Geochemical and mineralogical characterisation of the Caribou Zn-Pb VMS deposit, Bathurst Mining Camp, New Brunswick, Canada

PhD Thesis
2022

Foteini Drakou
I declare that this thesis has not been submitted as an exercise for a degree at this or any other university and it is entirely my own work.

I agree to deposit this thesis in the University’s open access institutional repository or allow the library to do so on my behalf, subject to Irish Copyright Legislation and Trinity College Library conditions of use and acknowledgement.

Foteini Drakou
Acknowledgements

I would like to thank my PhD supervisor, Sean McClenaghan, for his support and mentorship throughout this project. I am also grateful to Balz Kamber, who gave me the opportunity to work on this project and supervised my work for the first years. I would also like to thank all my colleagues and staff in the TCD Geology Department for all the great time we spent together that make my time in the department very enjoyable. Thanks are due to the geology department’s technical and administrative staff; Frank Hendron, Maura Morgan, Cora McKenna, Gary O’Sullivan, Paul Guyett, Leona O’Connor and Noel McGinley and Sarah Guerin, for their support. During this journey I was very lucky to meet John Caulfield and Siobhná Burke that became my friends and a massive moral support at different periods of my PhD. Finally, I would like to thank my family for the encouragement and their love.
# Table of Contents

**CHAPTER 1: INTRODUCTION**

1.1 Thesis Context .................. 1
1.2 Layout of the thesis .......... 4

**CHAPTER 2: GENESIS OF VMS DEPOSITS**

2.1 Tectonic Setting ............... 6
2.3 Fluid transportation and chemical zonation .... 10

**CHAPTER 3: GEOLOGY** ............ 13

**CHAPTER 4: SAMPLING PROGRAM AND ANALYTICAL PROCEDURE** ......... 19

4.1 Sampling methods ............... 19
4.2 Analytical methods ............. 19
   4.2.1 Bulk rock geochemical analysis ........................................ 19
   4.2.2 Microscopy ................................................................. 25
      4.2.2.1 Optical microscopy ............................................... 25
      4.2.2.2 Scanning Electron Microscopy .................................. 25
   4.2.2.2.1 SEM – Energy Dispersive Spectrometry (EDS) .................. 26
   4.2.2.2.3 SEM- Cathodoluminescence (CL) .................................. 28
   4.2.2.3 Laser Ablation – Inductively Coupled Plasma – Mass Spectrometry 28
      4.2.2.3.1 LA-ICP-MS mapping ............................................... 30
      4.2.2.3.2 LA-ICP-MS spot analyses ........................................ 33
      4.2.2.3.3 LA-ICP-MS Data reduction protocol ........................................ 35
   4.3 Data manipulation and statistical methods ......................... 38

**CHAPTER 5: WHOLE-ROCK LITHOGEOCHEMISTRY** ................. 42

5.1 Introduction ....................... 42
5.2 Correlation patterns across the geochemical dataset .............. 42
5.3 Metal zonation .................... 61
   5.3.1 Characteristics of sulphide facies .................................. 62
      5.3.1.1 Cu sulphide facies .................................................. 62
      5.3.1.2 Py sulphide facies .................................................. 70
      5.3.1.3 Zn-Pb sulphide facies ............................................. 73
   5.3.2 Hydrothermal stratigraphy .............................................. 79
5.4 Discussion ........................ 89
CHAPTER 6: ORE PETROGRAPHY

6.1 Introduction 94
6.2 Petrographic description 95
   6.2.1 Pyrite 98
   6.2.1.2 Intra-mineral trace element signatures of pyrite 103
   6.2.2 Sphalerite 112
   6.2.3 Galena 115
   6.2.4 Chalcopyrite 116
   6.2.5 Arsenopyrite 116
   6.2.6 Tetrahedrite and Sb-Ag sulfosalts 118
   6.2.8 Magnetite and hematite 119
   6.2.7 Cassiterite 121
6.3 Discussion 126

CHAPTER 7: MINERAL CHEMISTRY 138

7.1 Introduction 138
7.2 Trace element distribution 138
   7.2.1 Qualitative intra-mineral trace element variations 139
   7.2.2 Quantitative trace element variation 146
   7.2.2.1 Vertical zonation 147
   7.2.2.2 Lateral zonation 157
7.3 Discussion 159

CHAPTER 8: CONCLUSION 164

CHAPTER 7: REFERENCES 166
CHAPTER 1

Introduction

1.1 Thesis Context

Global commodity price volatility and the rising demand of less abundant specialty metals (e.g., ECEs) has led to exploration and mining of more complex mineral deposits. The geometry, geochemistry and geometallurgy of these mineralised systems accounts for much of the complexity requiring an in-depth investigation and understanding of the mineral deposit.

Energy critical elements (ECEs) are scarce elements that have experienced increased demand since they are integral to emerging energy-related technologies. The criticality of ECEs has been assessed on the basis of economic importance and supply risk, and largely vary on the geopolitical position of countries and their resources. The term “energy critical elements” was stemmed from a joint meeting of the American Physical Society (APS) and Materials Research Society (MRS) that took place in 2009 discussing the availability of material resources needed for new energy technologies (Jaffe et al., 2011; Hurd et al., 2012; Grandell et al., 2016). Later, many countries adopted the terminology and began investigating and establishing their own policies for the ECEs.

Thirty raw materials have been identified as critical based on the most recent 2020 European Union (EU) list, these include but are not limited to antimony (Sb), beryllium (Be), bismuth (Bi), cobalt (Co), gallium (Ga), germanium (Ge), hafnium (Hf), Rare Earth Elements (REEs), indium (In), magnesium (Mg), niobium (Nb), Platinum Group Metals (PGMs), scandium (Sc), tantalum (Ta), tungsten (W), lithium (Li), titanium (Ti) and strontium (Sr). Several of these raw materials are extracted and (or) refined in China, with EU imports of Be, Co, Ga, Ge, In, Mg and REEs coming entirely from China. This dependency
on Chinese exports has only been exacerbated by China redirecting production to internal industries and manufacturing (Hein et al., 2013). Although mitigation strategies have been developed (i.e., encourage recycling, investigation for substitution option; Moss et al., 2013) the demand for these elements cannot be supplanted.

Beyond a few exceptions, ECEs are not found in concentrations high enough to support their individual production, and they are exclusively recovered as by-products from smelters during the refining process (Jaffe et al. 2011; Hein, 2013). This inevitable connection between base metals and their by-products is attributed to similar crustal (fluid) sources and the hydrothermal evolution of the mineral deposits. Cobalt, PGMs, Mo, Se and Te are often recovered as by-products from Cu deposits, while Ge, In, Ag, Sb and Bi are principally found in Zn-Pb deposits (Hagelüken and Meskers, 2010; Nassar et al., 2015; John and Taylor, 2016).

The Volcanogenic Massive Sulphide (VMS) type of deposits constitutes an important source of the world’s base metal supply supporting the global economy for decades (Piercey, 2009; Barrie and Hannington, 1999). Due to their polymetallic nature that often includes several ECEs, these deposits are an attractive prospect for mineral exploration. Nevertheless, the complexity that describes this type of mineralisation in terms of mining and mineral processing of ores, requires continuous surveying and investigation throughout the mining lifecycle.

Insights on ore geochemistry complements the geological model, underlying the presence of significant grade heterogeneity and elemental zonation patterns that occur within the ore body. Textural information plays a key role to designing the ore comminution and further downstream processing. The major and trace element mineral chemistry is focussed on the principal mineral carriers of commodity metals (e.g., Pb –
galena, Zn – sphalerite, Cu – chalcopyrite), highlighting associations between the recoverable metal and other credit elements. Ore and gangue minerals are also viewed and evaluated as a potential source of penalty elements. Once the concentrations of these elements exceed a defined threshold in concentrates, financial penalties may be incurred at the smelters reducing the mine revenue.

This study provides a detailed geochemical and mineralogical characterisation of the Caribou Mine, a complexly deformed polymetallic Zn-Pb-Ag-(Au) VMS deposit that is situated in Bathurst Mining Camp, New Brunswick, Eastern Canada.

Historically, the Bathurst Mining Camp (BMC) has been a significant producer of Zn, Pb and Cu as well as by-product Ag, Au and Sb (Petruk and Schnarr, 1981). The BMC hosts over 40 VMS deposits with the Brunswick No. 12 Mine dominating production up until its closure in 2013. The Caribou Mine restarted operations in 2021 (Trevali Mining Corporation) after a brief hiatus and is currently the only active mine in the BMC, of great importance to the Glencore Pb smelter in nearby Belledune, New Brunswick.

The Caribou deposit is known for its characteristic fine-grained massive sulphide mineralisation, a characteristic that poses a major issue for the metal recovery, Pb and Ag in particular. These very fine-grained sulphides (<30 microns) are believed to have been modified by a lower grade of greenschist facies metamorphism than the rest of the BMC (i.e., Brunswick No.12); hence the limited P-T conditions did not allow the sulphides to extensively recrystallise as other deposits in the BMC that are coarser-grained and resulting in higher metal recoveries during mineral processing. Mineralogically, the Caribou ore body consists of pyrite, sphalerite, galena, chalcopyrite, magnetite, arsenopyrite, tetrahedrite and cassiterite as well as a wide range of silicates, carbonates and abundant quartz. The relative abundance of these minerals varies from stratigraphic
footwall to the hanging wall, exhibiting a distinctive metal zonation in Au, Ag, Sb, Bi, Co, In, Sn, Ga, Cd, As, Se, and Hg.

This project focuses on the North West Lens system (NLS) of the Caribou deposit which is composed of three stockwork proximal ore lenses (lenses 1, 2 and 3), while there is a brief reference to the ore mineral chemistry of distal portions of the deposit in lenses 4 and 5. The NLS exhibits the best-developed mineralogical and geochemical zonation of the deposit due to its proximity to a high temperature stockwork feeder zone in the footwall of the massive sulphide lenses. Through a thorough geochemical and mineralogical study, additional information regarding the metal deportment in sulphide minerals are made available, investigating the contents of base metals (Zn, Pb, Cu), precious metals (Au, Ag), Energy Critical Elements (In, Sn, Sb, Co) and deleterious elements (As, Hg, Cd) that dominate the geochemistry of the deposit.

1.2 Layout of the thesis

This study provides an integrated approach to ore characterisation of the Caribou Zn- Pb lenses in order to map and identify the distribution patterns of credit elements within the North Lens System (NLS) - with a focus on ECEs and precious metals. This work provides insight on the potential for the by-product recovery of a wide range of elements and proposes geochemical proxies for the exploration of VMS deposit and other zoned mineralised systems.

The three core chapters (5,6 and 7) of this thesis concern the study of three different aspects of the Caribou mineralisation. These chapters have self-contained results and discussion sections with their contents described in the following sections. Chapter 2 provides a context on the fundamentals of the common hydrothermal processes
responsible for the formation and the evolution of the VMS deposits and their resulting geometry and mineralisation type. Chapter 3 presents the geology of the Bathurst Mining Camp focusing on the stratigraphy of the California Lake Group which is the host tectonostatigraphic unit of the Caribou deposit. Chapter 4 provides a detailed description of sampling and the analytical techniques (bulk-rock geochemistry, optical microscopy, SEM, LA-ICP-MS) employed as part of this study. Chapter 8 concludes the findings of Chapters 5, 6 and 7.

Chapter 5 describes the geochemical zonation that has been identified in the North Lens system of the Caribou deposit. Additionally, it includes a comparative study of the three sulphide facies observed in the deposit highlighting the typical elemental association found within each of the three facies.

Chapter 6, provides a detailed textural characterisation of the mineralisation, identifying petrographic difference between the sulphide facies and various hydrothermal generations within the same phases where possible. The textural information gathered allows the reconstruction of a comprehensive paragenetic sequence of the mineralisation.

After presenting the whole rock lithogeochemical zonation of the deposit and mineralogy of the sulphide facies, Chapter 7 builds upon chapter 5 and 6, presenting the trace element mineral chemistry of the most abundant mineral phases. These trace element signatures constitute, to some degree, a record of the hydrothermal processes that led to the large-scale vertical and lateral geochemical zonation of the deposit. Hence, these geochemical signatures provide insight into the genesis of the deposit and can be used as targets for mineral exploration of VMS deposits or other zoned hydrothermal ore systems.
CHAPTER 2
Genesis of VMS deposits

Volcanogenic Massive Sulphide (VMS) deposits are a significant contributor to the world’s base (Zn, Pb, Cu) and precious metal (Ag, Au) supply (Piercey, 2009). They are considered a major exploration target on account of their polymetallic nature that makes them less susceptible to fluctuations in metal prices (Mercier-Langevin et al., 2011). They are sources of Cu, Zn, Pb, Ag and Au, but can also contain economic concentrations of Co, Sn, Bi, Sb, Te, In, Ga and Ge; deleterious elements such as Se, Tl, As, Cd and Hg are commonly present in elevated concentrations (Barrie and Hannington, 1999; Galley, 2003; Tornos et al., 2015).

Approximately, 850 VMS deposits of varying size and metal composition are found preserved in a wide range of volcano-sedimentary terrains around the globe (Galley et al., 2007). They commonly occur in clusters, with their distribution controlled by syn-sedimentary structures and the underlying volcanic stratigraphy (intrusions?) (Galley, 2003). Thus, VMS mineralisation can trend along linear rifts, such as the Cadillac fault zone in Abitibi belt or they aggregate in districts such as the Bathurst Camp in eastern Canada and the Hokuroko District in Japan.

2.1 Tectonic Setting

The formation of VMS deposits is more favourable within extensional geodynamic regimes that allow for the circulation and recycling of metalliferous hydrothermal fluids. Nevertheless, VMS deposits preserved in the geological record are formed in a range of supra-subduction settings: nascent-arc, rifts and back-arc settings (Allen and Wei hed, 2002; Galley et al., 2007).
Most seafloor sulphide deposits formed along ancient ocean spreading centres are not preserved. This is attributed to oxidation, erosion, or more importantly their subduction during the basin closure (Galley et al., 2007), with only a small fraction of these deposits have been successfully obducted onto the continental crust.

2.2 Geometry and formation of the VMS deposits

After the discovery of hydrothermal activity in the Red Sea (Degens and Ross, 1969) and the 1977 discovery of the hydrothermal vents at the Galapagos Rift (Corliss et al., 1978), hydrothermal activity in the modern seafloor has drawn the attention of researchers (Rona, 1988; Hannington et al., 1995; Tivey, 2007). The seafloor massive sulphide (SMS) deposits are considered modern analogues of ancient VMS deposits preserved throughout the geological record and feature similar geometry and formation processes.

SMS deposits are characterised by accumulations of polymetallic massive sulphides at or near the seafloor and are spatially and genetically linked to coeval volcanism. They are formed by ascending mineralising fluids venting through hydrothermal vents. These vents are sulphide-sulphate structures with a central orifice (chimneys) or multiple fluid conduits (spires) that vent high temperature (ca. 350°C) metal-enriched fluids (Tornos et al., 2015). The precipitation of sulphides is initiated as the hot fluids are mixed with the cold seawater in the ambient seafloor environment. When chimneys are overgrown and structurally unstable, they collapse and integrate into breccia mounds (Galley et al., 2007).

Two principle hydrothermal vent types (black and white smokers) have been identified based on their composition and temperature of formation. Black smokers are
Figure 2.1: Representation of an active hydrothermal mount consisting a Seafloor Massive Sulphide (SMS) deposit that is considered as the active equivalent of the VMS deposits (after Tivey, 2007).
formed by hot Cu-Fe–rich hydrothermal fluids, whereas cooler Zn-Pb–rich fluids (typically enriched in Au) vent from the “white smoker” chimneys on the low temperature peripheries (flanks) of the sulphide mound (Hannington et al., 1995). White and black smokers are formed in similar ways, however, the seawater entrainment along the down-flowing limb of the system results in a chemical and thermal differentiation of the white smoker fluids (Tivey, 2007).

Large particles discharged from these conduits can precipitate immediately on the seafloor; at the same time, others are suspended in clouds of particles achieving the neutral buoyancy (typically at 300m above the seafloor) and spread laterally (Rona, 1988 and references therein; Fig 2.1). Once these buoyant plumes meet ocean currents, the particles quickly disperse over a large area, a fact that makes this process inefficient for the formation of economically important sulphide mounds or lenses (Tornos et al., 2015).

In the modern seafloor, the oxidizing conditions do not often allow for exhalative facies to be preserved as sulphide particles rapidly oxidise and are dispersed by ocean currents, forming extensive surficial oxidised sheets (i.e., gossan at TAG mound and relict MIR mound; Hannington, 1995).

When exhalation occurs during the immature and/or waning stage of hydrothermal activity, the fluids produced are rich in Fe ± Mn ± Si ± S instead of base metals and can form stratiform beds of ferromanganiferous exhalite (Galley et al., 2007). A well-known occurrence of Fe-rich exhalite is the Algoma-type iron formation at Austin Brook in the BMC that extends laterally for several km along the Brunswick Horizon (Peter and Goodfellow, 1996).

Hydrothermal fluids venting from the chimneys represent only a minor fraction of the total fluid discharge. Diffuse flow and the resultant replacement of the host rock is the
dominant process in formation of the VMS deposits (Rona et al., 1993). At depth, the system is confined by stockwork (stringer) type mineralization that represents the feeder zone for most VMS systems. The stockwork consists of disseminated sulphides and sulphide-rich veins that are interpreted to be the focal point for the ascending hydrothermal fluids along syn-sedimentary (volcanic) faults (Galley et al., 2007).

The morphology of VMS deposits varies impressively when compared to other mineral deposit types, as different mineralisation processes (styles) are in control of metal transport across a range of depositional settings. An ideal geometry that synthesises all the styles of VMS mineralisation (Galley et al., 2007; Tornos et al., 2015) is described by three distinct sections: a) One or more mound-shaped stratiform to stratabound massive sulphide bodies at the top; b) an underlying, downward-narrowing, funnel-like discordant to semi-concordant stockwork that leads downward to the feeder/stringer zone and; c) distal exhalative sediments that mainly occur as iron-formation. In most cases, the exhalative sediments are accumulated far from the core structure.

