µg/L	-	-	-	-	-	-	-
Thulium	Tm	µg/L	0	0.18	0.18	0.19	0%	5%	5%
Tin **	Sn	µg/L	3	<3.0	<3.0	<3.0	0%	0%	0%
Titanium	Ti	µg/L	3	<3.0	<3.0	<3.0	0%	0%	0%
Tungsten	W	µg/L	1	<0.5	<0.5	<0.5	0%	0%	0%
Uranium	U	µg/L	0	4.6	4.6	4.5	0%	2%	2%
Vanadium	V	µg/L	0	34	34	36	0%	6%	6%
Ytterbium	Yb	µg/L	0	1.1	1.1	1.1	0%	0%	0%
Yttrium	Y	µg/L	1	17	16	17	6%	0%	6%
Zinc	Zn	µg/L	10	38000	37000	41000	3%	8%	10%
Zirconium	Zr	µg/L	0	<0.1	<0.1	<0.1	0%	0%	0%

				Sample name	LN-BP-W	LN-BP-W	LN-BP-W
				Sample type	FA	FA	FA
				Sample number	No11	No11	% Diff No 11
	Symbol	Units	Detection limit	Lab Duplicate			
Metals							
Aluminium	Al	µg/L	5	6300	6200	2%	
Antimony	Sb	µg/L	2	2	2	0%	
Arsenic	As	µg/L	2	4.0	3.3	19%	
Barium	Ba	µg/L	0	45	40	12%	
Beryllium	Be	µg/L	0	0.24	0.28	15%	
Boron	B	µg/L	1000	1000	1000	0%	
Cadmium	Cd	µg/L	0	7.8	6.9	12%	
Calcium	Ca	µg/L	300	36000	32000	12%	
Cerium	Ce	µg/L	1	12	11	9%	
Cesium	Cs	µg/L	-	-	-	-	
Chromium	Cr	µg/L	5	5	5	0%	
Cobalt	Co	µg/L	0	100	89	12%	
Copper	Cu	µg/L	5	3900	3800	3%	
Dysprosium	Dy	µg/L	0	1.2	1.1	9%	
Erbium	Er	µg/L	0	0.64	0.58	10%	
Europium	Eu	µg/L	0	0.57	0.45	24%	
Gadolinium	Gd	µg/L	0	1.7	1.6	6%	
Gallium	Ga	µg/L	5	5	5	0%	
Germanium	Ge	µg/L	1	1	1	0%	
Hafnium	Hf	µg/L	-	-	-	-	
Holonium	Ho	µg/L	0	0.22	0.21	5%	
Iridium	Ir	µg/L	1	1	1	0%	
Iron	Fe	µg/L	50	17000	15000	13%	
Lanthanum	La	µg/L	0	5.2	4.8	8%	
Lead	Pb	µg/L	0	53	48	10%	
Lithium	Li	µg/L	2	4.6	4.0	14%	
Lutetium	Lu	µg/L	0	0.061	0.059	3%	
Magnesium	Mg	µg/L	30	3300	2900	13%	
Manganese	Mn	µg/L	0	1000	1100	10%	
Molybdenum	Mo	µg/L	10	10	10	0%	
Neodymium	Nd	µg/L	0	7.4	6.6	11%	
Nickel	Ni	µg/L	1	91	81	12%	
Niobium	Nb	µg/L	0	0	0	0%	
Palladium	Pd	µg/L	-	-	-	-	
Phosphorus	P	µg/L	1000	1000	1000	0%	
Platinum	Pt	µg/L	0	0	0	0%	
Potassium	K	µg/L	200	2000	1800	11%	
Praseodymium	Pr	µg/L	0	1.7	1.6	6%	
Rhenium	Re	µg/L	0	0	0	0%	
Rhodium	Rh	µg/L	0	0	0	0%	
Rubidium	Rb	µg/L	1	5.0	4.5	11%	
Ruthenium	Ru	µg/L	0	0	0	0%	
Samarium	Sm	µg/L	0	1.4	1.3	7%	
Selenium	Se	µg/L	1	28	25	11%	
Silver	Ag	µg/L	0	2.1	1.8	15%	
Sodium	Na	µg/L	200	19000	16000	17%	
Strontium	Sr	µg/L	1	120	100	18%	
Sulfur	S	µg/L	1000	4600000	4600000	0%	
Tantalum	Ta	µg/L	0	0	0	0%	
Terbium	Tb	µg/L	0	0.23	0.21	9%	
Tellurium	Te	µg/L	1	1	1	0%	
Thalium	Tl	µg/L	0	2.3	2.1	9%	
Thorium	Th	µg/L	-	-	-	-	
Thulium	Tm	µg/L	0	0.080	0.078	3%	
Tin **	Sn	µg/L	3	3.0	3.0	0%	
Titanium	Ti	µg/L	3	3	3	0%	
Tungsten	W	µg/L	1	1	1	0%	
Uranium	U	µg/L	0	0.43	0.39	10%	
Vanadium	V	µg/L	0	0	0	0%	
Ytterbium	Yb	µg/L	0	0.46	0.38	19%	
Yttrium	Y	µg/L	1	7.7	6.4	18%	
Zinc	Zn	µg/L	10	120	110	9%	
Zirconium	Zr	µg/L	0	0.23	0	79%	