2.3 Fluid transportation and chemical zonation

As noted by Large (1977), VMS deposits exhibit distinct mineralogical and chemical zonation. In this, he explained the metal zonation as an effect of progressive change in chemistry of hydrothermal fluids while the fluids approach the seafloor and mix with seawater. Many VMS deposits are characterised by a Cu-rich base that passes stratigraphically upwards to a Zn±Pb-rich top. This spatial separation of the Zn-rich and Cu-rich facies of the system is resulted by the strong thermal gradient existing within the upflow zone of both VMS and SMS systems (Hannington et al., 1995). Thus, if the upwelling
fluid flow or the temperature gradient is disturbed, the development of the chemical zonation is significantly complicated (Allen and Weihed, 2002).

For the most part, Au is associated with the Zn-Pb facies of the deposits, (Hurley and Crocket, 1985); rarely, the Cu facies is found equally enriched in the Au (i.e., Mt. Lyell, Large, 1990). The bimodal distribution of Au has been attributed to its transport mechanism by two dominant Au complexes (bisulphide and chloride complexes) that results in Au deposition under a range of physicochemical conditions. In particularly, Huston and Large (1989) suggest that Au is transported as Au(HS)$_2^-$ within the Zn-Pb-rich top of the systems, while AuCl$_2^-$ is prominent along the basal Cu-rich facies and stringer zone. This theory differs from that of Moss and Scott (2001) that they proposed that AuHS$^0$ is the dominant gold carrier. Based on observations made in the PACMANUS vent field (Papua New Guinea), they claimed that the reduction of sulphur activity [a(H$_2$S)] is adequate to trigger Au precipitation from the AuHS$^0$ complex across the hydrothermal column.

Individual chimneys are also characterised by a smaller scale variable chemical composition. In the white smoker, the highest Au concentration is found in proximity to the fluid conduit within the chimney structure. The centre of the chimney is characterised by high Au and Sb concentrations, while higher values of As and Ag contents occur at the outer margin of the structure (Hannington et al., 1995).

In mineralogical terms, chalcopyrite - pyrite - magnetite ± pyrrhotite are dominant near the base of the sulphide body and within the stringer zone; whereas, the top of the lenses is dominated by banded pyrite-sphalerite ± galena mineralization. The mineralogical and chemical zonation is influenced by the strong temperature gradient of mineral precipitation. For instance, pyrrhotite is confined to the lower parts of the VMS
lenses; its formation takes place in a deep low-permeability high-temperature zone along grain boundaries in the host rock (Libbey and Williams-Jones, 2016). When the upwelling hydrothermal fluids enter the more permeable convective reservoir, they are mixed and equilibrated with relatively cooler fluids, a phenomenon that results in temperature drop of the mineralising fluids and the precipitation of chalcopyrite (Large, 1977). The presence of hydrothermal magnetite is often pronounced; however, it can be misidentified as secondary magnetite that is formed later during metamorphism (Makvandi et al., 2016).

Late hydrothermal events, metamorphism and deformation are responsible for modifying the primary zonation as well as the overall architecture of VMS deposits. The flow of hydrothermal fluids through earlier formed mound-like bodies can lead to remobilization of the primary metal sulphides. This process is referred to as “zone refining” (Eldridge et al., 1983) whereby hot upwelling Cu-rich flows passing through the lower section of the mounds, replace Zn-Pb-Ag-Au mineralisation with Cu-Fe sulphides. The Zn-Pb-Ag-Au mineralisation that dissolves progressively re-precipitates at the cooler upper and lateral margin of the mound and ultimately results in Cu-enriched as well as massive pyritic cores with a thin, base metal-enriched outer margin (Hannington et al., 1998). A protracted hydrothermal history usually leads to Au enrichment of the top of the lenses, similar to those described in the modern seafloor (e.g., TAG hydrothermal field: Hannington et al., 1995). In addition, regional deformation is likely to result in finely banded ore (Galley et al., 2007). This phenomenon is facilitated by the dynamic remobilisation of sulphides and is better developed in low grade ore with mixed silicate-sulphide assemblage due to the rheolytic contrast; the strain is usually focussed on the lower strength layer while the more competent layer accommodate strain by disaggregation and boutinage (Gilligan and Marshall, 1987).
CHAPTER 3
Geology

The Bathurst Mining Camp (BMC) is situated in northern New Brunswick, Canada. It is one of the largest mining camps worldwide hosting a cluster of numerous Volcanogenic Massive Sulphide deposits (VMS). Beyond Caribou, Brunswick No. 12, Brunswick No. 6 and Heath Steele were in production at some point.

Volcanic rocks in the Bathurst Camp formed within a continental to transitional oceanic back-arc basin (similar to the Japan Sea back-arc basin), above a southeast-directed subduction zone (van Staal et al., 2003). The volcanic rocks represent ensialic to ensimatic portions of the Tetagouche – Exploits basin formed as a result of rifting of the Popelogan Arc between 475 and 455 Ma. Subsequent closure of the Tetagouche – Exploits back-arc basin through northwest-directed subduction from the late Ordovician (Caradocian) to Silurian (Ludlovian) resulted in the development of an accretionary wedge, referred to as the Brunswick Subduction Complex (van Staal, 1994). A number of allochthonous to para-autochthonous thrust sheets (nappes) can be recognized within the imbricated accretionary wedge on the basis of their distinctive stratigraphic sequences. These nappes have undergone intense polyphase deformation and associated lower- to upper-greenschist facies metamorphism (van Staal and Williams, 1984, van Staal et al., 1988) and have been subsequently folded into shallow and steep structures (van Staal et al., 2003).

The oldest rocks in the Bathurst Camp belong to the Miramichi Group and consist of a continentally derived turbidite sequence of quartz wacke, quartzite, siltstone, and black shale of Cambrian to Early Ordovician age (ca. 490-478 Ma; Sullivan and van Staal, 1990). The Miramichi Group is conformably to disconformably overlain by Ordovician felsic
Figure 3.1: Geological map of the north section of the Bathurst Mining Camp (from McClenaghan et al., 2009).
mafic volcanic rocks and associated sedimentary rocks of Sheephouse Brook, Tetagouche and California Lake groups. These three groups represent three different joint and tectonic nappes of volcanic stratigraphy in the BMC that are collectively referred to as the Bathurst Supergroup (van Staal et al., 2003).

The largest massive sulphide accumulations occur in two distinct horizons: the Brunswick Horizon hosted by the Nepisiguit Falls Formation of the Tetagouche Group and the Caribou Horizon hosted by the Spruce Lake Formation in the California Lake Group. The California Lake Group (Fig. 3.1), which is divided into four formations that in ascending stratigraphic order are: Spruce Lake, Mount Brittain, Canoe Landing Lake, and Boucher Brook formations. The two dominantly felsic volcanic units, Spruce Lake (host to the Caribou VMS deposit) and Mount Brittain formations, formed from high temperature partial melts of a crustal block (Lentz, 1999; Rogers and van Staal, 2003). Further extension within the back-arc basin led to the eruption of mafic volcanic rocks of the Boucher Brook Formation. In particularly the Spruce Lake Formation is characterised by light green dacitic to rhyolitic volcanic rocks with intercalated tholeitic basalt (McCutcheon et al., 2000), also including polymictic fragmental rocks and crystal tuffs (Staal et al., 1991).

An oceanic crustal sequence of tholeitic basalt, lithic wacke, limestone, and shale assigned to the Fournier Group, structurally overlies the California Lake Group, and represents extension in ensimatic portions of the Tetagouche – Exploits back-arc basin (van Staal et al., 2003).

The Caribou VMS deposit has been described by several researchers (Roscoe, 1971; Davis, 1972; Helmstaedt, 1973; Cavelero, 1993), with the most recent description of its geology and genesis provided by Goodfellow (2003). Within the Spruce Lake nappe, which is structurally bound by the Mount Brittain sulphides are hosted within sedimentary and
Figure 3.2: Geological map of the Caribou deposit after Goodfellow, 2003 and McClenaghan et al., 2009. Cross-section along the NLS is included in Figure 3.3. The position of samples used for the LA-ICP-MS analyses of the pyrite chemistry are annotated in the map (see results of LA-ICP-MS spot analyses in Chapter 8).
Figure 3.3: Cross-section within the NLS interesting the Spruce Lake formation including the sulphide lenses and the feeder zone modified from Goodfellow (2003).
felsic volcaniclastic rocks of the Spruce Lake Formation. Footwall rocks consist of laminated to thinly bedded black, to dark grey shale interbedded with feldspathic sandstone and light grey siltstone. These rocks are hydrothermally altered and cut by a sulphide feeder zone, which is best preserved in the western end of the deposit (Figs. 3.2-3.3). The sulphide feeder zone is directly overlain by a stratiform massive sulphide unit, which consists of a vent complex (Cu-rich) and bedded sulphide (Zn–Pb-rich) facies (Goodfellow, 2003). Massive sulphides form a very sharp contact with hanging wall rocks, which consist of feldspar-phyric crystal tuff and ash tuff.

The deposit consists of six en echelon massive sulphide lenses extending for 1.5 km around the Caribou Synform (Fig. 3.1; Roscoe, 1971; Cavelero, 1993). The strike-length of the largest lens is 305 m with massive sulphides extending from surface to a depth of at least 1200 m. the Caribou deposit has endured protracted deformational episodes that were accompanied by a low-grade regional greenschist metamorphic overprint. Due to the low-grade nature of metamorphism (Currie et al., 2003), the sulphide minerals have not extensively recrystallised. At least four phases of deformation have affected the rocks at the Caribou deposit (van Staal et al., 1990; van Staal et al., 2003). Early D1 and D2 events gave rise to isoclinal folds and a strong penetrative axial planar schistosity ranging from a slatey cleavage in sedimentary rocks to a spaced cleavage in felsic volcanic rocks. Three sets of kink folds post-date the schistosity, forming before and during the creation of the Caribou Synform. The F4 Caribou Synform (Fig. 3.1; Roscoe, 1971) formed as a large-scale, dextral kink on the northwest limb of the Tetagouche Antiform. The west limb is vertical and the east limb dips 80° to 95° NW. The axial plane strikes 25° with a dip of 75° to 80° W and plunges 75° to the northwest (Cavelero, 1993).
CHAPTER 4
Sampling Program and Analytical Procedure

4.1 Sampling methods

During the sampling campaign in October 2015, samples of massive sulphides were collected from 10 underground diamond drill holes. The core samples originate from four E-W cross-sections distributed from the north to south across the Northwest Lens Systems (NLS) of the Caribou deposit. The sampling was limited to mineralised lenses with all of the samples containing massive or disseminated sulphides. Neither samples from the vein material cutting the mineralisation nor the host rock were submitted for analysis.

The sampled core was quartered using a water-cooled masonry saw at the provincial core repository in Madran, New Brunswick. Then, the samples were dried and transferred to labelled bags. The remaining core was returned to the core trays and labelled for reference. A total of 144 samples of quarter core - each no longer than 80cm - were collected for geochemical analysis. For each geochemical sample interval, one to three samples (a total of ~300 slabs) of quarter core were collected and shipped to Trinity College Dublin.

4.2 Analytical methods

4.2.1 Bulk rock geochemical analysis

A number of core samples were collected (n=144) in order to identify the chemical signatures associated with the mineralisation and the modifications that occurred during the protracted metamorphic and deformational history of the system. These samples were submitted to Activation Laboratories (Ancaster, Canada) for major and trace element
whole-rock analysis. In preparation for analysis, samples were crushed and pulverized using a soft iron swing mill to minimize any possible contamination of trace elements. The iron contamination was estimated to be no more than 50 ppm and therefore does not significantly affect the geochemistry of Fe-rich massive sulphide samples.

In addition to the core samples of unknown composition, 11 standards (OREAS 621) were added to the sample set for quality control and quality assurance. This certified reference material originates from a VMS deposit in Western Australia which is characterised by similar mineral assemblages with Caribou deposit. Furthermore, the OREAS 621 is certified for most of the elements of interest, having been subjected to different digestions methods including 4-acid digestion and Na-peroxide fusion that are used for this study. From a mineralogical and analytical viewpoint, OREAS 612 is an ideal reference material to assess the quality of the acquired geochemical data set.

Three different analytical packages were ordered: Ultratrace 5 (UT5), Ultratrace 7 (UT7) and 8-Peroxide (8PF). The samples for the analytical package UT5 were subjected to four-acid digestion, while prior to analyses of UT7 and 8PF packages the samples were digested with peroxide fusion. The analyses were performed using Inductively Coupled Plasma - Mass Spectrometry (ICP-MS), Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES) and Instrument Neutron Activation Analysis (INAA).