			Sample name	LN-VWD-W	LN-VWD-W	LN-VWD-W
			Sample type	FFA	FFA	FFA
			Sample number	No27	No27	%Diff No 27
	Symbol	Units	Detection limit	Lab Duplicate		
Metals						
Aluminium	Al	µg/L	5	190000	190000	0%
Antimony	Sb	µg/L	2	2	2	0%
Arsenic	As	µg/L	2	320	320	0%
Barium	Ba	µg/L	0	9.8	9.4	4%
Beryllium	Be	µg/L	0	41	41	0%
Boron	B	µg/L	1000	1000	1000	0%
Cadmium	Cd	µg/L	0	110	110	0%
Calcium	Ca	µg/L	300	460000	460000	0%
Cerium	Ce	µg/L	1	290	290	0%
Cesium	Cs	µg/L	-	-	-	-
Chromium	Cr	µg/L	5	110	110	0%
Cobalt	Co	µg/L	0	820	830	1%
Copper	Cu	µg/L	5	22000	21000	5%
Dysprosium	Dy	µg/L	0	31	30	3%
Erbium	Er	µg/L	0	16	16	0%
Europium	Eu	µg/L	0	10	11	10%
Gadolinium	Gd	µg/L	0	38	38	0%
Gallium	Ga	µg/L	5	33	35	6%
Germanium	Ge	µg/L	1	15	15	0%
Hafnium	Hf	µg/L	-	-	-	-
Holonium	Ho	µg/L	0	6.0	6.0	0%
Iridium	Ir	µg/L	1	1	1	0%
Iron	Fe	µg/L	50	450000	450000	0%
Lanthanum	La	µg/L	0	130	130	0%
Lead	Pb	µg/L	0	7.1	6.8	4%
Lithium	Li	µg/L	2	71	70	1%
Lutetium	Lu	µg/L	0	1.8	1.8	0%
Magnesium	Mg	µg/L	30	66000	67000	2%
Manganese	Mn	µg/L	0	34000	32000	6%
Molybdenum	Mo	µg/L	10	10	10	0%
Neodymium	Nd	µg/L	0	150	150	0%
Nickel	Ni	µg/L	1	890	900	1%
Niobium	Nb	µg/L	0	0.11	0.12	9%
Palladium	Pd	µg/L	-	-	-	-
Phosphorus	P	µg/L	1000	1600	1500	6%
Platinum	Pt	µg/L	0	0	0	0%
Potassium	K	µg/L	200	1000	970	3%
Praseodymium	Pr	µg/L	0	36	35	3%
Rhenium	Re	µg/L	0	0	0	0%
Rhodium	Rh	µg/L	0	0	0	0%
Rubidium	Rb	µg/L	1	11	11	0%
Ruthenium	Ru	µg/L	0	0	0	0%
Samarium	Sm	µg/L	0	35	34	3%
Selenium	Se	µg/L	1	22	22	0%
Silver	Ag	µg/L	0	0.85	0.91	7%
Sodium	Na	µg/L	200	45000	45000	0%
Strontium	Sr	µg/L	1	2800	2800	0%
Sulfur	S	µg/L	1000	5300000	5000000	6%
Tantalum	Ta	µg/L	0	0	0	0%
Terbium	Tb	µg/L	0	5.6	5.6	0%
Tellurium	Te	µg/L	1	4.3	4.2	2%
Thalium	Tl	µg/L	0	0.52	0.48	8%
Thorium	Th	µg/L	-	-	-	-
Thulium	Tm	µg/L	0	2.1	2.0	5%
Tin **	Sn	µg/L	3	3.0	3.0	0%
Titanium	Ti	µg/L	3	10	6.0	50%
Tungsten	W	µg/L	1	1	1	0%
Uranium	U	µg/L	0	18	18	0%
Vanadium	V	µg/L	0	23	22	4%
Ytterbium	Yb	µg/L	0	13	13	0%
Yttrium	Y	µg/L	1	180	180	0%
Zinc	Zn	µg/L	10	6500	6500	0%
Zirconium	Zr	µg/L	0	2.2	1.9	15%

		Sample name		DAR-1-W	DAR-1-W	DAR-1-W
		Sample type	UA	UA	UA	
		Sample number	No29	No29	%Diff 29	
Symbol	Units	Detection limit	Lab Duplicate			
Metals						
Aluminium	Al	µg/L	5	360000	360000	0%
Antimony	Sb	µg/L	2	3.3	3.7	11%
Arsenic	As	µg/L	2	830	990	18%
Barium	Ba	µg/L	0	9.7	9.6	1%
Beryllium	Be	µg/L	0	53	53	0%
Boron	B	µg/L	1000	1000	1000	0%
Cadmium	Cd	µg/L	0	200	200	0%
Calcium	Ca	µg/L	300	440000	430000	2%
Cerium	Ce	µg/L	1	580	590	2%
Cesium	Cs	µg/L	-	-	-	-
Chromium	Cr	µg/L	5	84	83	1%
Cobalt	Co	µg/L	0	1000	1000	0%
Copper	Cu	µg/L	5	20000	19000	5%
Dysprosium	Dy	µg/L	0	74	74	0%
Erbium	Er	µg/L	0	36	37	3%
Europium	Eu	µg/L	0	26	25	4%
Gadolinium	Gd	µg/L	0	92	92	0%
Gallium	Ga	µg/L	5	76	69	10%
Germanium	Ge	µg/L	1	29	28	4%
Hafnium	Hf	µg/L	-	-	-	-
Holonium	Ho	µg/L	0	14	14	0%
Iridium	Ir	µg/L	1	1	1	0%
Iron	Fe	µg/L	50	660000	660000	0%
Lanthanum	La	µg/L	0	270	270	0%
Lead	Pb	µg/L	0	4.8	3.4	34%
Lithium	Li	µg/L	2	130	130	0%
Lutetium	Lu	µg/L	0	3.5	3.5	0%
Magnesium	Mg	µg/L	30	140000	140000	0%
Manganese	Mn	µg/L	0	47000	47000	0%
Molybdenum	Mo	µg/L	10	10	10	0%
Neodymium	Nd	µg/L	0	350	350	0%
Nickel	Ni	µg/L	1	930	910	2%
Niobium	Nb	µg/L	0	0.22	0.21	5%
Palladium	Pd	µg/L	-	-	-	-
Phosphorus	P	µg/L	1000	6300	6300	0%
Platinum	Pt	µg/L	0	0	0	0%
Potassium	K	µg/L	200	1300	1400	7%
Praseodymium	Pr	µg/L	0	80	81	1%
Rhenium	Re	µg/L	0	0	0	0%
Rhodium	Rh	µg/L	0	0	0	0%
Rubidium	Rb	µg/L	1	9.8	9.6	2%
Ruthenium	Ru	µg/L	0	0	0	0%
Samarium	Sm	µg/L	0	82	83	1%
Selenium	Se	µg/L	1	25	23	8%
Silver	Ag	µg/L	0	0	0	0%
Sodium	Na	µg/L	200	28000	28000	0%
Strontium	Sr	µg/L	1	2000	2000	0%
Sulfur	S	µg/L	1000	1800000	1800000	0%
Tantalum	Ta	µg/L	0	0.067	0.070	4%
Terbium	Tb	µg/L	0	14	14	0%
Tellurium	Te	µg/L	1	2.2	2.2	0%
Thalium	Tl	µg/L	0	0	0	0%
Thorium	Th	µg/L	-	-	-	-
Thulium	Tm	µg/L	0	4.5	4.5	0%
Tin **	Sn	µg/L	3	3.00	3.00	0%
Titanium	Ti	µg/L	3	24	26	8%
Tungsten	W	µg/L	1	1	1	0%
Uranium	U	µg/L	0	24	24	0%
Vanadium	V	µg/L	0	26	26	0%
Ytterbium	Yb	µg/L	0	26	27	4%
Yttrium	Y	µg/L	1	400	390	3%
Zinc	Zn	µg/L	10	13000	13000	0%
Zirconium	Zr	µg/L	0	2.3	2.4	4%