The first analytical package ordered was the UT5, in which a total of 59 elements were analysed (Ag, As, Au, Ba, Be, Bi, Br, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, In, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, Pb, Pr, Rb, Re, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tm, U, V, W, Y, Yb, Zn and Zr). From this package, 20 elements (including Au and Ag) were measured by INAA, while the remaining 39 elements were analysed using ICP-MS. Sample preparation for the UT5 analysis uses a four-acid digestion
<table>
<thead>
<tr>
<th>Element</th>
<th>Ultratrace 5</th>
<th>Ultratrace 7</th>
<th>8-Peroxide</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>INNA &amp; ICP-MS</td>
<td>ICP-MS &amp; ICP-OES</td>
<td>Na₂O fusion</td>
</tr>
<tr>
<td>Ag</td>
<td>0.05 - 100,000 ppm</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Al</td>
<td>-</td>
<td>0.01 - 25 %</td>
<td>0.01 - 50 %</td>
</tr>
<tr>
<td>As</td>
<td>0.5 - 100,000 ppm</td>
<td>5 - 10,000 ppm</td>
<td>0.01 - 10 %</td>
</tr>
<tr>
<td>Au</td>
<td>2 - 30,000 ppb</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>10 - 10,000 ppm</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ba</td>
<td>1 - 100,000 ppm</td>
<td>3 - 10,000 ppm</td>
<td>-</td>
</tr>
<tr>
<td>Be</td>
<td>0.1 - 1,000 ppm</td>
<td>3 - 10,000 ppm</td>
<td>0.001 - 1 %</td>
</tr>
<tr>
<td>Bi</td>
<td>0.02 - 2,000 ppm</td>
<td>2 - 10,000 ppm</td>
<td>-</td>
</tr>
<tr>
<td>Br</td>
<td>0.5 - 5,000 ppm</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ca</td>
<td>0.01 - 50 %</td>
<td>0.01 - 50 %</td>
<td>0.01 - 50 %</td>
</tr>
<tr>
<td>Cd</td>
<td>0.1 - 1,000 ppm</td>
<td>2 - 10,000 ppm</td>
<td>-</td>
</tr>
<tr>
<td>Ce</td>
<td>0.1 - 10,000 ppm</td>
<td>0.8 - 5,000 ppm</td>
<td>-</td>
</tr>
<tr>
<td>Co</td>
<td>0.1 - 5,000 ppm</td>
<td>0.2 - 5,000 ppm</td>
<td>0.002 - 10 %</td>
</tr>
<tr>
<td>Cr</td>
<td>1 - 100,000 ppm</td>
<td>30 - 10,000 ppm</td>
<td>0.01 - 60 %</td>
</tr>
<tr>
<td>Cs</td>
<td>0.05 - 5,000 ppm</td>
<td>0.1 - 10,000 ppm</td>
<td>-</td>
</tr>
<tr>
<td>Cu</td>
<td>0.2 - 10,000 ppm</td>
<td>2 - 10,000 ppm</td>
<td>0.005 - 40 %</td>
</tr>
<tr>
<td>Dy</td>
<td>0.1 - 5000 ppm</td>
<td>0.3 - 5,000 ppm</td>
<td>-</td>
</tr>
<tr>
<td>Er</td>
<td>0.1 - 1,000 ppm</td>
<td>0.1 - 5,000 ppm</td>
<td>-</td>
</tr>
<tr>
<td>Eu</td>
<td>0.05 - 100 ppm</td>
<td>0.1 - 1,000 ppm</td>
<td>-</td>
</tr>
<tr>
<td>Fe</td>
<td>0.01 - 50 %</td>
<td>0.05 - 75 %</td>
<td>0.05 - 100 %</td>
</tr>
<tr>
<td>Ga</td>
<td>0.1 - 500 ppm</td>
<td>0.2 - 10,000 ppm</td>
<td>-</td>
</tr>
<tr>
<td>Gd</td>
<td>0.1 - 5,000 ppm</td>
<td>0.1 - 5,000 ppm</td>
<td>-</td>
</tr>
<tr>
<td>Ge</td>
<td>0.1 - 500 ppm</td>
<td>0.7 - 5,000 ppm</td>
<td>-</td>
</tr>
<tr>
<td>Hf</td>
<td>1 - 5,000 ppm</td>
<td>10 - 5,000 ppm</td>
<td>-</td>
</tr>
<tr>
<td>Hg</td>
<td>10 - 10,000 ppb</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ho</td>
<td>0.1 - 1,000 ppm</td>
<td>0.2 - 1,000 ppm</td>
<td>-</td>
</tr>
<tr>
<td>In</td>
<td>0.1 - 100 ppm</td>
<td>0.2 - 1,000 ppm</td>
<td>-</td>
</tr>
<tr>
<td>K</td>
<td>0.01 - 5 %</td>
<td>0.1 - 25 %</td>
<td>0.1 - 100 %</td>
</tr>
<tr>
<td>La</td>
<td>0.1 - 10,000 ppm</td>
<td>0.4 - 10,000 ppm</td>
<td>-</td>
</tr>
<tr>
<td>Li</td>
<td>0.5 - 400 ppm</td>
<td>3 - 10,000 ppm</td>
<td>0.01 - 10 %</td>
</tr>
<tr>
<td>Lu</td>
<td>0.1 - 100 ppm</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mg</td>
<td>0.01 - 10 %</td>
<td>0.01 - 30 %</td>
<td>0.01 - 30 %</td>
</tr>
<tr>
<td>Mn</td>
<td>1 - 10,000 ppm</td>
<td>3 - 10,000 ppm</td>
<td>0.01 - 100 %</td>
</tr>
<tr>
<td>Mo</td>
<td>0.05 - 10,000 ppm</td>
<td>1 - 10,000 ppm</td>
<td>-</td>
</tr>
<tr>
<td>Na</td>
<td>0.01 - 20 %</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Nb</td>
<td>0.1 - 500 ppm</td>
<td>2.4 - 10,000 ppm</td>
<td>-</td>
</tr>
<tr>
<td>Nd</td>
<td>0.1 - 10,000 ppm</td>
<td>0.4 - 5,000 ppm</td>
<td>-</td>
</tr>
<tr>
<td>Ni</td>
<td>0.5 - 100,000 ppm</td>
<td>10 - 10,000 ppm</td>
<td>0.005 - 40 %</td>
</tr>
<tr>
<td>Pb</td>
<td>0.5 - 5,000 ppm</td>
<td>0.8 - 5,000 ppm</td>
<td>0.01 - 30 %</td>
</tr>
<tr>
<td>Pr</td>
<td>0.1 - 1,000 ppm</td>
<td>0.1 - 1,000 ppm</td>
<td>-</td>
</tr>
<tr>
<td>Rb</td>
<td>0.2 - 5,000 ppm</td>
<td>0.4 - 10,000 ppm</td>
<td>-</td>
</tr>
<tr>
<td>Re</td>
<td>0.001 - 100 ppm</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Element</td>
<td>Detection Limits</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>-----------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>0.01 - 20 %</td>
<td>0.01 - 60 %</td>
<td></td>
</tr>
<tr>
<td>Sb</td>
<td>0.1 - 10,000 ppm</td>
<td>2 - 10,000 ppm</td>
<td></td>
</tr>
<tr>
<td>Sc</td>
<td>0.1 - 1,000 ppm</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Se</td>
<td>0.1 - 10,000 ppm</td>
<td>0.8 - 10,000 ppm</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>-</td>
<td>0.01 - 60 %</td>
<td>0.01 - 100 %</td>
</tr>
<tr>
<td>Sm</td>
<td>0.1 - 100 ppm</td>
<td>0.1 - 1,000 ppm</td>
<td>-</td>
</tr>
<tr>
<td>Sn</td>
<td>1 - 200 ppm</td>
<td>0.5 - 10,000 ppm</td>
<td>-</td>
</tr>
<tr>
<td>Sr</td>
<td>0.2 - 1,000 ppm</td>
<td>3 - 10,000 ppm</td>
<td>-</td>
</tr>
<tr>
<td>Ta</td>
<td>0.1 - 10,000 ppm</td>
<td>0.2 - 10,000 ppm</td>
<td>-</td>
</tr>
<tr>
<td>Tb</td>
<td>0.1 - 100 ppm</td>
<td>0.1 - 1,000 ppm</td>
<td>-</td>
</tr>
<tr>
<td>Te</td>
<td>0.1 - 500 ppm</td>
<td>6 - 10,000 ppm</td>
<td>-</td>
</tr>
<tr>
<td>Th</td>
<td>0.1 - 10,000 ppm</td>
<td>0.1 - 1,000 ppm</td>
<td>-</td>
</tr>
<tr>
<td>Ti</td>
<td>-</td>
<td>0.01 - 50 %</td>
<td>0.01 - 30 %</td>
</tr>
<tr>
<td>Tl</td>
<td>0.05 - 500 ppm</td>
<td>0.1 - 1,000 ppm</td>
<td>-</td>
</tr>
<tr>
<td>Tm</td>
<td>0.1 - 1,000 ppm</td>
<td>0.1 - 1,000 ppm</td>
<td>-</td>
</tr>
<tr>
<td>U</td>
<td>0.1 - 10,000 ppm</td>
<td>0.1 - 10,000 ppm</td>
<td>-</td>
</tr>
<tr>
<td>V</td>
<td>1 - 1,000 ppm</td>
<td>5 - 10,000 ppm</td>
<td>-</td>
</tr>
<tr>
<td>W</td>
<td>1 - 10,000 ppm</td>
<td>0.7 - 10,000 ppm</td>
<td>0.005 - 20 %</td>
</tr>
<tr>
<td>Y</td>
<td>0.1 - 10,000 ppm</td>
<td>0.1 - 1,000 ppm</td>
<td>-</td>
</tr>
<tr>
<td>Yb</td>
<td>0.1 - 5,000 ppm</td>
<td>0.1 - 1,000 ppm</td>
<td>-</td>
</tr>
<tr>
<td>Zn</td>
<td>0.5 - 100,000 ppm</td>
<td>25 - 10,000 ppm</td>
<td>0.01 - 40 %</td>
</tr>
<tr>
<td>Zr</td>
<td>1 - 5,000 ppm</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**Table 4.1**: Element lists and detection limits of the three bulk-rock analytical packages acquired for this study.
which can be problematic for the complete digestion of restate phases. The results of these analyses failed the quality control test (accuracy: 66% and precision: 7.4%), therefore the same samples and standards were reanalysed using a Na-Peroxide fusion digestion (UT7).

The UT7 analytical package offers analysis of 55 elements (Al, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Ho, In, K, La, Li, Mg, Mn, Mo, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Se, Si, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, and Zn) with ICP-MS and ICP-OES. Due to the high abundance of Zn, Pb, Cu and As contents, the concentrations determined for the samples exceeded the instrumental detection limit, thus, the same sample pulps were assayed using ICP-OES (8PF package). The analytical package 8PF includes the analyses of the following 19 elements: Al, As, Be, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Ni, Pb, S, Si, Ti, W and Zn.

With respect to the problematic geochemical package (UT5), a number of elements show poor precision of >10% (Ba, Cr, Cs, Hf, Se, In, Mg, Sr and Lu). Poor precision correlated somewhat with poor accuracy. The 11 OREAS 621 standards together with 30 standards introduced by the lab were used to test the precision and accuracy of the analyses. All 11 OREAS standards contained at least 12 elements which failed to be within two standard deviations of the certified value. More specifically, of the 462 individual elemental analyses throughout the 11 standards, 159 analyses were greater or less than two standard deviations of the certified value, equating to an overall accuracy of only 66% at two standard deviations. Within the standard set inserted by the lab, it was only possible to assess accuracy for two standards, DNC-1a and SdMAR-M2, showing low overall accuracies at 67% and 39%, respectively and using a testing level of two standard deviations from certified values. Chromium, Hf, Yb and Lu were consistently over-reported with Ag, Cs, U,
Cu, Bi, In, Mg, Nb, Rb and Sr underreported, by two to five standard deviation from the certified value.

The sample set was too small to detect whether drift contributed to inaccuracy. There was, however, noticeable drift in values for individual standards. The fourth and the ninth OREAS 621 standards show consistently lower values across the range of elements. Lastly, all blanks passed with no issues and the duplicate samples performed generally well with variation around the mean averaging 7.4 % precision by the half-absolute relative difference method. Taking these findings into account, the problem with this analytical package was associated with the digestion procedure and volatilization losses.

In contrast to the compromised quality of the analyses of specific elements from the UT5 dataset, the results released for the UT7 and 8P packages are consistent and accurate. The quality control program showed that the average values for accuracy and precision are 94 % and 2.6 % respectively.

In summary, the bulk-rock geochemical dataset consists of 22 elements compiled over the three analytical packages. The majority of them are acquired from the UT7 package (Sn, In, Cd, Ga, Ge, Co, Sb, Bi, Se, Mo, Mn and Tl) and 8P package (Zn, Pb, Cu, Fe, S, As), except for the Au, Ag, Ni and Hg analyses that derive from UT5. In particular, Au and Ag are analysed by INAA, a technique that does not require any pre-treatment of the samples such that suspected to have influenced the accuracy and precision of the UT5 dataset. Besides, UT7’s Ni is replaced by UT5’s Ni analyses, since the latter are described by LODs that are an order of magnitude inferior and thus more suitable to the depleted Ni composition of the samples. Accuracy and precision values are presented here for Au (100% accuracy and 1.4% precision), Ag (36% accuracy and 4.28% precision) and Ni (100% accuracy and 4.27% precision), while the quality of the Hg analyses could not be tested as
the OREAS 621 standard is not certified for this element. Regarding the poor accuracy of the Ag analysis, this Ag data was compared with the Ag assay analyses performed by the company during the initial assessment of the drilling program. This comparison shows that the Ag data acquired for this study is within the range of the known Ag assays.

4.2.2 Microscopy

A total of 27 polished 30 μm-thin sections of massive sulphides were prepared at the Geology department at the University of New Brunswick for petrographic and micro-analytical study. In addition, three thin sections, part of Sean H. McLenaghan collection, were added to this study. These thin sections, cut from core samples collected in 2009, represent samples of surface drill holes intersecting the stratigraphic top of the mineralisation.

4.2.2.1 Optical microscopy

A total of 27 polished thin sections were studied under reflected light. Potential analytical targets were determined from petrographic examination of 10 of these thin sections. Prior to microanalytical study, high resolution stitched images of the entire thin sections were acquired using an Olympus BX60 reflected and transmitted light microscope equipped with a SC50 CMOS Olympus colour camera.

4.2.2.2 Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) analyses were performed on selected sulphide samples to obtain major element mineral chemistry and micro-imaging. Two multi-detector SEM systems were used for this work, both of which are hosted at the
Centre for Microscopy and Analysis, Trinity College Dublin. The first system, on which most of the micro-imaging and spot analyses were carried out, is a Tescan Mira XMU field emission scanning electron microscope (FE-SEM, TESCAN, Brno, Czech Republic) operating under high vacuum conditions. The second system is a Tescan Tiger Mira3 Variable Pressure Field Emission Scanning Electron Microscope (VP-FE-SEM, TESCAN, Brno, Czech Republic). Both systems are equipped with a Tescan CL detector and an Oxford X-MaxN 150 mm² Energy Dispersive Spectrometer (EDS) detectors operating via AZtec software (Oxford Instruments). Tiger Mira3 which has been consistently used for large scale EDS mapping, as it is equipped with a second EDS detector that allows for faster data acquisition.

In preparation for the SEM work, the thin sections were carbon coated (Cressington 208 Carbon, high-resolution carbon coater) with a continuous coating layer of 15nm in order to obtain an evenly conductive sample surface. Backscattered electron images (BSE images) were acquired at 20 keV to yield compositional information through the mechanism of atomic number contrast. For imaging of galena, the accelerating voltage was reduced to 15 keV to eliminate the charging effect.

4.2.2.2.1 SEM – Energy Dispersive Spectrometry (EDS)

Major element mineral chemistry was determined by EDS. All chemical analyses were acquired with a focused beam using an accelerating voltage of 20 KV and a beam current of 0.25 nA measured in the Faraday cup. Compositional data from both samples and standards were obtained using a spot size of 10 nm at a magnification of 31,000x. Standardisation was made at the beginning of each analytical session using natural minerals (pyrite, sphalerite, chalcopyrite), alloys (PbTe, InAs, HgTe) and metals (Ag, Au, Co,
Sb, Sn, Ni). Minor beam current drifts were controlled by frequent analysis of a Co standard. The live counting time was set at 60 seconds or 400,000 accumulated counts, while analytical conditions maintained the EDS detector’s dead-time at approximately 30%. The long processing times aim to improve deconvolution of the neighbouring overlapping element energy lines, such those found between S (Kα - 2.31) and Pb (Mα 2.34), as well as As (Lα - 1.28) and Se (Lα - 1.38)). The detection limit of this technique is ca. 0.1 wt. % (Reed, 2005).

Major element semi-quantitative EDS maps were acquired targeting compositional heterogeneity within individual grains as well as different mineral phases across an entire thin section. During the mapping, the complete spectrum is collected at once and saved for each individual pixel. In this way, the user is able to recall information from the stored data, process and export the data retrospectively.

For this study, two maps of entire thin sections were obtained in order to spatially locate minute mineral phases that were expected to be present considering the corresponding whole-rock chemistry data. As such, Sn distribution maps were acquired to spatially constrain the position of cassiterite grains with size smaller than 10 μm. Following this, the same areas were studied in detail performing quantitative spot analyses with SEM-EDS.

Full section major element maps were obtained by producing a montage of individual X-ray maps with 15% overlap. These maps were collected in a “standardless” procedure with the aim of visualising the major element distribution, carrying no significant quantitative information. Thus, the intensities of the energy peaks are converted to approximate concentrations using theoretical data already constrained for the system (Reed, 2005).
The TIGER MIRA3 SEM with the two EDS detectors was employed for the acquisition of these large maps in a shorter time. In order to further reduce the instrument live time, the maps were acquired with low process times that allow for the collection of higher total count rates in a shorter time period. During the post-processing, the individual frames were aligned and stitched into single maps which were subsequently processed as true maps in order to apply the background correction and resolve the energy overlaps in the collected spectrum. A different colour is assigned to each element on the map.

4.2.2.3 SEM- Cathodoluminescence (CL)

Cathodoluminescence response was investigated for a limited number of specimens. TIGER MIRA3 SEM was used for these analyses that is equipped with a Tescan CL detector. The SEM was set-up for the CL at 10KeV acceleration voltage, considerably lower than the one used for the SEM-EDS spot analyses. This time, beam intensity was not adjusted based on a measurement in the Faraday cup, instead, it was intuitively tested based on the CL response. Hence, a beam intensity of 11 was found to give the clearest signal. For the CL image acquisition, the image scan speed was lowered to improve the image resolution, capturing one image every ca. 12 minutes.

4.2.2.3 Laser Ablation – Inductively Coupled Plasma – Mass Spectrometry

A suite of trace elements was analysed with LA-ICP-MS in order to determine the trace element composition of the ore minerals as well as illustrate chemical variations along their grain boundaries.

All data were obtained at Trinity College Dublin on a ThermoFisher Scientific iCAP-Qc quadrupole mass spectrometer (MS, Thermo Fisher Scientific, Waltham, MA, USA) that
is coupled with a 193 nm excimer Ar-F laser Teledyne Photon Machines G2 (Teledyne Technologies, Inc., Thousand Oaks, CA, USA), equipped with a HelEx II active 2-volume ablation cell (Teledyne Cetac Technologies, Omaha, NE, USA). A short residence time of the ablation products is achieved by using a He-Ag carrier gas. A typical He flow rate of 0.20 L/min is introduced to both the large outer cell and the small inner volume (cup) of the sample chamber. The cup also receives a small volume of N$_2$ flow (ca. 7 mL/min) that promotes signal sensitivity and impedes the formation of oxides. The Ar nebulizer gas (0.7 L/min) is added to the sample-gas mixture downstream of the laser cell and is controlled by the mass spectrometer operation software.

The laser is operated with Chromium 2.3 software (Teledyne Photon Machines, Inc., Thousand Oaks, CA, USA) and data acquisition is executed with Qtegra 2.2 (ThermoFisher Scientific, Waltham, MA, USA) in time-resolved peak-hopping analysis mode.

The analyte list for both mapping and spot analysis experiments includes $^{34}$S, $^{55}$Mn, $^{57}$Fe, $^{59}$Co, $^{60}$Ni, $^{69}$Ga, $^{63}$Cu, $^{66}$Zn, $^{73}$Ge, $^{75}$As, $^{77}$Se, $^{95}$Mo, $^{107}$Ag, $^{112}$Cd, $^{113}$In, $^{115}$In, $^{119}$Sn, $^{124}$Sn, $^{197}$Au, $^{199}$Hg, $^{121}$Sb, $^{125}$Te, $^{205}$Tl, $^{208}$Pb and $^{209}$Bi. The isotopes analysed were thoroughly inspected for potential interferences forming between the make-up gas and the ablated samples (May and Wiedmeyer, 1998). Individual dwell times were selected for each analyte based on their relative abundance on the unknown and standards. For major elements such as Fe, Cu, Zn and As, short dwell times and high-resolution mode were selected in order to avoid acquisition of large count rates that deteriorates the detector’s performance on the long term.

Sulphur is a major constituent of all mineral analysed and has been used as an internal element standard on analyses of sulphide minerals (Martin et al., 2019). However,
isotopes of S significantly interfere with O isotopes, producing a high and variable background that results in high Limit of Detections (LODs) and inaccurate measurements. $^{34}$S was analysed across the experiments, as it interferes exclusively with $^{17}$O ($^{17}$O+$^{17}$O=$^{34}$S) which is the least abundant O isotope. Nevertheless, for the experiments conducted on this study, $^{57}$Fe and $^{66}$Zn were used as internal standard, due to their homogeneous distribution across the various mineral phases and their low interference levels.

Initial instrument calibration was performed at the beginning of each analytical secession using NIST SRM 612 (Jochum et al., 2011), in order to optimise the instrument sensitivity. This glass standard was not included in any of the experiments due to the considerably lower concentrations in the elements of interest. Each experiment was bracketed by 2 x 2 NIST SRM 610 standard that used to monitor the instrument performance. In the course of the experiment MASS1 (Wilson et al., 2002), MUL (Onuk et al., 2016) and UQAC were analysed as external calibration standards.

4.2.2.3.1 LA-ICP-MS mapping

Trace element distribution maps were produced by ablating a set of lines of equal length and processed as a single experiment. A 1-2 μm line overlap was employed in order to ensure that there are not un-ablated gaps left on the maps. Each line is generated by the ablation of numerous overlapping square spots on a constantly moving stage. These lines were aligned parallel to the gas flow trajectories in order to reduce the possibility of resampling of previously ablated material.