			Sample name	LN-AB2	LN-AB2	LN-AB2
			Sample type	UA	UA	UA
			Sample number	No42	No42	%Diff 42
Symbol	Units	Detection limit	Lab Duplicate			
Metals						
Aluminium	Al	µg/L	5	26	28	7%
Antimony	Sb	µg/L	2	2	2	0%
Arsenic	As	µg/L	2	2	2	0%
Barium	Ba	µg/L	0	0	0	0%
Beryllium	Be	µg/L	0	0	0	0%
Boron	B	µg/L	1000	1000	1000	0%
Cadmium	Cd	µg/L	0	0.058	0.097	50%
Calcium	Ca	µg/L	300	300	300	0%
Cerium	Ce	µg/L	1	1	1	0%
Cesium	Cs	µg/L	-	1	1	0%
Chromium	Cr	µg/L	5	5	5	0%
Cobalt	Co	µg/L	0	42	42	0%
Copper	Cu	µg/L	5	5	5	0%
Dysprosium	Dy	µg/L	0	0	0	0%
Erbium	Er	µg/L	0	0	0	0%
Europium	Eu	µg/L	0	0	0	0%
Gadolinium	Gd	µg/L	0	0	0	0%
Gallium	Ga	µg/L	5	5	5	0%
Germanium	Ge	µg/L	1	1	1	0%
Hafnium	Hf	µg/L	-	1	1	0%
Holonium	Ho	µg/L	0	0	0	0%
Iridium	Ir	µg/L	1	1	1	0%
Iron	Fe	µg/L	50	64	50	25%
Lanthanum	La	µg/L	0	0	0	0%
Lead	Pb	µg/L	0	15	15	0%
Lithium	Li	µg/L	2	2	2	0%
Lutetium	Lu	µg/L	0	0	0	0%
Magnesium	Mg	µg/L	30	30	30	0%
Manganese	Mn	µg/L	0	0	0	0%
Molybdenum	Mo	µg/L	10	10	10	0%
Neodymium	Nd	µg/L	0	0	0	0%
Nickel	Ni	µg/L	1	1	1	0%
Niobium	Nb	µg/L	0	0	0	0%
Palladium	Pd	µg/L	-	0.23	0.19	19%
Phosphorus	P	µg/L	1000	1000	1000	0%
Platinum	Pt	µg/L	0	0	0	0%
Potassium	K	µg/L	200	200	200	0%
Praseodymium	Pr	µg/L	0	0	0	0%
Rhenium	Re	µg/L	0	0	0	0%
Rhodium	Rh	µg/L	0	0	0	0%
Rubidium	Rb	µg/L	1	1	1	0%
Ruthenium	Ru	µg/L	0	0	0	0%
Samarium	Sm	µg/L	0	0	0	0%
Selenium	Se	µg/L	1	1.7	1.4	19%
Silver	Ag	µg/L	0	0.72	0.64	12%
Sodium	Na	µg/L	200	200	200	0%
Strontium	Sr	µg/L	1	1	1	0%
Sulfur	S	µg/L	1000	5500000	5600000	2%
Tantalum	Ta	µg/L	0	0	0	0%
Terbium	Tb	µg/L	0	0	0	0%
Tellurium	Te	µg/L	1	1	1	0%
Thalium	Tl	µg/L	0	0	0	0%
Thorium	Th	µg/L	-	0	0	0%
Thulium	Tm	µg/L	0	0	0	0%
Tin **	Sn	µg/L	3	0	0	0%
Titanium	Ti	µg/L	3	3	3	0%
Tungsten	W	µg/L	1	1	1	0%
Uranium	U	µg/L	0	0	0	0%
Vanadium	V	µg/L	0	0	0	0%
Ytterbium	Yb	µg/L	0	0	0	0%
Yttrium	Y	µg/L	1	1	1	0%
Zinc	Zn	µg/L	10	10	10	0%
Zirconium	Zr	µg/L	0	0.12	0	18%

		Sample name		IN28-W	IN28-W	IN28-W
		Sample type		FA	FA	FA
		Sample number		No46	No46	%Diff 46
Symbol	Units	Detection limit	Lab Duplicate			
Metals						
Aluminium	Al	µg/L	5	15000	15000	0%
Antimony	Sb	µg/L	2	2	2	0%
Arsenic	As	µg/L	2	110	110	0%
Barium	Ba	µg/L	0	8.6	8.2	5%
Beryllium	Be	µg/L	0	1.7	1.8	6%
Boron	B	µg/L	1000	1700	1800	6%
Cadmium	Cd	µg/L	0	9.1	9.0	1%
Calcium	Ca	µg/L	300	160000	160000	0%
Cerium	Ce	µg/L	1	2.7	2.6	4%
Cesium	Cs	µg/L	-	-	-	-
Chromium	Cr	µg/L	5	5	5	0%
Cobalt	Co	µg/L	0	56	54	4%
Copper	Cu	µg/L	5	28000	27000	4%
Dysprosium	Dy	µg/L	0	1.6	1.6	0%
Erbium	Er	µg/L	0	0.62	0.63	2%
Europium	Eu	µg/L	0	0.46	0.38	19%
Gadolinium	Gd	µg/L	0	2.1	2.0	5%
Gallium	Ga	µg/L	5	5	5	0%
Germanium	Ge	µg/L	1	1.4	1.4	0%
Hafnium	Hf	µg/L	-	-	-	-
Holonium	Ho	µg/L	0	0.27	0.28	4%
Iridium	Ir	µg/L	1	1	1	0%
Iron	Fe	µg/L	50	23000	23000	0%
Lanthanum	La	µg/L	0	0.88	0.92	4%
Lead	Pb	µg/L	0	0.58	0.50	15%
Lithium	Li	µg/L	2	450	440	2%
Lutetium	Lu	µg/L	0	0.053	0.053	0%
Magnesium	Mg	µg/L	30	28000	28000	0%
Manganese	Mn	µg/L	0	3200	3300	3%
Molybdenum	Mo	µg/L	10	10	10	0%
Neodymium	Nd	µg/L	0	2.3	2.2	4%
Nickel	Ni	µg/L	1	39	37	5%
Niobium	Nb	µg/L	0	0	0	0%
Palladium	Pd	µg/L	-	-	-	-
Phosphorus	P	µg/L	1000	1000	1000	0%
Platinum	Pt	µg/L	0	0	0	0%
Potassium	K	µg/L	200	12000	12000	0%
Praseodymium	Pr	µg/L	0	0.43	0.45	5%
Rhenium	Re	µg/L	0	0	0	0%
Rhodium	Rh	µg/L	0	0	0	0%
Rubidium	Rb	µg/L	1	120	120	0%
Ruthenium	Ru	µg/L	0	0	0	0%
Samarium	Sm	µg/L	0	1.1	1.1	0%
Selenium	Se	µg/L	1	1	1	0%
Silver	Ag	µg/L	0	0	0	0%
Sodium	Na	µg/L	200	68000	67000	1%
Strontium	Sr	µg/L	1	990	1000	1%
Sulfur	S	µg/L	1000	270000	270000	0%
Tantalum	Ta	µg/L	0	0	0	0%
Terbium	Tb	µg/L	0	0.32	0.33	3%
Tellurium	Te	µg/L	1	1	1	0%
Thalium	Tl	µg/L	0	0.29	0.28	4%
Thorium	Th	µg/L	-	-	-	-
Thulium	Tm	µg/L	0	0.082	0.070	16%
Tin **	Sn	µg/L	3	3	3	0%
Titanium	Ti	µg/L	3	3	3	0%
Tungsten	W	µg/L	1	1	1	0%
Uranium	U	µg/L	0	3.0	2.8	7%
Vanadium	V	µg/L	0	0	0	0%
Ytterbium	Yb	µg/L	0	0.44	0.45	2%
Yttrium	Y	µg/L	1	6.9	7.2	4%
Zinc	Zn	µg/L	10	2000	2100	5%
Zirconium	Zr	µg/L	0	0	0	0%