During the mapping experiments the HelEx II laser ablation cell and the mass spectrometer were connected using a small diameter polytetrafluoroethylene tubing system, the ‘Aerosol Rapid Introduction System’ (ARIS, Teledyne Photon Machines, Inc.,
This tubing (1.3 mm inner diameter, 372 mm in length) delivers the sample to the mass spectrometer with minimal wash-in and wash-out time (<20 μm) to baseline, enabling the user to resolve individual single pulses even when ablation is performed at a high repetition time (up to 60 Hz).

The number of analytes of each experiment was restricted to 5-11 isotopes for each run and were selected relative to the trace-element chemistry of the analysed minerals. The dwell times were variable according to the relative abundance of the analytes which were determined by running a test experiment. Individual dwell times range from 20 to 60 ms that add to a total dwell time of shorter than 330 ms in order to ensure frequent measurements of each analyte. Overall, 20 ms is the shortest dwell time used on experiments involve the ARIS tubing, in order to avoid oscillations on the signal.

The mapping experiments conducted under different stage speed (15-30 μm/s), nominal beam size (8-12 μm/s), fluence (1.0-1.2 J/cm²) and frequency (39-40 Hz) parameters that serve best the purpose of the individual experiments. For all mapping experiments, a 20 s pause time preceded the analysis of each line.

Beam size, scan speed and total dwell time of the experiments are interlinked parameters that dictate the spatial resolution of the experiment. While beam size determines the y-resolution, x-resolution is calculated as stage speed [μm/s] × (total dwell time [s] + detector’s dead time [s]).

As part of this study, two types of LA-ICP-MS maps were generated: (a) “single mineral maps” and (b) “large scale maps” across different mineral phases. Data acquisition was designed adopting two different protocols tailored to the resolution requirements of the individual type.
The “single mineral maps” present the intra-mineral trace element variations of a single mineral phase. The experiments designed herein are based on protocols followed by Ubide et al., (2015) and Zhou et al., (2017). In particular, the ablated area – usually not exceeding the 0.25 mm² - includes the crystals of interest and the immediate surrounding matrix. These experiments are conducted under the following conditions: beam size of 10-12 μm, stage speed of 20 μm/s and a total dwell time of 170-180 ms. The short total dwell time allows only for the analysis of 5-6 analytes per run including the internal standard. Considering the large number of analytes needed per map, the experiments were repeated with identical parameters, but different analyte list and corresponding dwell times. The parameters under these experiments were conducted resolve an individual pixel’s aspect ratio of approximately 4:1 (x-resolution to y-resolution). In an attempt to avoid decreasing the laser beam size (10-12 μm), over-resolving for the x-resolution were used as an alternative approach to discern mineral feature with a size similar to laser spot. The acquisition time for these experiments may exceed two hours.

The “large scale maps” illustrate the relative trace element abundance across the different minerals, intersecting more than one mineral phases. These experiments are designed to have equal x- and y-resolution by applying faster stage speed (ca. 30 μm/s) and a longer total dwell time (ca. 330 ms). The size of these experiments usually extends up to 1mm² and their acquisition last about an hour.

Each map was bracketed by two NIST SRM 610 (external standard) and two MASS1 (quality control standard) line scans with the same laser parameters as the map. For most of the experiments, no standards introduced in the course of the mapping. It is found that when the succession of the line scans on the unknown is interrupted by analysis on standard, artefacts are generated on the 2D element maps. These artefacts are present in
the maps where the analytes are significantly depleted in the reference material compared to the unknown. These artefacts are caused by the extreme drop of the baseline following the analysis of the standard line scans and the subsequent low overall count rate of the first ablated lines when the analysis on the unknown resumes. Through the progression of the experiments, the count rate adds up to the previous level shows no evidence of these 2-3 line scans long artefacts that appear after the analyses of the standards.

4.2.2.3.2 LA-ICP-MS spot analyses

Spot analyses were acquired for pyrite, sphalerite and chalcopyrite. Samples were analysed in time-resolved mode using a square laser aperture with maximum size 25 by 25 μm - depending on the sample’s grain size - at a frequency of 5-10 Hz, shot count of 150-250 and fluence of 1.0-1.3 J/cm² (see Table 4.2).

A combination of matrixed-matched primary and secondary standards (MASS1, UQAC and MUL) were used for the spot experiments, running frequent analyses of the standards for every 25 spot analyses of the unknown. Background (effectively a gas blank) was measured for 120 seconds prior the analysis followed by a 16 second washout period post-ablation. A long background line was also recorded at the end of each experiment. The spot analyses were acquired using an in-house developed adjustable signal smoothing device that connects the laser with the mass spectrometer.

Spot analysis on pyrite and sphalerite acquired with the same laser parameters: 25 by 25 μm beam size, fluence of 1.1 J/cm², 150 shot counts, and 5 Hz repetition rate. However, different calibration and internal element standards were used for the data reduction, using MASS1 with $^{57}\text{Fe}$ for pyrite, and $^{66}\text{Zn}$ with MASS1 and MUL for sphalerite spot analyses.
<table>
<thead>
<tr>
<th></th>
<th>Beam (μm)</th>
<th>Fluence (J/cm²)</th>
<th>Shot counts</th>
<th>Frequency (Hz)</th>
<th>Internal STD</th>
<th>External STD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td>25 X 25 (square)</td>
<td>1.1</td>
<td>150</td>
<td>5</td>
<td>$^{57}$Fe</td>
<td>MASS1</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>25 X 25 (square)</td>
<td>1.1</td>
<td>150</td>
<td>5</td>
<td>$^{66}$Zn</td>
<td>MUL &amp; MASS1</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>18 X 18 (square)</td>
<td>1.3</td>
<td>150</td>
<td>6</td>
<td>$^{57}$Fe</td>
<td>MASS1</td>
</tr>
</tbody>
</table>

**Table 4.2:** Summary of the laser parameters and standards used for the LA-ICP-MS spot analysis on sulphide minerals.
Chalcopyrite analysis performed using 18 μm square beam size, a fluence of 1.3 J/cm², 150 shot counts and 6 Hz. The beam sizes were smaller than the pyrite and sphalerite experiments due to the considerably finer size of chalcopyrite grains in one of the specimens. $^{57}\text{Fe}$ were used as an internal element standard calibrating for MASS1.

4.2.2.3.3 LA-ICP-MS Data reduction protocol

Data reduction for both types of LA-ICP-MS experiments was performed with the software package lolite 3.5 (The University of Melbourne, VIC, Australia), implemented in Igor Pro 6.37 (WaveMetrics Inc, Portland, OR, USA). After importing the raw data as time-resolved waves into lolite, baseline intervals were defined from beam intensity and then the individual integration windows were manually adjusted for all element channels. The best-fitted spine type was selected for baseline subtraction.

The laser log file was synchronised with the ICP-MS data file to define integration intervals for reference material and samples. The primary and secondary standard integrations were interpolated using a suitable spline type.

Maps were generated through lolite stitching the line scan data into two-dimensional maps using the Data Reduction Scheme “Trace-Elements” in “Semi-Quantitative” mode that perform no correction for the internal element standard. Concentration limits were selected to highlight the inhomogeneity for each analyte.

Concentration data were obtained for spot analyses by applying the DRS “Trace-Elements” in “Quantitative” mode, using an external standard (MASS1 or MUL) together with an internal element standard ($^{57}\text{Fe}$ or $^{66}\text{Zn}$) that was earlier measured on the SEM-EDS. EDS analyses show that pyrite, sphalerite and chalcopyrite composition is stoichiometric as follows:
• 46.55 wt. % Fe for pyrite standardising with MASS1
• 64.06 wt. % Zn for sphalerite with MUL and MASS1
• 30.43 wt. % Fe for chalcopyrite with MASS1.

All types of inclusions identified in the spot profiles were maintained along the data reduction unless they significantly influence the shape and the overall count rate of the integration. In the latter case, the entire integration is discarded. Figure 4.1 shows the raw count profiles of Fe (green) and Pb (blue) of three individual pyrite spot analysis. The displayed CPS scale is true only for Fe. During the data reduction, the first spot analysis was discarded due to the intersection of galena towards the bottom of the ablation pit. The principal behind avoiding adjustments of the integration window to fit only inclusion-free section of the signal is that bias is introduced in the calculation of the elemental compositions. If, for instance, the integration window is shortened including only the first half of the spot profile, a higher average count rate of in the internal element standards will be applied for the correction resulting in underreporting of all other elemental concentration of the particular spot analysis.

The calculated values for each spot analysis are accompanied by an error and the limit of detection (LOD). The LOD is the lowest value that can be quantified for a give spot analysis. This value is both element-specific and experiment-specific as its calculation is based on the baseline spine, the background CPS and the dwell time of the individual elements. In the summary statistics table, only the mean LOD value is reported per element. Thus, some of the analysis existing in the dataset may be lower than the reported mean LOD value, however, these analyses were over detection limit for the LOD calculated specific for the corresponding spot analysis. Values below LOD are automatically assigned by the software as “below detection limit”.

36
Figure 4.1: Iron (green) and Pb (blue) profiles of three spot analyses on pyrite. The first spot analysis is discarded due to intersections of a galena grain.
4.3 Data manipulation and statistical methods

The individual datasets acquired during this study were compiled using Microsoft Excel 2013. Computation of summary statistics (e.g., mean, median etc.), correlation coefficients (Spearman’s) and Principal Component Analysis (PCA) were performed using statistical software and data analysis in ioGAS 7.0 (IMDEX), PAST 2.0 (National History Museum, University of Oslo, Norway), CoDaPack 3.0 (Department of Computer Science and Applied Mathematics, University of Girona, Spain) and Excel. In addition to the above-mentioned statistical treatment, downhole profiles, binary plots, histograms and box and whisker plots were used as visual supplements to descriptive statistics.

For the bulk-rock geochemical analyses, data below the instrumental detection limit (LOD) are assigned a set value of half the detection limit in order to facilitate the statistical treatment of the dataset. However, these assigned values are not discussed or included in the descriptive statistics tables (Table 5.1), instead they are reported as below detection limit (<LOD), followed by the calculated LOD value. From the total of 144 geochemical samples, 10 or less individual measurements per element returned values beyond the calculated LODs. The frequency of these measurements is also included in Table 5.1. Data below LOD derived from the LA-ICP-MS analyses were discarded from the dataset before applying statistics.

Most statistical tests assume that datasets consist of normally distributed populations. However, the majority of the geological data appeared positively skewed and typically follow a multimodal distribution (Rock, 1988; Reimann and Filzmoser, 2000), with data acquired for this project to be no exception. Figure 4.2 consists of 20 histograms that illustrate the distribution of an equal number of major and trace elements across the whole-rock geochemical dataset acquired for this study. As anticipated, none of the
histograms represents a normally distributed population. In particular, Zn, In, Cd, Hg and Sb are described by bimodal distributions, while elements such as Cu, Bi and Ge that follow strong unimodal distributions are right-skewed (positively skewed).

With such datasets, the typical parameters of descriptive statistics that are used to measure the central tendency (e.g., mean) and dispersion (e.g., standard deviation) of the data may be misleading. This is especially relevant for distributions that have more than one mode, where the concept of central tendency in practically meaningless. Hence, in an attempt to give a fair description of the distributions median and median absolute deviation (MAD) are preferred instead of mean and standard deviation, respectively (Reimann and Filzmoser, 2000).

In order to evaluate the associations between different variables (i.e., elemental concentrations), the spearman’s rank-order correlation coefficient ($\rho$) is employed (Spearman, 1904). This non-parametric correlation type requires a monotonic relationship between the pair of variables that is incurred after rank-transformation. The calculation of this coefficient type uses the distance between the ranked values instead of the original variables, based on the following formula:

$$\rho = 1 - \frac{6 \sum d^2}{n(n^2 - 1)}$$

where $d$ is the distance between the corresponding ranks of each variable and $n$ is the sample size.

According to Ramsey (1989), the significance of the Spearman’s correlation coefficient was assessed by calculating the $\rho_{crit}$ based on the Student’s t distribution applied on a given population size ($n$) and degrees of freedom ($df = n - 2$)

$$t = \rho_{crit} \sqrt{\frac{df}{1 - \rho_{crit}^2}}$$
Figure 4.2: Histograms of major and trace element distribution of the 144 who-rock samples analysed as part of this study.
Only if $|\rho| \geq \rho_{\text{crit}}$ the described correlation is significant.

Spearman’s rank-order correlation coefficient is a great tool for exploratory data analysis. As such, it is used in this study to highlight elemental covariations within the individual facies and across the complete bulk-rock geochemistry dataset. Spearman’s rank coefficient overcomes the issue of the non-normal distribution and eliminates the influence of outliers.

However, geological dataset also suffers from a closure problem (Aitchison, 1983). Compositional data of bulk-rock geochemistry or mineral chemistry are expected to sum up to a constant number - in most cases 100% (Rollinson, 1992). A suitable data transformation should be applied to open the closed data when these multi-variant data are plotted on a lower-dimensional space, such that occur in Principal Component Analyses (PCA). Isometric log-ration (ilr), additive log-ratio (alr) and centred log-ratio (clr) are the most common transformation applied for this purpose (Egozcue et al., 2003; Filzmoser et al., 2009). In this study, centred log-ratio transformation was applied to the raw dataset prior to PCA. A Residual Value (RV) is added to each sample in order to satisfy the constant-sum constraints. During the clr transformation, the log of individual analyses is divided by the geometric mean of the specific variable (in this case element) across the dataset.

Principal Component Analysis allows for the representation of complex relationships between a large number of variables by reducing the dimensionality of the dataset. Similarly, in this study, PCA is used to explore and interpret hidden relationships across the compositional data but also to corroborate classifications performed during core logging when no compositional data were yet available.
5.1 Introduction

The Caribou deposit is an ideal deposit for the study of metal zonation in VMS systems. It consists of 6 en echelon lenses that occur in the core of a synformal structure that plunges steeply to the north. Each of these lenses exhibits individually the same vertical zonation. Past studies (Cavelero, 1970; Jambor, 1986; Goodfellow, 2003) have investigated the genesis, metal zonation and structure of the caribou deposits.

In this chapter, the whole-rock major and trace element chemistry is presented, discussing correlations and distribution patterns within both individual drill holes and sulphide facies, as well as the entire dataset. Descriptive statistics, correlation coefficients and Principal Component Analysis (PCA) are employed to extract information from the geochemical dataset (see Chapter 4.3). As mentioned in the previous chapter, the samples analysed are derived from four different cross-sections across the Northwest Lens System (NLS) of the Caribou deposit.

5.2 Correlation patterns across the geochemical dataset

A total of 144 samples of massive sulphide were analysed for their major and trace element composition. Iron, Zn, Pb and Cu comprise the base metal suite that dominates the chemistry of this sulphide deposit. The median values of metal concentrations of all 144 samples are as follows: 36.6 wt. % Fe, 6.49 wt. % Zn, 1.88 wt. % Pb, 0.33 wt. % Cu, 0.16 wt. % As, 1,225 ppb Au, 49 ppm Ag and 200 ppm Sn. The summary statistics for the entire bulk-rock dataset is found in Table 5.1.
To obtain a more comprehensive insight into elemental correlations, the Spearman rank-order correlation coefficient ($\rho$) is employed. For a 99% confidence level ($N=144$), the critical value ($\rho_{\text{crit}}$) is calculated to be 0.19 based on a Student’s $t$-distribution (see Chapter 4.3). Hence, $\rho$ values equal or higher than 0.19 (positive correlation) and equal or lower than -0.19 (negative correlation) are assigned as statistically significant. However, considering that the Spearman’s correlation coefficient is a measure of a monotonic relationship between the variables (i.e., elemental composition) of the dataset, variables with $\rho$ values outside the interval [-0.19, +0.19] could also found to be correlated but this relationship would not be characterised by a monotonic pattern. Therefore, the exploratory study of the geochemical dataset with the calculation of the $\rho$ values is followed by the examination of the binary plots of the same elements in order to confirm or reject the relationship between the two variables.

The Spearman’s rho ($\rho$) values, calculated across the entire dataset, are presented in Table 5.2, along with the elemental binary plots in order to graphically display the bulk-rock elemental associations (Figs. 5.1-5.4). In this section, geochemical variations across the entire dataset are described and illustrated en masse, including anomalous (outlier) data points, which are also included in the calculation of the summary statistics (Table 5.1) and the correlation coefficients (Table 5.2). These anomalous values do not compromise the quality of the dataset on the grounds of the large population size and the use of Spearman’s correlation that eliminates the influence of these outliers in the calculation of the $\rho$ values. The colour of the data points signifies the sulphide facies that each of the samples belongs to. In this section, there is limited reference to this facies categorisation, while it is discussed in detail in Chapter 5.3.
Table 5.1: Summary table of the whole-rock geochemistry of 144 samples analysed by ICP-MS and ICP-OES after Na-peroxide fusion digestion, except Au, Ag, Hg that were analysed by INAA. Median and Median Absolute Deviation (MAD) are calculated for the entire dataset before outlier’s rejection take place. Minimum and maximum values and the extreme outliers are displayed in the table. Outliers marked with an asterisk (*) are rejected along the procedure and not used for the calculation of descriptive statistics in Chapter 5.3. The frequency of measurements returned values beyond the detectable range (below or above LODs) is given in the last column of the tables.
Table 5.2: Spearman rank-order correlation matrix of the bulk-rock geochemistry of 144 samples of massive sulphides from the Caribou deposit. For 99% confidence level $\rho_{\text{crit}}$ is estimated to be 0.19, based on a student’s t-distribution.
Figure 5.1: Binary plots of base metals of economic interest (Zn, Pb, Cu) with selected elements that display significant Spearman correlation (99% Confidence level, $\rho>0.19$; Table 5.2)
Figure 5.1: (continued)
Zinc exhibits a positive Spearman correlation with Pb ($\rho=0.79$), Cd (0.98), Sn (0.86), In (0.48), Ag (0.65), Sb (0.56), As (0.46), Au (0.41), Ga (0.53), Tl (0.52), Mo (0.43), Hg (0.36) and Ni (0.29). The positive correlative behaviour identified between Zn, Cd and Sn is chiefly associated with Cd and Sn substitution into sphalerite lattice. Zinc concentrations range from below detection limit ($< 0.01$ wt. %) to 15 wt. % Zn; except for one outlier that reaches up to 19.2 wt. % Zn. This outlier does not exceed the four standard deviations from the mean criterion; however, its rejection is based on the fact that the sample fails to adhere to the linear relationship of Zn-Cd (Fig 5.1A) and Zn-Sn (Fig 5.1B) that are attested by any other data point of the dataset. Overall, Zn concentrations have a median value of 6.49 wt. % Zn.

Lead concentrations also vary, reaching up to 6.14 wt. % Pb with a median value of 1.88 wt. % Pb. Lead exhibits a significant correlation with Ag (0.82), Zn, Cd (0.75), Sn (0.76), As (0.57), Sb (0.71), Au (0.56), Tl (0.58), Ga (0.51), Mo (0.46), Hg (0.27), Ni (0.34) and In (0.22). The predominant positive correlation between Pb and Ag (Fig 5.1C) can be explained by assuming that galena is the principal mineral host of Ag. Nevertheless, Zn, Cd and Sn covariations with Pb (Fig 5.1 D-F) can be reconciled merely with the co-existence of galena and sphalerite in the same samples. Lead and Ag have considerably larger atomic radius than Zn that impede their incorporation into sphalerite. Additionally, it is indicated by the Pb-Co binary plot on Figure 5.1G and the $\rho$ value of -0.58 that Pb behaves antithetically with Co across the entire dataset. However, upon closer examination, two contrasting associations can be identified between Zn-Pb rich and Zn-Pb depleted samples.

Copper is the least abundant base metal in the deposit and occurs primarily as chalcopyrite. Copper abundance ranges from 0.026 to 3.06 wt. % Cu (median 0.33 wt. % Cu)
and covaries with Co (0.68; Fig. 5.1H), Se (0.57; Fig. 5.1I) and Bi (0.50; Fig. 5.1J). Four samples with anomalously high Cu concentrations (1.93 to 3.06 wt. %) are identified. These high concentrations can be readily explained by the greater chalcopyrite abundance that can be seen macroscopically in hand specimens. Copper exhibits a significant negative correlation with Zn (-0.52; Fig.5.1K), Pb (-0.52; Fig.5.1L) and all the elements associated with these two elements. These antithetic associations of Cu with the other base metals follow a broad metal zonation that is commonly developed in the VMS systems during the zone refining process (Large, 1977). 

Gold has a median value of 1,225 ppb across the entire dataset. It exhibits high variability ranging from 37 to 4,710 ppb, displaying higher concentrations within the Zn-Pb facies. Overall, BMC is characterised by low Au concentrations, and only the Caribou deposit stands out as one of the most Au-rich deposit of the camp. However, comparing the VMS deposits in the global scale, Caribou is not considered auriferous (Mercier-Langevin et al., 2011). Gold covaries with As (0.74), Ag (0.72), Sb (0.72), Tl (0.56), Pb, Zn, Sn (0.42), Cd (0.40), Ga (0.39), Ni (0.35), In (0.21), Mo (0.39) and Bi (0.19). The strong positive correlation between Au and As (Fig. 5.2A) is indicative of their common mineral carrier. This has been extensively studied across the different mineralising systems, suggesting a refractory nature of Au in arsenian pyrite and arsenopyrite (Fleet et al., 1993; McClennaghan et al., 2004; Reich et al., 2005; Deditius et al., 2014). Similarly, Ag, Sb and Tl enter into pyrite and arsenopyrite lattice (Cabri et al., 1989, 2000; Deditius and Reich, 2016) and this is reflected on the positive correlation of these elements with Au (Fig. 5.2 B-D).

Overall, contents of Silver range from 3.4 to 236 ppm Ag, beyond an outlier with an absolute concentration of 380 ppm Ag (Fig 5.1C). This sample is being retained in the dataset as it is also characterised by an outlying Bi concentration, suggesting the presence
of Ag-Bi-rich sulphosalt or galena. However, due to the negative Pb-Bi correlation (-0.2),
galena is very unlikely to be the host of Bi in the deposit. The median value of Ag is 49 ppm.
Silver shows a positive correlation with Pb, Au, Sb (0.73), Sn (0.68), Zn, Cd (0.63), As (0.64),
Ga (0.52), Ni (0.52), Tl (0.61), Mo (0.39), In (0.34). On the binary plots of Ag with other
elements (Fig. 5.1C, 5.2B, 5.2E-I), a discernible set of 14 Ag-rich samples - including the
outlier - forms a separate cluster. Namely, this group is characterised by approximately
100 ppm higher Ag contents than the rest of the samples and elevated Sb contents (Fig. 5.2F).
Furthermore, it shows consistently medium to low As (Fig. 5.2E) and Co (Fig. 5.2I)
contents compared to the other samples of the Zn-Pb facies, whereas the concentrations
of the remaining elements are within the range. The cluster of the 14 Ag-rich outlying sam-
ples consists entirely of samples from the Zn-Pb facies of the system, specifically from the
medium and high-grade zone. According to Goodfellow (2003), the presence of this dis-
cernible cluster is attributed to Ag-rich tetrahedrite; the presence of other Sb-Ag sulpho-
salts was confirmed by SEM (see Chapter 6).

*Tin* displays elevated concentrations with a median value of 206 ppm Sn. It ranges
from 3.4 to 593 ppm Sn, with the exception of an outlier with 1160 ppm Sn (Fig. 5.1B).
Overall, Sn exhibits a strong positive correlation with Pb, Zn, Cd (0.84), Ag, In (0.54), Tl
(0.60), Sb (0.57), Ga (0.54), Sb (0.57), As (0.45), Mo (0.45), Au and Hg (0.39). The elemental
covariations of Sn are illustrated in the Figures 5.1B, 5.1F, 5.2H and 5.3A-B. The sample
with the outlying Sn content requires an extensive petrographic investigation to account
for its anomalous value (see Chapter 6).

*Indium* contents are described by a median value of 12.9 ppm In (0.3 up to 39.8
ppm In). Cadmium (0.55), Sn, Zn, Ga (0.39), Ag, Bi (0.28), Pb, Au and Tl (0.19) covary with
Figure 5.2: Binary plots between the precious metals (Au, Ag) and other elements of interest that correlate significantly with them (Table 5.2).
Figure 5.2: (continued).
Figure 5.3: Binary plots of energy critical elements (Sn, In, Ga, Ge, Co) and other elements of interest that display significant Spearman rank-order correlation coefficient values (Table S.2)
Figure 5.3: (continued).
In. Significant positive correlations feature the relationship between In and Zn, Sn (Fig. 5.3B), Cd (Fig. 5.3C), and Ga (Fig. 5.3D), possibly owing to their incorporation of these elements into the mineral sphalerite. Inspecting the Figures 5.3C-D, it is further noted that the relationships of In-Cd and In-Ga are described by heteroscedasticity, a characteristic that is not identifiable by the Spearman’s correlation coefficient due to the transformation preceded the calculations of the $\rho$ values. This example signifies the necessity to generate graphic representations of the calculated correlation and it is better understood by comparing two plots of similar $\rho$ value but different degree of scedasticity (e.g., Fig. 5.3B-C and Fig. 5.3E-F).

*Cadmium* abundance has a median value 142.5 ppm Cd, ranging from detection limit (<2 ppm) up to 370 ppm, and correlates positively with Zn (Fig. 5.1A), Sn (Fig. 5.3A), Pb (Fig. 5.1E), In (Fig. 5.3C), Ag, Au, Sb (0.51), As (0.43), Ga (0.54), Tl (0.46), Mo (0.36) and Hg (0.31).

Elevated concentrations of *Gallium* and *Germanium* are usually associated with the polymetallic type deposits, where these elements are typically bound in sphalerite. Increased mobility of Ge and Ga that typically occurs during metamorphism can explain the sub-economical concentrations. However, in Caribou deposit and the BMC, the low contents are more likely an indicator of source and hydrothermal fluid that were depleted in these elements. Namely, the median value of Ga is 5.7 ppm (0.8 to 20.5 ppm Ga) and 5 ppm for Ge (2.9 up to 11.5 ppm Ge). Gallium exhibits significant correlations with Zn, Cd (Fig. 5.3E), Sn (Fig. 5.3F), Pb (Fig. 5.3G), Ag (Fig. 5.3H), Ni (0.49), Au, In, Sb (0.41), Tl (0.30) and As (0.29), whereas Ge shows only moderate positive correlations with Se (0.33) and Co (0.29) that are illustrated on the Figures 5.3 I-J.
Nickel and Cobalt are present in low concentrations with median values of 2.8 ppm Ni and 47.3 ppm Co, respectively. Overall, Ni concentration ranges from below detection limit to 92.5 ppm and shows a positive correlation with In, Ga, Sb (0.45), Tl (0.39), Cd, Pb, As (0.36), Au, Mn (0.31) and Zn (0.29). Cobalt is by an order of magnitude more abundant than Ni, with its concentration ranging from 0.7 to 875 ppm and covaries with Se (0.77; Fig.5.3K), Cu (Fig.5.1H), Ge (Fig.5.3J) and Bi (0.27). Based on the calculated $\rho$ values, Co is expected to show significant negative correlation with other 11 elements including Pb, Sb, As, Zn, Cd, Ag, Au, Mo, Tl, Sn and Ga. However, this is not confirmed from the binary plots, or at least not for the entire dataset. These negative values only represent the Zn-Pb rich samples of the dataset that constitutes the most populous subset of the dataset. Figure 5.3L illustrates the two contrasting trends identified between the Zn-Pb rich and the Zn-Pb depleted samples that are expressed as an overall negative $\rho$ value.

Overall, Arsenic concentration has a median value of 0.16 wt. % As and ranges from 0.03 to 4.43 wt. % As, showing positive correlations with Sb (0.78), Au, Ag, Pb, Zn, Cd, Sn, Tl (0.57), Mo (0.57), Ga, Ni and Hg (0.24). Samples found exceeding the defined outlier’s rejection threshold for As are also described by anomalously high Au (Fig 5.2A) and Sb (Fig 5.4A) contents and, as such retained to the dataset for a detailed petrographic examination (see Chapter 6). These samples more likely associated with occurrences of arsenopyrite. However, arsenian pyrite accounts for most of As in the VMS system owing to its high abundance. From the binary plots, it can be inferred that the correlations of As with Ag (Fig. 5.2E) and Pb (Fig. 5.4B) are significantly influenced by the 11 high As-content samples as well as the discernible Ag-rich cluster.

Antimony exhibits positive correlations with As (Fig. 5.4A), Au (Fig. 5.2C), Ag (Fig. 5.2F), Pb, Zn, Cd, Sn, Tl (0.79), Mo (0.65), Ga, Ni and Hg (0.43). Antimony abundance ranges
from 63 to 998 ppm and has a median value of 238 ppm Sb. All the samples with substantially high Sb concentrations are associated somewhat with the samples of the Ag-rich cluster. Besides, as shown from the binary plots, samples with the highest Sb-contents are consistently associated with high Pb concentrations (Fig. 5.4C), whereas Indium concentration ranges from low to moderate levels (Fig. 5.4D).

*Mercury* exhibits strong positive correlation with Tl (0.68) and Mo (0.58) that is illustrated in the Figures 5.4E and 5.3F, and also covaries with Sb, Sn, Cd, Zn and Pb. Mercury ranges from 140 ppb to over detection limit (>10,000 ppb Hg) with a median value of 2,155 ppb Hg. Beyond a few exceptions, the highest concentrations of Hg are typically detected in samples of the Zn-Pb facies with all 7 samples that returned values over the limit of detection to belong to this facies.

*Bismuth* concentration has a median value of 72.5 ppm and ranges from the detection limit (<2 ppm) up to 323 ppm. An extreme outlier of 458 ppm Bi concentration is retained in the dataset for reasons stated earlier in this chapter. Bismuth covaries with Cu (Fig. 5.1J), In (Fig. 5.4G), Co (0.27) and Au. As earlier mentioned, the anticipated principal residence of Bi in galena has not been corroborated due to the negative correlation of Bi with Pb (-0.20).

*Selenium* exhibits a positive correlation with Cu (Fig.5.1I), Ge (Fig.5.3I) and Co (Fig.5.3K), whereas it shows significantly negative correlations with other metalloids such as Sb and As. Eventually, these negative ρ values are proved to be associated with two contrasting trends that occur among the Zn-Pb facies subset and the remaining samples of the dataset. Overall, Se ranges from 3.3 to 110 ppm, beyond an outlier of 127 ppm that is discounted on the four standard deviation basis. Overall, Se composition has a median value of 12.3 ppm Se.
Figure 5.4: Binary plots of selected elements associated with the sulphide mineral phases. Linear grouping of data at lower level is an analytical artefact of instrumental detection limit.
Figure 5. 4: (continued).
Molybdenum is limited to low concentrations ranging from detection limit (<1ppm) to 23ppm with a median of 6ppm Mo. Molybdenum covaries with Tl (0.73), Sb, Hg, Pb, Zn, Sn, Cd, Au, Ag and Mn. An outlier of 44 ppm Mo is excluded from the dataset, based on the $4\sigma$ rejection criteria and its prominent distance from the established linear relationship on the plots of Mo-Tl (Fig.5.4H) and Mo-Sb (Fig.5.4I). The visual inspection of the significant correlations is complicated since the binary plots are affected by the linear grouping of the dataset. This is an artefact generated as the measurements return values close the lower limit of detection.

Although Manganese and Thallium are not of economic interest in the Caribou deposit, these elements have been used as proximal (Mn halo) and distal (Tl halo) exploration vectors (Large et al., 2001). Overall, the median value of Mn is 1,450 ppm (268 to 4,080 ppm Mn) and covaries with Tl (0.41), As (0.38), Sb (0.35), Au (0.40), Ag (0.33), Sn (0.33), Pb (0.32) and Mo (0.32). Thallium ranges from 0.8 to 127 ppm, with an outlier lying at 169 ppm Tl. The Tl contents of the samples has a median of 11.6 ppm. Antimony (Fig. 5.4J), Hg (Fig. 5.4E), As, Mo (Fig. 5.4F), Ag, Au (Fig. 5.2D), Sn (Fig. 5.4K), Pb (Fig. 5.4L), Zn, Cd, In, Ga, Mn and Ni significantly correlate with Tl.

In general, two groups of elements exhibit strong correlation across the geochemical dataset. The element groups are (A) Zn-Pb-Cd-Sn-As-Hg-Sb-Tl-Mo-Au-Ag and (B) Cu-Co-Se. The two groups have the unique characteristic that - each of the elements of the group has a positive correlation with all elements of the same group and significant negative correlation with all elements of the other group. In order to present the significant negative correlation between the elements of group A and group B, Spearman’s rank correlation values of the leading (most abundant) element of the first groups is compared with the elements of the second group and vice versa. The leading elements are Zn for the
group A and Cu for the group B. Hence, Zn exhibits strong negative correlations with Cu (-0.52), Co (-0.52) and Se (-0.46); whereas Cu displays a negative correlation with Zn, Pb (-0.52), Tl (-0.51), Mo (-0.46), Cd (-0.45), Sn (-0.40), As (-0.42), Hg (-0.42), Sb (-0.51), Ag (-0.31) and Au (-0.27).

5.3 Metal zonation

The results presented in this chapter confirm the presence of three principal sulphide facies that are documented by Goodfellow (2003). These are (i) a Cu sulphide facies at the base of the hydrothermal stratigraphic sequence, overlain by (ii) a Py sulphide facies and (iii) a well-developed Zn-Pb facies at the top that typically occupies the largest sections of the stratigraphic column. In some drill holes, the presence of an additional zone was identified. This is a magnetite – rich zone (Mag zone) which extends between the upper part of the Cu facies and the lower section of Zn-Pb facies; according to Cavelero (1993), the Mag zone is absent in the eastern lenses of the deposit.

Each of the ore lenses shows a similar stratigraphic metal zonation from the Cu base to a Zn-rich top, with abrupt or gradual transitions between the two facies. Mineralogically, pyrite is the dominant mineral in all three sulphide facies. Chalcopyrite is the principal Cu mineral that occurs but is not limited to the Cu facies. The Cu facies is related to the stringer or feeder zone of the system; however, chalcopyrite is more abundant and occurs in disseminated form. Sphalerite and galena represent the Zn and Pb minerals and, while sphalerite is more abundance than galena, they both occur in the Zn-Pb facies as distinct wispy bands within massive pyrite. For the most part, galena is associated with sphalerite bands but less often it forms discrete bands without following sphalerite distri-
bution. This erratic distribution of galena is often reflected in the whole-rock chemistry of the samples.

As a follow up to the geochemical characterisation, statistics of the absolute elemental concentrations and elemental association of the individual sulphide facies are presented in this section. A total of 144 samples are placed within discrete sulphide facies based on the petrographic information collected during core logging, supported by the chemical signatures identified from the whole-rock geochemistry. Overall, three samples are rejected from the dataset due to their outlying compositions. Data are rejected when the measurements obtained are not considered representative of the true chemistry of the samples, and they are attributed to contamination or analytical issues. Outlying measurements that met specific criteria are retained in the dataset (see Chapter 5.2). All outliers are summarised in Table 5.1, with rejected values to be marked with an asterisk (*). Out of the 141 samples retained for further statistical analyses, 25 samples are allocated to Cu facies, 7 to Py facies and 109 to Zn-Pb facies subset. The summary statistics of the individual sulphide facies are shown in Table 5.3.