			Sample name	P-ARD17-W	P-ARD17-W	P-ARD17-W
			Sample type	UA	UA	UA
			Sample number	No65	No65	%Diff 65
Symbol	Units	Detection limit	Lab Duplicates			
Metals						
Aluminium	Al	µg/L	5	2300	2100	9%
Antimony	Sb	µg/L	2	4.7	4.7	0%
Arsenic	As	µg/L	2	34	34	0%
Barium	Ba	µg/L	0	21	21	0%
Beryllium	Be	µg/L	0	0	0	0%
Boron	B	µg/L	1000	1000	1000	0%
Cadmium	Cd	µg/L	0	2.1	1.9	10%
Calcium	Ca	µg/L	300	2300	2400	4%
Cerium	Ce	µg/L	1	1.0	0.93	7%
Cesium	Cs	µg/L	-	-	-	-
Chromium	Cr	µg/L	5	5	5	0%
Cobalt	Co	µg/L	0	3.4	3.4	0%
Copper	Cu	µg/L	5	610	600	2%
Dysprosium	Dy	µg/L	0	0.23	0.22	4%
Erbium	Er	µg/L	0	0.12	0.11	9%
Europium	Eu	µg/L	0	0.059	0.055	7%
Gadolinium	Gd	µg/L	0	0.19	0.23	19%
Gallium	Ga	µg/L	5	5	5	0%
Germanium	Ge	µg/L	1	1	1	0%
Hafnium	Hf	µg/L	-	-	-	-
Holonium	Ho	µg/L	0	0	0	0%
Iridium	Ir	µg/L	1	1	1	0%
Iron	Fe	µg/L	50	5100	5000	2%
Lanthanum	La	µg/L	0	0.41	0.41	0%
Lead	Pb	µg/L	0	4.9	4.9	0%
Lithium	Li	µg/L	2	2	2	0%
Lutetium	Lu	µg/L	0	0	0	0%
Magnesium	Mg	µg/L	30	710	690	3%
Manganese	Mn	µg/L	0	1500	1500	0%
Molybdenum	Mo	µg/L	10	10	10	0%
Neodymium	Nd	µg/L	0	0.71	0.64	10%
Nickel	Ni	µg/L	1	3.3	3.9	17%
Niobium	Nb	µg/L	0	0	0	0%
Palladium	Pd	µg/L	-	-	-	-
Phosphorus	P	µg/L	1000	1000	1000	0%
Platinum	Pt	µg/L	0	0	0	0%
Potassium	K	µg/L	200	1200	1300	8%
Praseodymium	Pr	µg/L	0	0.15	0.14	7%
Rhenium	Re	µg/L	0	0	0	0%
Rhodium	Rh	µg/L	0	0	0	0%
Rubidium	Rb	µg/L	1	6.3	6.1	3%
Ruthenium	Ru	µg/L	0	0	0	0%
Samarium	Sm	µg/L	0	0.18	0.17	6%
Selenium	Se	µg/L	1	1	1.1	10%
Silver	Ag	µg/L	0	0	0	0%
Sodium	Na	µg/L	200	1100	1100	0%
Strontium	Sr	µg/L	1	9.7	9.8	1%
Sulfur	S	µg/L	1000	20000	18000	11%
Tantalum	Ta	µg/L	0	0	0	0%
Terbium	Tb	µg/L	0	0	0	0%
Tellurium	Te	µg/L	1	1	1	0%
Thalium	Tl	µg/L	0	0	0	0%
Thorium	Th	µg/L	-	-	-	-
Thulium	Tm	µg/L	0	0	0	0%
Tin **	Sn	µg/L	3	0	0	0%
Titanium	Ti	µg/L	3	3	3	0%
Tungsten	W	µg/L	1	1	1	0%
Uranium	U	µg/L	0	0.19	0.17	11%
Vanadium	V	µg/L	0	0	0	0%
Ytterbium	Yb	µg/L	0	0	0	0%
Yttrium	Y	µg/L	1	1.3	1.4	7%
Zinc	Zn	µg/L	10	1800	1600	12%
Zirconium	Zr	µg/L	0	0.76	0.83	9%

			Sample name	P-EC-W	P-EC-W	P-EC-W
			Sample type	FA	FA	FA
			Sample number	No 84	No 84	%Diff 84
Symbol	Units	Detection limit	Lab Duplicates			
Metals						
Aluminium	Al	µg/L	5	39000	38000	3%
Antimony	Sb	µg/L	2	2	2	0%
Arsenic	As	µg/L	2	4.7	3.9	19%
Barium	Ba	µg/L	0	32	32	0%
Beryllium	Be	µg/L	0	7.0	7.1	1%
Boron	B	µg/L	1000	1000	1000	0%
Cadmium	Cd	µg/L	0	1100	1100	0%
Calcium	Ca	µg/L	300	370000	360000	3%
Cerium	Ce	µg/L	1	62	63	2%
Cesium	Cs	µg/L	-	1	1.2	18%
Chromium	Cr	µg/L	5	5	5.1	2%
Cobalt	Co	µg/L	0	370	360	3%
Copper	Cu	µg/L	5	5500	5400	2%
Dysprosium	Dy	µg/L	0	10	10	0%
Erbium	Er	µg/L	0	5.1	5.1	0%
Europium	Eu	µg/L	0	4.2	4.0	5%
Gadolinium	Gd	µg/L	0	13	13	0%
Gallium	Ga	µg/L	5	10	8.9	12%
Germanium	Ge	µg/L	1	3.4	3.8	11%
Hafnium	Hf	µg/L	-	1	1	0%
Holonium	Ho	µg/L	0	2.0	2.0	0%
Iridium	Ir	µg/L	1	1	1	0%
Iron	Fe	µg/L	50	36000	34000	6%
Lanthanum	La	µg/L	0	29	30	3%
Lead	Pb	µg/L	0	120	120	0%
Lithium	Li	µg/L	2	32	32	0%
Lutetium	Lu	µg/L	0	0.49	0.52	6%
Magnesium	Mg	µg/L	30	16000	16000	0%
Manganese	Mn	µg/L	0	34000	38000	11%
Molybdenum	Mo	µg/L	10	10	10	0%
Neodymium	Nd	µg/L	0	40	41	2%
Nickel	Ni	µg/L	1	110	100	10%
Niobium	Nb	µg/L	0	0	0	0%
Palladium	Pd	µg/L	-	1.8	1.8	0%
Phosphorus	P	µg/L	1000	1000	1000	0%
Platinum	Pt	µg/L	0	0	0	0%
Potassium	K	µg/L	200	5000	4700	6%
Praseodymium	Pr	µg/L	0	8.9	9.1	2%
Rhenium	Re	µg/L	0	0	0	0%
Rhodium	Rh	µg/L	0	0	0	0%
Rubidium	Rb	µg/L	1	13	13	0%
Ruthenium	Ru	µg/L	0	0	0	0%
Samarium	Sm	µg/L	0	11	11	0%
Selenium	Se	µg/L	1	3.8	3.4	11%
Silver	Ag	µg/L	0	0	0	0%
Sodium	Na	µg/L	200	13000	13000	0%
Strontium	Sr	µg/L	1	910	890	2%
Sulfur	S	µg/L	1000	360000	480000	29%
Tantalum	Ta	µg/L	0	0	0	0%
Terbium	Tb	µg/L	0	1.9	1.9	0%
Tellurium	Te	µg/L	1	0.73	0.60	20%
Thalium	Tl	µg/L	0	10	10	0%
Thorium	Th	µg/L	-	0	0	0%
Thulium	Tm	µg/L	0	0.66	0.65	2%
Tin **	Sn	µg/L	3	0	0	0%
Titanium	Ti	µg/L	3	3	3	0%
Tungsten	W	µg/L	1	1	1	0%
Uranium	U	µg/L	0	8.1	8.1	0%
Vanadium	V	µg/L	0	0	0	0%
Ytterbium	Yb	µg/L	0	3.9	3.9	0%
Yttrium	Y	µg/L	1	67	66	2%
Zinc	Zn	µg/L	10	22000	25000	13%
Zirconium	Zr	µg/L	0	0	0	0%