5.3.1 Characteristics of sulphide facies

5.3.1.1 Cu sulphide facies

As previously mentioned, the Cu sulphide facies occurs at the base of the hydrothermal column and is present in most of the studied drill holes. It is enriched in Cu, exhibiting a median value of 0.674 wt. % Cu. The median Zn and Pb grades are 1.28 wt. % Zn and 0.21 wt. % Pb. Beyond the elevated Cu concentrations, this facies is also characterised by relatively higher Co and Se contents in comparison with the other two sulphide facies.
|                | Zn wt.% | Pb wt.% | Cu wt.% | Au ppb | Ag ppm | Sn ppm | In ppm | Cd ppm | Ga ppm | Ge ppm | Ni ppm | Co ppm | As ppm | Sb ppm | Hg ppb | Bi ppm | Se ppm | Mo ppm | Mn ppm | Tl ppm |
|----------------|---------|---------|---------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| **Zn-Pb facies (n=109)** |         |         |         |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |
| Median          | 7.39    | 2.34    | 0.298   | 1,450  | 57.4   | 235    | 13.8   | 169    | 7.1    | 4.8    | 3.2    | 29     | 0.19   | 282    | 72     | 10.4   | 7      | 1,580  | 16.9   |
| Min             | 1.15    | 0.10    | 0.026   | 209    | 6.3    | 36.7   | 0.3    | 26     | 1.2    | 2.9    | <LOD   | 0.7    | 0.04   | 85     | 140    | <LOD   | 3.3    | 2      | 491    | 1.8    |
| Max             | 15.00   | 5.68    | 0.677   | 4,710  | 380    | 1,160  | 39.8   | 363    | 20.5   | 11.5   | 92.5   | 268    | 4.43   | 998    | >LOD   | 458    | 110    | 23     | 4,080  | 169    |
| **Py facies (n=7)** |         |         |         |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |
| Median          | 1.19    | 0.09    | 0.370   | 388    | 14.5   | 32.6   | 4.9    | 28     | 1.8    | 5.7    | 0.7    | 178.0  | 0.05   | 102    | 2050   | 69     | 29.7   | 4      | 804    | 3.3    |
| Min             | 0.12    | 0.06    | 0.287   | 153    | 6.5    | 10.0   | 1.3    | 4      | 0.8    | 5.2    | <LOD   | 42.7   | 0.05   | 69     | 500    | 36     | 19.3   | 2      | 480    | 1.1    |
| Max             | 2.14    | 0.49    | 0.576   | 603    | 26.6   | 45.2   | 13.1   | 53     | 3.1    | 7.2    | 1.2    | 262.0  | 0.11   | 139    | 3,170  | 114    | 43.7   | 5      | 1,090  | 8.9    |
| **Cu facies (n=25)** |         |         |         |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |
| Median          | 1.28    | 0.21    | 0.674   | 465    | 23.5   | 67.3   | 11.5   | 36     | 3.4    | 5.9    | 1.9    | 391    | 0.06   | 117    | 1,220  | 86     | 32.5   | 4      | 1,090  | 3.3    |
| Min             | <LOD    | 0.02    | 0.401   | 37     | 3.4    | 3.4    | 1.5    | <LOD   | 1.4    | 3.7    | <LOD   | 37.5   | 0.03   | 63     | 220    | 31     | 3.7    | <LOD   | 268    | 0.9    |
| Max             | 3.55    | 1.36    | 3.060   | 3,330  | 49.1   | 176    | 25.9   | 90     | 14.8   | 9.0    | 28.8   | 874    | 0.41   | 324    | 8,330  | 323    | 99.7   | 14     | 2,770  | 25.8   |

**Table 5.3:** Summary statistics of the bulk-rock geochemistry of samples from all sulphide facies.
Figure 5.5: Histograms of major and trace element distribution of 25 samples from the Cu sulphide facies.
Table 5.4: Spearman rank-order correlation matrix of the bulk-rock geochemistry on the 25 samples allocated to the Cu facies of the system. For 95% confidence level $\rho_{(\text{crit})}$ is estimated to 0.34.
Twenty-five samples are allocated to the Cu facies and a total of 20 histograms (Fig. 5.5) are generated, displaying the concentrations of base metals (Zn, Pb, Cu), precious metals (Au, Ag), energy critical elements (In, Ga, Ge, Sn, Sb, Co, Ni), deleterious elements (As, Hg, Cd) and other elements of interest (Bi, Se, Mo, Tl, Mn).

These histograms show that within the Cu facies, Zn, Pb and Ag follow a bimodal distribution. These elements are typically abundant in the Zn-Pb facies, but the concentration measured in these samples are not high enough to be associated with the Zn-Pb facies. Thus, the second mode of the distribution is more likely associated with a transitional zone located between the Cu and the Zn-Pb facies.

Similarly, such transitional subset can be identified in the histograms of In and Cd at a peak of ~23 ppm and ~80 ppm, respectively. The other two higher frequency peaks at 3 and 10-18 ppm for In, and at 10 ppm and 45 ppm for Cd, represent the true bimodal distribution of these elements across the Cu facies. Copper, As, Hg, Mo, Ni and Ga show evidence of high concentration outliers, with some of the outlying samples (e.g., As, Hg and Ni distributions) to be considered as part of the transitional zone mentioned earlier. Whereas outlying Cu and Ga contents belong to the typical Cu facies.

Gold and Tl display a heavily tailed distribution (Fig. 5.5), having only a small number of samples on the upper tail. From these two histograms, the covariation between Au and Tl is inferred, as the high concentration outliers of the two elements are associated with the same set of samples.

It is worth mentioning that a seemingly unimodal distribution may not be representative of the original distribution and can result from the mixture of two modes with adjacent peaks. This is more profound since the resolution of the histograms is limited by the small population size of the dataset of the Cu facies. This argument can explain the
seemingly unimodal distribution of Sn (Fig. 5.5), while there is evidence that Sn exhibits a bimodal distribution.

The critical value ($\rho_{(i)\text{crit}}$) of the Cu facies subset (n=25) with 95% confidence level was estimated to be 0.34. Elemental correlations unveiled for the Cu facies of the systems are dissimilar to those identified for the entire data set. This observation demonstrates the importance of applying correlative statistics on the individual subsets (sulphide facies), as the correlations attested for the entire dataset predominantly portray correlation among samples of the most populous subset (Zn-Pb facies; n=111 before the outlier rejection).

Across the Cu facies, Cu covaries with In (0.74), Ga (0.68), Ni (0.64), Ag (0.50), and Sn (0.36), and ranges from 0.401 to 3.06 wt. % (median 0.67 wt. %). It is notable that the Cu facies is the only facies of the deposit where a Cu-Ni positive correlation is identified.

Overall, Zn exhibits a positive Spearman’s correlation with Cd (0.97), Sn (0.79), Pb (0.67), As (0.51), Ag (0.61), Ga (0.48), Sb (0.46), Au (0.46) and Bi (0.45). Zinc composition ranges from below detection limit (< 0.01 wt. %) to 3.55 wt. % with a median value of 1.28 wt. % Zn.

Indium concentrations in the Cu facies range from 1.5 to 25.9 ppm (median 11.5 ppm In). These concentrations are only slightly lower than those obtained from the Zn-Pb facies. Indium exhibits positive correlation with Cu (0.74), Pb (0.63), Au (0.61), Ag (0.77), Sn (0.72), Bi (0.54), Tl (0.51), Cd (0.44) and Sb (0.44), Ga (0.42) and Ni (0.42). Spearman’s correlation coefficient between In and Zn is less prominent (0.38), indicating that sphalerite is not the principal host of In for this facies.

Cadmium abundance is described by a median of 36 ppm and ranges from the detection limit (<2 ppm) to 90 ppm. As noted earlier, Cd shows a strong corre-
ation with Zn and also covaries with Sn (0.83), In, Pb (0.68), Au (0.54), Ag (0.64), As (0.46), Bi (0.53), Tl (0.42) and Ga (0.41).

Tin exhibits positive correlation with Pb (0.83), Zn, Cd, In, Ag (0.86), Au (0.68), Bi (0.64), Tl (0.60), Sb (0.55), As (0.48), Mo (0.43), Ga (0.43) and Ge (0.42). Tin is variable along the Cu facies and ranges from 3.4 to 176 ppm (median 67.3 ppm). The highest Sn contents correspond to samples with elevated Zn contents and suggest the presence of sphalerite.

Lead abundance shows a median value of 0.21 wt. % Pb and ranges from 0.02 to 1.36 wt. % Pb. It exhibits a positive correlation with Zn, Sn, Cd, In, Ag (0.89), Au (0.79), Bi (0.72), Tl (0.68), Mo (0.59), Sb (0.60), As (0.38) and Hg (0.39). Lead correlations with As (0.38) is considerably weaker than that calculated for the whole dataset.

Silver shows a strong positive correlation with Pb even within the individual sulphide facies. In addition to Pb, Ag correlates with Zn, Au (0.81), Sn (0.86), In, Cd, Bi (0.81), Tl (0.70), As (0.49), Sb (0.53), Mo (0.53) and Ge (0.37). The absolute abundance of Ag ranges from 3.4 to 49.1 ppm (median 23.5 ppm Ag).

Gold concentration has a median value of 465 ppb Au and ranges from 37 to 3,330 ppb Au. Due to their strong positive correlation, Au and Ag share positive correlations with the same set of elements and for the most part with similar strength. In particular, Au exhibits positive correlation with Ag, Bi (0.92), Tl (0.78), Pb, Sn, Zn In, Mo (0.65), Ge (0.57), Cd, As (0.41), Sb (0.41) and Hg (0.37).

Gallium and Germanium occur in low concentrations with median values of 3.4 ppm and 5.9 ppm, respectively. In particular, Ga covaries with Cu, Ni (0.48), Zn, Sn, In and Cd; while Ge exhibits positive correlations with Au, Bi (0.55), Tl (0.52), Sn and Mo (0.43).
Arsenic ranges from 0.03 to 0.41 wt. % As (median 0.06 wt. % As) and correlates with Zn, Sn, Cd, Ag, Au, Bi (0.45), Sb (0.4), Tl (0.41) and Pb. At the stratigraphic lower section of the hydrothermal column and especially in the Cu facies, there is a notable depletion in As.

Antimony exhibits positive correlation with a similar element group as As. Hence, Tl (0.74), Hg (0.63), Mo (0.62), Pb, Ag, Au, As, Sn, Bi (0.41), Zn, In and Cd are elements which shows a significant correlation with Sb. Antimony ranges from 63 to 324 ppm and averages 133 ppm (mean 117 ppm Sb).

Overall, Mercury concentrations reach up to 8,330 ppb and have a median value of 1,220 ppb Hg. Within the Cu facies, Hg exhibits moderate correlations with Tl (0.70), Sb (0.63) and Mo (0.65), and weak correlations with Au, Pb, Ge, Ag and Bi (0.32).

Bismuth is relatively more abundant in the Cu facies than the stratigraphically overlying Py facies and ranges from 31 to 323 ppm (median 86 ppm). Bismuth covaries with Au, Ag, Tl (0.70), Pb, Sn, Mo (0.63), Ge (0.55), In, Cd, As, Zn, Sb and Hg.

Nickel concentration ranges from below detection limit (0.5 ppm Ni) to 28.8 ppm Ni (median 1.9 ppm) and exhibiting a positive correlation with Cu, Ga and In.

Cobalt is relatively abundant across the Cu facies with a median of 391 ppm (37.5 to 874 ppm Co); it does not show any significant positive or negative correlation within the Cu facies.

The Cu sulphide facies is found relatively enriched in Selenium. It has a median value of 32.5 ppm, ranging from 3.7 to 99.7 ppm. Selenium does not covary with other elements, instead, it shows negative correlations with many of them, including but not limited to Bi (-0.84), Au (-0.80), Tl (-0.74), and Ag (-0.73). The fact that Se is not correlated with any of the major and trace elements that dominate the chemistry of the sulphide
minerals indicates that the bulk-rock Se variations are controlled by different processes. Similarly, terrigenous factors may have influenced Se signatures as implied by the strong positive correlations of Se with Al and Y.

*Molybdenum* abundance does not vary considerably along the stratigraphic column. In Cu facies, Mo concentration ranges from below detection limit (<1 ppm) to 14 ppm Mo (median 4 ppm Mo) and exhibits positive correlation with Tl (0.78), Sb, Hg, Bi, Pb, Au, Ag, Sn and Ge.

*Thallium* is depleted in the Cu facies and exhibits a significant positive correlation with Au, Ag, Mo, Sb, Hg, Bi, Pb, Sn, As, In, Cd and Zn. Its concentration ranges from 0.9 to 25.8 ppm Tl (median 3.3 ppm Tl).

Lastly, *Manganese* composition ranges from 268 to 2,770 ppm Mn (median 1,090 ppm Mn) and exhibits weak positive correlations with In (0.36), Bi (0.34) and Au (0.33).

### 5.3.1.2 Py sulphide facies

The Py facies has the lowest overall base metal contents (median values 1.19 wt. % Zn and 0.09 wt. % Pb) and corresponding depletion in Ag, Sb, Bi and Sn. Copper concentrations in the Py facies are notably lower than the Cu facies with a median of 0.370 wt. % Cu. The Pyrite facies is identified in only two of the 10 drill holes examined.

A total of seven samples have been assigned to the Py facies. This statistically small population discourages the generation of histograms. Therefore, the analysis is limited to general observations that the element distribution is more variable and less predictable than the other facies.
Table 5.5: Spearman Rank-order correlation matrix of the bulk-rock geochemistry of 7 samples for the Py facies. For 95% confidence level ρ_{(ii)crit} is estimated to 0.67.
The limited sample size does not support the application of correlative statistics; however, the Spearman’s rho is calculated, and the correlations are examined together with the elemental binary plots in order to confirm the correlations. For 95% confidence level, the critical value ($\rho_{(i)\text{crit}}$) of this subset (n=7) is calculated to 0.67.

As previously stated, the Py sulphide facies is defined by low Zinc concentrations (median 1.19 wt. % Zn) and ranges from 0.12 to 2.14 wt. % Zn. Zinc displays a linear relationship with Cd (0.75). Lead contents are equally limited and range from 0.06 to 0.49 wt. % Pb (median 0.09 wt. % Pb). Significant correlations indicated by the Spearman’s rank coefficient are not confirmed as the samples are described by very low or very high-level concentrations without the medium range concentrations. Copper covaries with Ge (0.86) and Co (0.71) and its concentration ranges from 0.287 to 0.576 wt. % Cu (median 0.37 wt. % Cu).

Tin (median 32.6 ppm), Cadmium (median 28 ppm), Indium (median 4.9 ppm) and Antimony (median 102 ppm) abundances are the lowest identified within the three facies. Similarly, Gallium contents are the lowest determined across the hydrothermal column, with a median value of 1.8 ppm Ga, showing no evidence of correlation with other elements. Germanium concentration range is similar to the Cu facies and has a median value of 5.7 ppm. Germanium exhibits a significant correlation with Co.

Arsenic contents are similar to those found in the Cu facies and ranges from 0.05 to 0.11 wt. % As (median 0.05 wt. %). Mercury concentration is slightly less abundant compared to the Cu facies and ranges from 500 ppb up to 3,170 ppb Hg (median 2,050 ppb Hg).

Gold exhibits a positive correlation with Ag (0.96) and Bi (0.85), with concentrations ranging from 153 to 603 ppm (median 388 ppm Au). Silver ranges from 6.5 to 26.6 ppm Ag (median 14.5 ppm Ag) and bismuth concentrations have a median value of 69 ppm Bi.
Cobalt covaries with Ge (0.93) having variable absolute concentrations that range from 42.7 to 262 ppm. Selenium concentrations have a mean of 29.7 ppm Se and show a significant correlation with Mn (0.75). Manganese contents of the Py facies are the lowest found compared to the other sulphide facies with a mean value of 804 ppm Mn. Besides Se, Mn also covaries with Mo (0.70). Thallium occurs depleted with concentrations lower than 8.9 ppm Tl.

5.3.1.3 Zn-Pb sulphide facies

Volumetrically speaking, the Zn-Pb sulphide facies is the most abundant hydrothermal facies in the systems and is intersected in all 10 drill holes. It is particularly enriched in Zn, Pb, Au, Ag, In, Cd, Sn, As, Hg and Sb with their concentrations varying across the facies. In an attempt to better decipher the variability and complex chemistry within the Zn-Pb facies, the 109 samples that comprise this facies are further discriminated into grade zones, based largely on the whole-rock Zn concentrations. These zones are described as high (>9 wt. % Zn; 36 samples), medium (6 up to 9 wt. % Zn; 41 samples) and low-grade zones (<6 wt. % Zn; 32 samples).

Histograms illustrate the distribution of 20 elements along the Zn-Pb facies (Fig. 5.6), with only a few of them to show unimodal and even quite normal distributions (e.g., Zn and Cd). Tin, As, Bi, Ni and Tl distributions are highly skewed owing to high concentration outliers. The outlying values likely related to samples with high abundance in accessory mineral phases that directly control the distribution of the above elements (e.g., arsenopyrite, cassiterite, sulphosalts; see Chapter 6). Gold, Ag, Sb and Ge are bimodally distributed with the higher content population to consist of a limited number of samples. Three differ-
ent populations can be identified in In and Ga distributions that suggest that the two elements are associated with the same mineral carriers. Mercury exhibits a similar distribution pattern with In and Ga; the peak in Hg distribution, occurring in the upper tail of the histogram, is caused by the clustering of all analyses exceeding the instrumental detection limit (10,000 ppb Hg). Namely, seven out of the 9 samples allocated to this class returned values over the detection limit. Samples representing the transitional zone are effectively concealed by the overall large size of the subset, apart from the high-concentration samples featured in Co and Se distribution.

The further discrimination of the samples into the grade zones does not provide with any additional information regarding the chemistry of the Zn-Pb facies. As explained earlier, this classification is based on the Zn content. Zinc, along with Cd, that consistently covary, are the only elements feature a clear separation of their distributions in respect to the zones. On the contrary, Pb distribution by no means follows a similar separation on its distribution. Although samples of the low-grade zone are described by a somewhat lower Pb concentrations than the medium and high-grade zones, several high-grade samples are also described by a relative depletion in Pb. However, this was already known, as galena, which accounts for the lead distribution in the deposits, exhibits an erratic distribution. Finally, it is inferred that variability describes the Zn-Pb facies is not related with the interlayering of the zones of different grade.

For the Zn-Pb facies, the critical value ($\rho_{(iii)\text{crit}}$) is calculated to 0.22 for a confidence level of 99%. The application of the Spearman’s rank-order correlation coefficient identifies significant elemental correlations for the given confidence level that are either positive ($\rho_{(iii)\geq 0.22}$) or negative ($\rho_{(iii)\leq -0.22}$).
Overall, Zinc concentrations show a median value of 7.39 wt. % and range from 1.15 to 15 wt. % Zn, whereas Pb range from 0.10 to 5.68 wt. % Pb (median 2.34 wt. % Pb, 0.10 to 6.14 wt. % Pb). Zinc exhibits significant correlations with Cd (0.97), Sn (0.79), Pb (0.59), In (0.44), Ag (0.33), Ga (0.30) and Hg (0.28). Similarly, Pb correlates with Zn, Cd (0.52), Sn (0.52), Sb (0.45), Ag (0.64), Ga (0.32), Tl (0.31), as well as, Ni (0.30), Au (0.28), and As (0.25). Moreover, both Zn and Pb exhibit significant negative correlations with Bi and Cu.

Cadmium exhibits a very strong correlation with Zn, likewise, Sn (0.68), In (0.55) and Pb. Moderate to weak \( \rho \) values characterise the association of Cd with Ga (0.30) and Ag (0.30). Cadmium abundance ranges from 26 up to 363 ppm (median 170 ppm Cd).

Tin contents are the highest determined across the three facies. It varies from 36.7 to 1,160 ppm Sn with a median of 235 ppm Sn. Tin exhibits positive correlation with Zn, Cd, Pb, In (0.47), Ag (0.38), Tl (0.35), Ga (0.35) and Hg (0.31).

Indium contents are higher within the Zn-Pb facies, however, the overall In concentration in the deposit is significantly low (median 13.8 ppm In; 0.3 to 39.8 ppm In). Indium covaries with Cd, Sn, Zn, Cu (0.39), Co (0.33), Ga (0.31) and Bi (0.29).

Gold is distinctly enriched in the Zn-Pb sulphide facies with a median concentration of 1,450 ppb Au and ranges from 209 to 4,710 ppb Au. Gold displays positive correlations with As (0.69), Sb (0.62), Ag (0.58), Ni (0.40), Tl (0.33), Ga (0.31) and Pb.

Contents of Silver are considerably higher than those in the Py and the Cu facies, with a median value of 57.4 ppm Ag (6.3 to 380 ppm Ag) and covary as a function of Pb, suggesting Ag substitution into galena and sulphosalts. Silver also shows positive correlations with Au, Ni (0.57), Sb (0.53), As (0.41), Ga (0.38), Sn, Tl (0.37), Zn and Cd.

Arsenic concentration reaches up to 4.43 wt. % with a median of 0.19 wt. % As. It positively correlates with Au, Sb (0.68), Mo (0.45), Ag, Ni (0.37), Tl (0.35) and Pb.
Figure 5.6: Histogram of major and trace element distribution of 109 samples from the Zn-Pb sulphide facies
<table>
<thead>
<tr>
<th></th>
<th>Zn</th>
<th>Pb</th>
<th>Cu</th>
<th>Au</th>
<th>Ag</th>
<th>Sn</th>
<th>In</th>
<th>Cd</th>
<th>Ga</th>
<th>Ge</th>
<th>Ni</th>
<th>Co</th>
<th>As</th>
<th>Sb</th>
<th>Hg</th>
<th>Bi</th>
<th>Se</th>
<th>Mo</th>
<th>Mn</th>
<th>Tl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>1.00</td>
<td>0.59</td>
<td>-0.22</td>
<td>0.03</td>
<td>0.33</td>
<td>0.72</td>
<td>0.44</td>
<td>0.97</td>
<td>0.30</td>
<td>-0.11</td>
<td>0.17</td>
<td>-0.12</td>
<td>0.04</td>
<td>0.17</td>
<td>0.28</td>
<td>-0.29</td>
<td>-0.05</td>
<td>0.16</td>
<td>0.06</td>
<td>0.21</td>
</tr>
<tr>
<td>Pb</td>
<td>1.00</td>
<td>-0.25</td>
<td>0.28</td>
<td>0.64</td>
<td>0.52</td>
<td>-0.03</td>
<td>0.52</td>
<td>0.32</td>
<td>-0.27</td>
<td>0.30</td>
<td>-0.25</td>
<td>0.27</td>
<td>0.45</td>
<td>0.10</td>
<td>0.31</td>
<td>-0.31</td>
<td>-0.24</td>
<td>0.19</td>
<td>0.23</td>
<td>0.31</td>
</tr>
<tr>
<td>Cu</td>
<td>1.00</td>
<td>-0.03</td>
<td>0.04</td>
<td>-0.06</td>
<td>0.39</td>
<td>-0.10</td>
<td>0.04</td>
<td>0.00</td>
<td>-0.07</td>
<td>0.47</td>
<td>-0.17</td>
<td>-0.31</td>
<td>-0.39</td>
<td>0.62</td>
<td>0.44</td>
<td>-0.37</td>
<td>-0.07</td>
<td>-0.38</td>
<td>0.23</td>
<td>0.33</td>
</tr>
<tr>
<td>Au</td>
<td>1.00</td>
<td>0.58</td>
<td>0.05</td>
<td>-0.08</td>
<td>0.00</td>
<td>0.31</td>
<td>-0.26</td>
<td>0.40</td>
<td>-0.30</td>
<td>0.69</td>
<td>0.62</td>
<td>-0.05</td>
<td>0.13</td>
<td>-0.31</td>
<td>0.11</td>
<td>0.32</td>
<td>0.33</td>
<td>0.23</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>1.00</td>
<td>0.38</td>
<td>0.14</td>
<td>0.30</td>
<td>0.38</td>
<td>-0.26</td>
<td>0.57</td>
<td>-0.11</td>
<td>0.41</td>
<td>0.53</td>
<td>-0.05</td>
<td>0.20</td>
<td>-0.23</td>
<td>0.07</td>
<td>0.23</td>
<td>0.37</td>
<td>0.23</td>
<td>0.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>1.00</td>
<td>0.47</td>
<td>0.68</td>
<td>0.35</td>
<td>-0.12</td>
<td>0.25</td>
<td>0.16</td>
<td>0.05</td>
<td>0.21</td>
<td>0.31</td>
<td>-0.12</td>
<td>-0.02</td>
<td>0.20</td>
<td>0.21</td>
<td>0.35</td>
<td>0.21</td>
<td>0.35</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>In</td>
<td>1.00</td>
<td>0.55</td>
<td>0.31</td>
<td>0.06</td>
<td>0.05</td>
<td>0.33</td>
<td>-0.23</td>
<td>-0.22</td>
<td>0.03</td>
<td>0.29</td>
<td>0.24</td>
<td>-0.14</td>
<td>0.05</td>
<td>0.05</td>
<td>0.10</td>
<td>0.05</td>
<td>0.10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>1.00</td>
<td>0.33</td>
<td>-0.12</td>
<td>0.14</td>
<td>-0.05</td>
<td>-0.02</td>
<td>0.07</td>
<td>0.19</td>
<td>-0.19</td>
<td>0.03</td>
<td>0.05</td>
<td>0.05</td>
<td>0.11</td>
<td>0.11</td>
<td>0.11</td>
<td>0.11</td>
<td>0.11</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ga</td>
<td>1.00</td>
<td>-0.01</td>
<td>0.35</td>
<td>0.02</td>
<td>0.02</td>
<td>0.20</td>
<td>0.00</td>
<td>-0.01</td>
<td>0.03</td>
<td>-0.13</td>
<td>-0.01</td>
<td>0.11</td>
<td>0.11</td>
<td>0.11</td>
<td>0.11</td>
<td>0.11</td>
<td>0.11</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>1.00</td>
<td>-0.33</td>
<td>0.12</td>
<td>-0.24</td>
<td>-0.07</td>
<td>0.08</td>
<td>0.01</td>
<td>0.27</td>
<td>-0.02</td>
<td>-0.69</td>
<td>-0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>1.00</td>
<td>-0.08</td>
<td>0.37</td>
<td>0.48</td>
<td>0.10</td>
<td>0.06</td>
<td>-0.13</td>
<td>0.29</td>
<td>0.26</td>
<td>0.46</td>
<td>0.46</td>
<td>0.46</td>
<td>0.46</td>
<td>0.46</td>
<td>0.46</td>
<td>0.46</td>
<td>0.46</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>1.00</td>
<td>-0.30</td>
<td>-0.28</td>
<td>0.08</td>
<td>0.31</td>
<td>0.67</td>
<td>-0.16</td>
<td>-0.04</td>
<td>-0.07</td>
<td>0.07</td>
<td>0.17</td>
<td>0.07</td>
<td>0.17</td>
<td>0.07</td>
<td>0.17</td>
<td>0.07</td>
<td>0.17</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>1.00</td>
<td>0.68</td>
<td>0.11</td>
<td>-0.07</td>
<td>-0.27</td>
<td>0.45</td>
<td>0.27</td>
<td>0.35</td>
<td>0.27</td>
<td>0.35</td>
<td>0.27</td>
<td>0.35</td>
<td>0.27</td>
<td>0.35</td>
<td>0.27</td>
<td>0.35</td>
<td>0.27</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb</td>
<td>1.00</td>
<td>0.32</td>
<td>-0.26</td>
<td>-0.26</td>
<td>0.50</td>
<td>0.26</td>
<td>0.66</td>
<td>0.26</td>
<td>0.66</td>
<td>0.26</td>
<td>0.66</td>
<td>0.26</td>
<td>0.66</td>
<td>0.26</td>
<td>0.66</td>
<td>0.26</td>
<td>0.66</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg</td>
<td>1.00</td>
<td>-0.46</td>
<td>-0.01</td>
<td>0.56</td>
<td>0.15</td>
<td>0.68</td>
<td>0.15</td>
<td>0.68</td>
<td>0.15</td>
<td>0.68</td>
<td>0.15</td>
<td>0.68</td>
<td>0.15</td>
<td>0.68</td>
<td>0.15</td>
<td>0.68</td>
<td>0.15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi</td>
<td>1.00</td>
<td>0.20</td>
<td>-0.34</td>
<td>-0.13</td>
<td>-0.25</td>
<td>0.10</td>
<td>0.20</td>
<td>-0.34</td>
<td>-0.13</td>
<td>-0.25</td>
<td>0.10</td>
<td>0.20</td>
<td>-0.34</td>
<td>-0.13</td>
<td>-0.25</td>
<td>0.10</td>
<td>0.20</td>
<td>-0.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Se</td>
<td>1.00</td>
<td>-0.16</td>
<td>-0.32</td>
<td>-0.29</td>
<td>0.23</td>
<td>0.64</td>
<td>0.23</td>
<td>0.64</td>
<td>0.23</td>
<td>0.64</td>
<td>0.23</td>
<td>0.64</td>
<td>0.23</td>
<td>0.64</td>
<td>0.23</td>
<td>0.64</td>
<td>0.23</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>1.00</td>
<td>0.23</td>
<td>0.64</td>
<td>0.23</td>
<td>0.64</td>
<td>0.23</td>
<td>0.64</td>
<td>0.23</td>
<td>0.64</td>
<td>0.23</td>
<td>0.64</td>
<td>0.23</td>
<td>0.64</td>
<td>0.23</td>
<td>0.64</td>
<td>0.23</td>
<td>0.64</td>
<td>0.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>1.00</td>
<td>0.35</td>
<td>0.64</td>
<td>0.35</td>
<td>0.64</td>
<td>0.35</td>
<td>0.64</td>
<td>0.35</td>
<td>0.64</td>
<td>0.35</td>
<td>0.64</td>
<td>0.35</td>
<td>0.64</td>
<td>0.35</td>
<td>0.64</td>
<td>0.35</td>
<td>0.64</td>
<td>0.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tl</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.6: Spearman rank-order correlation matrix of the bulk-rock geochemistry on the 109 samples consist the Zn-Pb facies of the system. For 99% confidence level $\rho_{(ii)\text{crit}}$ is estimated to 0.22.
Antimony concentrations have a median value of 284 ppm and range from 85 to 998 ppm Sb. It exhibits positive correlations with As, Tl (0.66), Au, Ag, Mo, Ni (0.48) and Hg (0.32).

Mercury displays positive correlations with Tl (0.68), Mo (0.56), Sb, Sn and Zn. With respect to the absolute abundances, mercury contents within the Zn-Pb facies are the highest identified in the geochemical dataset with a median of 2,570 ppb Hg and range from 140 ppb up to concentrations above the detection limit (>10,000 ppb Hg).

Bismuth contents are slightly lower than the Cu facies and range from below detection limit to 458 ppm Bi (median 72 ppm Bi). Copper (0.62), Co (0.31) and In show positive correlations with Bi.

Although Gallium is more variable within the Zn-Pb facies, its overall concentrations levels are comparable to concentrations determined within the Cu and Py facies. Gallium ranges from 1.2 up to 20.5 ppm (median 7.1 ppm Ga) and exhibits covariations but only in a moderate to weak level. Particularly, Ga correlates with Ag, Sn, Ni, Cd, Pb, Au, In and Zn.

Germanium, in contrast, covaries only with Se (0.27). Germanium concentration ranges from 2.9 to 11.5 ppm Ge (median 4.8 ppm Ge) and exhibits significant negative correlation with the precious metals.

Thallium contents are significantly high in comparison to the other two sulphide facies (median 16.9 ppm, 1.8 up to 169 ppm Tl). Mercury, Sb and Mo (0.64) show strong correlations with Tl, Ni (0.46), Ag, Sn, As, Au and Pb show moderate to low correlation.

Nickel found relatively enriched in comparison with the stratigraphically lower facies. It was a median concentration of 10 ppm Ni and ranges from below detection limit to
92.5 ppm Ni. Silver, Sb, Tl, Au, As, Ga, Pb, Mo, (0.26) and Sn exhibit significant correlation with Ni.

_Cobalt_ is relatively depleted with concentration varying from 0.7 up to 268 ppm Co (median 27.1 ppm Co). Cobalt shows a strong positive correlation with Se (0.67), Cu (0.47), In and Bi.

_Copper_ contents of the Zn-Pb facies are lower than the other two facies. Particularly, Cu concentration ranges from 0.026 up to 0.677 wt.% (median 0.298 wt. % Cu). Copper correlates with Co, Bi (Figs. 5.1J), and In.

Within the Zn-Pb facies, _Selenium_ is characterised by a lower median concentration (median 10.4 ppm Se) compared to the other sulphide facies and ranges from 3.3 up to 110 ppm. Selenium exhibits a positive correlation with Co, Cu, Bi and In.

Overall _Molybdenum_ abundance shows a median value of 7 ppm Mo (2 up to 23 ppm Se) and correlates with Tl, Hg and Sb.

The concentrations of _Manganese_ in the Pb-Zn facies are described by a median value of 1,580 ppm Mn, that is similar to the concentrations of the Cu facies, yet the individual Mn contents vary considerably in the Zn-Pb facies, hosting samples with the highest Mn contents of the entire dataset. Manganese exhibits positive correlations with Tl, Au (0.32), Sb (0.26) and Ag (0.23); and a negative correlation with Ge (-0.69).

### 5.3.2 Hydrothermal stratigraphy

In the following sections, the hydrothermal stratigraphic column (Fig. 5.7) is presented in combination with chemostratigraphic profiles (Fig. 5.8). The majority of the drill holes intersect more than one lens, or they encounter a folded section of the lens that caused repetition in the sequence. These features are directly explained by the geometry
of the deposit and especially the en echelon placement of the ore lenses (see Chapter 3.2). Thus, Figure 5.7 illustrates the occurrences of the hydrothermal sulphide facies as they were identified during logging. In general, none of the studied drill holes exhibits the full stratigraphic succession, as such none of them are characterised by the “idealised” senso stricto stratigraphic sequence described earlier. Gaps in sampling are associated with intensive veining of non-sulphide minerals or intersections with the host rock.

The chemostratigraphic column of UGX-08-30 is presented in detail as it exemplifies the described zonation to a significant degree. At the stratigraphic top of the drill hole (Figure 5.7), there is a thin low-grade Zn-Pb zone followed by a thicker medium to high grade Zn-Pb zone. Immediately below, from 207 to 215m depth, there is a narrow section of Cu facies, which coincides with a magnetite zone. At depth, from 215 to 233m there is a barren pyrite facies. At the base of the drill hole, a narrow high-grade Zn-Pb zone appears just above the deeper occurring Cu facies.

Figure 5.8 shows chemostratigraphic profiles for 20 elements that are arranged in order of their geochemical behaviour. Zinc, Pb and Cu abundances (Fig. 5.8) generally follow the distribution of the sulphide facies, with Pb and Zn contents to show considerable variability within the Zn-Pb facies. The one-meter-thick deep occurrence of Zn-Pb facies is possibly a remnant of an early sphalerite and galena exhalite horizon that did not get remobilised during the zone refining process. The distribution of Cu is also not uniform within the Cu facies. The deeper occurrence of Cu facies is characterised by greater Cu grades and samples from this section belong to the discernible high Cu cluster described in Chapter 5.2 (see Figs. 5.1 H-L). Moving through the column and independently of the facies, a strong positive correlation describes the relationship between Sb and As and also among Zn, Cd and Sn. As presented earlier, these covariations are also true for the entire whole-
Figure 5.7: Schematic stratigraphic columns for the mineralised section from the UGX-08-3O drill hole from the NLS.
Figure 5.8: Whole-rock chemostratigraphic profiles show the major and trace element zonation across the mineralised section of the UGX-08-3O drill hole.
Figure 5.8: (continued).
Figure 5.8: (continued).
rock geochemical dataset. Gallium and Se show a prominent positive correlation along the Cu facies. Where magnetite is present (Mag zone) Se contents are elevated, however in that case, Ga does not share the same behaviour.