Sample	Symbol	Units	Certified Reference Material			
			Blank	QC	QC Target	%Diff
Fluoride	F	mg/L	<0.05	2.4	2.5	6%
Chloride	Cl	mg/L	<0.05	4.8	5.0	3%
Nitrite	NO ₂ ⁻	mg/L	<0.05	2.3	2.5	10%
Nitrate	NO ₃ ⁻	mg/L	<0.05	2.2	2.5	13%
Sulphate	SO ₄ ²⁻	mg/L	<0.10	4.5	5.0	10%

Sample	Symbol	Units	Sample name	LN-SP3-W	LN-SP3-W	P-WRD-W	P-WRD-W	%Diff 12	%Diff 16
			Sample type	FU	FU	FU	FU		
			Sample number	IC-12	IC-12	IC-16	IC-16		
			Detection limit	Lab Duplicates					
Fluoride	F	mg/L	<0.05	<2.0	<2.0	<5.0	<5.0	0%	0%
Chloride	Cl	mg/L	<0.05	<2.0	<2.0	<5.0	<5.0	0%	0%
Nitrite	NO ₂ ⁻	mg/L	<0.05	<2.0	<2.0	<5.0	<5.0	0%	0%
Nitrate	NO ₃ ⁻	mg/L	<0.05	3.8	3.9	<5.0	<5.0	1%	0%
Sulphate	SO ₄ ²⁻	mg/L	<0.10	690	690	2900	2900	0%	0%

			Sample name	IN13-W	IN13-W	LN-DW-B-11-W	LN-DW-B-11-W		
			Sample type	FU	FU	FU	FU	%Diff 4-5	%Diff 10-11
			Sample number	IC-4	IC-5	IC-6	IC-7		
Sample	Symbol	Units	Detection limit	Field Duplicates		Field Duplicates			
				2.3	2.0	<2.0	<2.0	15%	0%
Fluoride	F	mg/L	<0.05	140	140	<2.0	<2.0	0%	0%
Chloride	Cl	mg/L	<0.05	<2.0	<2.0	<2.0	<2.0	0%	0%
Nitrite	NO ₂ -	mg/L	<0.05	<2.0	<2.0	<2.0	<2.0	0%	0%
Nitrate	NO ₃ -	mg/L	<0.05	990	1000	820	870	1%	20%
Sulphate	SO ₄ 2--	mg/L	<0.10	4.3	4.3	2.8	2.8	0%	43%

				Sample name	P-WRD-W	P-WRD-W	P-ARD-14W	P-ARD-14W			
				Sample type					%Diff 16-17	%Diff 20-21	
				Sample number	IC-16 *	IC-17	IC-20	IC-21			
Sample	Symbol	Units	Detection limit	Field Duplicates		Field Duplicates					
				<5.0	<5.0	<0.10	<0.10		0%	0%	
Fluoride	F	mg/L	<0.05	<5.0	<5.0	0.55	0.48		0%	0%	
Chloride	Cl	mg/L	<0.05	<5.0	<5.0	<0.10	<0.10		0%	0%	
Nitrite	NO ₂ -	mg/L	<0.05	<5.0	<5.0	<0.10	<0.10		0%	0%	
Nitrate	NO ₃ -	mg/L	<0.05	2900	2600	55	53		11%	3%	
Sulphate	SO ₄ 2--	mg/L	<0.10	2.6	2.6	3.2	3.0		0%	5%	

Appendix G: Field photographs

IN23

IN23

IN23

IN2

IN2

IN-RMATR

LN-DW-B-11

LN-SP3

LN-PW2

LN-PW2

LN-BP

LN-BP

LN-BP

LN-VWD

LN-VWD

LN-VWD

P-WRD

P-ARD17

P-PD

P-PW1

P-EC

P-EC