High Au contents are limited to the Zn-Pb facies. The drill hole UGX-08-30 exhibits the highest Au contents of the dataset, including the sample with the highest Au concentration (4,710 ppb Au). The Au-rich samples are also high in As and Bi. Silver concentrations reach up to 80 ppm beyond a single outlier with anomalously high Ag content (160 ppm). This sample is characterised by relatively high Pb concentration and it is part of the set of 14 outlying Ag-rich samples described in Chapter 5.2.

Indium and Cd are abundant and covary within the Zn-Pb facies. Low concentration levels of In are also observed in the deeper Cu facies. Thallium and Hg show a positive correlation throughout the profile; however, this correlation is more prominent within the Zn-Pb facies where these elements occur in elevated concentrations.

In addition to descriptive statistics, Principal Component Analysis (PCA) is employed in order to visualise the chemical variation and separation within the samples of the NLS. The set of 22 major and trace elements used for the descriptive statistics are also employed for the PCA analysis. A Residual Value (RV) is added to each sample in order to satisfy the constant-sum constraints before applying the central log-ration (CLR) transformation (see Chapter 4.3). Two principal components - PC1 and PC2 - are presented in this section that account for 52% and 12% of the total variance, respectively (Figs. 5.9-5.10). The length of the vectors indicates the contribution of the element to the variance of the dataset, while the length of the orthogonal projections of each vector to PC1 and PC2 shows the relative contribution of the element to the variance expressed by the components. For the most part, Co, Pb, Se, Cu and Zn define PC1, while Tl, Hg, In, Zn, Cd, Bi and As define PC2.
Figure 5.9: Scree plot illustrates the variation captured by the 23 Principal Components.
Figure 5. 10: Multi-element PCA diagram of the whole-rock lithogeochemical dataset from the NLS.
Samples of the three sulphide facies of the NLS are readily separated on the PCA diagram. The nature of this separation is attributed to the large-scale zonation that extents from the proximal (Cu facies) to the distant stratigraphic horizons (Zn-Pb facies) of the NLS. As shown in Figure 5.10, samples from the high-grade Zn-Pb facies plot closer to the eigenvector of Zn and the medium and low-grade cluster are aligned towards the origin of the orthogonal plane. The first and fourth quadrants of the plot are dominated by samples from the Cu and Py facies of the dataset that is characterised by similar composition except for the Cu concentration. However, the moderate contribution of Cu vector (0.26) to PC1 is undermined by the significant contribution of Co (0.56) and Se (0.32) that together with Pb and Zn dictate the distribution pattern along the PC1. The field that the Zn-Pb facies cluster meets the Cu facies cluster is occupied by samples of the transitional zone. These are either Cu-enriched samples of Zn-Pb facies or samples from the Cu facies that show elevated Zn concentration.

Although the PC1 variation is linked to the distance of the samples from the feeder zone, PC2 primarily describes the chemical variation present within the individual sulphide facies. To a limited extend, the chemical variations occur within the individual facies follow the ore grades (e.g., low to high Zn-Pb facies) as indicated by the contribution of Zn, Cd and In, however the majority of the variance in the PC2 is captured by Tl, Hg, Bi and As, elements that occur as major constituents of minor and accessory mineral phases (e.g., arsenopyrite, tetrahedrite) that locally occur in great abundances forming the discernible outlying cluster described in the Chapter 5.2.

A small number of samples show significant deviation away from the main clusters of the dataset. These samples are associated with the anomalous concentration of ele-
ments that are major contributors to PC1 and PC2. Namely, the anomalously high concentrations of Tl and Hg, high Sb and no detectable Bi (<LOD) can explain the two low grade Zn-Pb outliers at the third quadrant of the PC1-PC2 biplot. Similarly, the three outlying samples from the Cu facies are described by the lowest Zn, Pb, Cd, In contents of the dataset and the highest concentration of Se and Co across the Cu facies.

5.4 Discussion

The Caribou deposit and specifically the Northwest Lens System (NLS) is characterised by a well-developed geochemical zonation. As described by Goodfellow (2003) the deposit comprises of three distinct sulphide facies: (i) a Cu sulphide facies at the base of the hydrothermal stratigraphic sequence, overlain by (ii) a Py sulphide facies and (iii) a Zn-Pb sulphide facies near the hanging wall that comprises the largest stratigraphic section of the mine sequence. A sparse magnetite-bearing zone occurs between the upper part of the Cu facies and the lower section of Zn-Pb facies.

The Cu facies of the deposit has a proportionally smaller tonnage compared to the volumetrically greater Zn-Pb facies. The NLS, for which this work is focused, is situated above the feeder zone, thus the drill holes intersect the full length of the Cu facies. Although other deposits in the BMC have better developed Cu facies, the Caribou deposit exhibits the highest Cu grades overall.

As previously stated, considering the entire geochemical dataset, two groups of elements are found to exhibit strong correlations across the geochemical dataset; these are: A) Zn-Pb-Cd-Sn-As-Hg-Sb-Tl-Mo-Au-Ag and B) Cu-Co-Se. These two element groups, in effect, represent the chemical signatures within the two dominant facies, where group A characterises the chemistry of the Zn-Pb facies and the group B the Cu facies of the deposit.
The bulk-rock elemental correlations that characterise the hydrothermal system can be attributed to two different mechanisms. The first mechanism concerns co-variations between elements accommodated in the same mineral host, while the second is associated with co-existent mineral phases.

The first case is described by the strongest positive correlations within the geochemical dataset. These positive correlations are exhibited due to the trace element substitutions into the lattice of an abundant mineral phase. Namely, Zn, Cd, Sn covariations are associated with Cd and Sn substitution into the lattice of sphalerite. Similarly, galena is the principal carrier of Ag, thus explain the positive correlation between Pb and Ag. In addition, the substitution of Au, Ag, Sb and Tl into arsenian pyrite and arsenopyrite explains the overall positive correlation of these elements with As.

Outlying populations disturbing these correlations may suggest the presence of a minor accessory mineral phases that occur locally in unusually high abundance. Such examples can be found in Figure 5.2E, where two clusters are plotted away from the main population of the dataset. The discernible set of 14 Ag-Sb-rich samples is explained by the presence of tetrahedrite (Goodfellow, 2003). Furthermore, the high As- low Ag cluster of the dataset is attributed to the anomalously high abundance of arsenopyrite (11 samples).

Mineral co-existence is the second mechanism influencing elemental covarations identified in the dataset. This mechanism results in moderate to weak correlations that are not facies-specific and can be found consistently throughout the deposit. The most common example is the positive correlation between Zn and Pb that is attributed to the fact that the greatest abundance of the sphalerite and galena which as the principal Zn and Pb mineral carriers, are found within the same stratigraphic horizons (facies) of the hydrothermal column and specifically at the stratigraphic top towards the hanging wall.
Similarly, covariation of Zn with Au can be explained, as the highest Au contents are typically found within the samples from the highest ore grades of the deposit.

Systematic elemental co-variation through co-existing minerals are found often observed in VMS deposits and are developed through the zone refining process. Zone refining is referred to as a continuous remobilisation of metals deposited at the base of mound-like body towards the top while the mound is increasing its size (Large, 1977; Eldridge et al., 1983; Huston and Large, 1989; Ohmoto, 1996). This process is triggered by a strong temperature gradient controlled by the hot upwelling fluids and can result in highly zoned VMS deposits such as those found in the BMC.

The zone refining model is supported by the strong Zn and Cu separation identified in the Caribou deposits as seen from the PCA diagram (Figure 5.10). One of the dominant reactions taking place during zone refining is the replacement of sphalerite by chalcopyrite that follows the reaction below:

\[
2 \text{CuCl}^0 + 2 \text{ZnS}_{(s)} + 2 \text{FeS}_{(s)} + 2\text{H}^+ + \frac{1}{2} \text{O}_2(aq) \rightarrow 2 \text{CuFeS}_2(s) + 2 \text{ZnCl}^+ + \text{H}_2\text{O} \quad (1)
\]

However, the earlier deposited sulphide facies are not entirely remobilised, leaving behind remnants of early sphalerite and galena-rich facies within the Cu facies of the system.

The separation of the Zn-Pb from the Cu facies has also been identified in the synchronous SMS deposits, where Zn-Pb sulphides are one to two orders of magnitude more enriched in Au than the higher temperature Cu facies, owing to the continuous recycling of the hydrothermal fluids and metals upwards (e.g., TAG hydrothermal field; Hannington et al., 1995).

According to McClenaghan et al., (2003), Au in Bathurst Mining Camp is associated with both Zn-Pb and Cu facies of the deposit. In particularly, Au found in the Zn-Pb facies
of the deposits systematically correlates with Sb, As and Ag, whereas Au that resides in the
vent complex is associated with Bi, Co and Cu. The vast majority of the Au-rich samples,
analysed for this work, come from the Zn-Pb facies, however, there is a limited number of
samples from the Cu facies that also exhibit elevated Au concentrations.

McClenaghan et al., (2003) explained this bimodal distribution of Au in many de-
posits of the BMC as an effect of different transportation and deposition mechanisms, with
AuCl$_2^-$ complex to transport Au in high temperature conditions deep within the mounds,
and Au(HS)$_2^-$ to carry Au in relatively lower temperature settings near the sea floor. The
reactions of Au precipitation for the two environments are the following:

\[
\text{AuCl}_2^- + \frac{1}{2} \text{H}_2^{(aq)} \rightarrow \text{Au}_{(s)} + 2\text{Cl}^- + \text{H}^+ \quad (2)
\]

\[
\text{Au(HS)}_2^- + \frac{1}{2} \text{H}_2^{(aq)} + \text{H}^+ \rightarrow \text{Au}_{(s)}^+ \quad (3)
\]

In the Caribou deposit, Au precipitation likely took place through the reaction 2 pathway,
where Au is transported as the Au(HS)$_2^-$ complex. However, similar to many VMS districts,
in the BMC, it is unlikely that Au had been initially deposited in both Cu and Zn-Pb facies
through reactions 1 and 2. Meanwhile, Au from the Cu facies could have been transported
to the top of the mound through zone-refining processes. In this way, the Caribou deposit
may have experienced a more intensive zone-refining than other deposits in the camp,
which more effectively remobilize the Au towards the stratigraphic top. If this is the case,
zone refining may also explain the elevated Au concentrations that occur at the strati-
graphic top of the Caribou lenses that are anomalously elevated compared to the other
deposits in the camp. Hence, Au enrichment is not only dictated by original metal endow-
ment, but also post-depositional remobilisation processes that concentrate Au within spe-
cific sulphide facies.
Similar to Au, the distribution of other elements can be modified through developed temperature gradients during early genesis. Particularly, for the Caribou deposit, Cu co-varies with Co and Se that are all found in highest concentrations within the Cu facies of the deposit. The high Co contents are possibly be taken up by pyrite, as is commonly found in most hydrothermal systems (see Libbey and Williams-Jones, 2016). Moreover, high concentrations of Cu, Co and Se are also found in the modern black smokers that are characterised as high temperature hydrothermal environments (Hannington et al., 1995).

Beyond Co and Se, temperature gradients have influenced the distribution of other trace elements in massive sulphides of Caribou deposit. Thallium, As and Sb, contents increase towards the Zn-Pb facies of the system where the highest whole-rock concentrations of these elements are measured. This observation, supported by chemostratigraphic profiles (Fig. 5.8) and the PCA (Fig. 5.10) diagram produced in this study, demonstrates a clear link between the whole-rock composition and proximity of facies (lenses) to the feeder stockwork zone. Goodfellow 2003 reported elevated Bi contents associated with the Cu facies of the Caribou sulphide lenses, however this observation is not confirmed from the present study. The Bi, Hg, In and Ga distribution does not exhibit systematic trends within the hydrothermal architecture of the Caribou deposit.
Chapter 6
Ore Petrography

6.1 Introduction

A subset of drill core slabs was selected to obtain a representative overview of ore petrography spanning the complete stratigraphic and compositional range of the Northwest Lens System (NLS) of the Caribou deposit. The petrographic samples are grouped and described according to the three sulphide facies as defined by the corresponding lithogeochemistry (Chapter 5).

A total of 27 polished thin sections of massive sulphides were prepared and examined under reflected light with the petrographic results presented in this section. Ten of these samples were additionally studied with in-situ micro-analytical techniques including Scanning Electron Microscopy (SEM) and Laser Ablation - Inductively Coupled Plasma - Mass Spectrometry (LA-ICP-MS).

This work aims to illustrate the ore textures, mineral association and acquire the major element composition of minerals of interest. SEM-EDS also allowed for the identification of minute mineral phases (e.g., sulfosalts) that were not recognised with the conventional reflected light microscopy. Insights gained from the SEM study are used for the selection of the targets for LA-ICP-MS analyses. These include both mapping and spot analyses, however, only the SEM-EDS and LA-ICP-MS maps are presented in this chapter (see Chapter 7 for results of the LA-ICP-MS spot analyses). LA-ICP-MS mapping was performed to highlight the trace element variations of composite grains which exhibit multiple generational growth. All the information is gathered with the objective of reconstruct the paragenetic sequence in the Caribou deposit.
6.2 Petrographic description

Numerous mineral phases are identified in the thin sections using reflected light microscopy and SEM. However, this project focusses on sulphide and oxide minerals that are believed to be genetically linked to the mineralisation, these include pyrite, sphalerite, galena, chalcopyrite, arsenopyrite, cassiterite, tetrahedrite, magnetite and hematite. Covellite and chalcocite are also present and associated with the supergene copper ore extracted by open-pit mining in 1970 (Cavelero, 1993). Nonetheless, the supergene zone has no tenable link with the deeper epigenetic Cu facies of the deposit and its study goes beyond the objective of this project. Gangue mineral phases consist of chlorite, phengite, quartz and carbonate minerals. Stilpnomelane and talc are also reported in the Caribou deposit (Jambor, 1979).

Mineral textures are particularly sensitive to variations in pressure and temperature. The protracted deformational episodes incurred by the Caribou massive sulphides and volcano-sedimentary host rocks were accompanied by greenschist facies regional metamorphism (325°C and 4-6 kbar; Currie et al., 2003). The footwall and hanging wall of the deposit have recorded a significant degree of ductile deformation, as shale and metavolcanic lithotypes of the Spruce Lake formation have been folded and sheared during D1. However, the overall low-grade greenschist facies metamorphism did not aid the substantial recrystallisation of sulphide grains resulting in fine-grained mineralisation.

With regards to the sulphide textures, the syn-metamorphic deformation has resulted in remobilisation of sphalerite, galena and chalcopyrite, inducing segregation banding and migration of these sulphides under ductile conditions (Cook et al., 1993; Craig and Vaughan, 1994). Such example is shown in Figure 6.1, a typical texture of the Zn-Pb facies, where sphalerite and galena banding follow the tectonic fabric.
Figure 6.1: Composite image of RL (left) and EDS layered map (on the right) illustrates banding of sphalerite (brown), galena (purple) and pyrite (green), a typical texture across the Zn-Pb facies; 15-FD-19-P7C.
Meso- and microscale observations, as such obtained in this study, are inadequate to delineate the extent of remobilisation (Gilligan and Marshall, 1987). However, it is assumed that since the chemical zonation of the systems is preserved, the distance of which this translocation occurs is limited within the individual sulphide facies and confined to few meters.

Under the same metamorphic and deformation conditions, refractory minerals (i.e., pyrite, arsenopyrite) show cataclastic behaviour, and often retain primary features. In the Caribou deposit, early textures are rarely preserved and limited to colloform and framboidal forms of pyrite (Chen, 1978). Pyrite also preserves growth bands formed in response to episodic hydrothermal flow in the system, providing the most complete record of the hydrothermal history of the mineralisation.

On the contrary, as previously mentioned textures exhibited by the common ore minerals (sphalerite, galena and chalcopyrite) are largely results of remobilisation and recrystallisation (re-equilibrate). Hence, most mineral textures identified and described in this chapter are not primary, adding a high degree of uncertainty in reconstructing the original paragenetic sequence of the system.

Overall, pyrite, sphalerite and galena are the most abundant sulphide minerals in the deposit. Chalcopyrite is less abundant occurring primarily within the Cu facies of the system. Arsenopyrite, magnetite, cassiterite and tetrahedrite are present in trace quantities. The ore textures described in this chapter is centred around the petrographic examination of the thin sections and evidenced in a series of reflected light and backscattered electron (BSE) microphotographs.
6.2.1 Pyrite

Pyrite is a ubiquitous sulphide mineral in the Caribou deposit and provides the most complete record of metamorphic textures, ranging from massive to granular in habit, colloform grains, framboids and more often recrystallised euhedral grains. There is no noticeable correlation between pyrite textures and the hydrothermal sulphide facies, in which they occur. Therefore, all textures can be found within a single thin section (i.e., 15-FD-32-P8A).

Framboidal pyrites are the least abundant pyrite texture identified across the NLS. They are particularly fine-grained and only identifiable during the SEM study. Pristine framboidal pyrites are found in a single petrographic sample that is part of the medium-grade Zn-Pb facies (15-FD-30-P7C; Fig. 6.2A). Similar to work documented by Chen (1978), the framboidal pyrite has ca. 10 μm diameter. The well-preserved framboids occur in fine-grained arsenopyrite and sphalerite groundmass with few galena inclusions. The limited size and scarce occurrences of the framboidal grains did not favour the in-situ analysis with SEM and LA-ICP-MS. More frequently, structures of framboidal pyrite are found partially or fully replaced by galena and silicate minerals (Figs. 6.2B-C). In this case, the diameter of these structures reaches up to 25 μm.

Colloform pyrite (Figs. 6.2D-H) is more abundant than framboidal pyrite. It occurs surrounded by gangue minerals (mainly silicates) or less frequently by sphalerite. There is no clear evidence for a genetic link between colloform pyrite and its matrix, however, it is here suggested that the silicate groundmass possibly represents the original matrix of the colloform grains, resembling remnants of hydrothermal conduits.

Colloform pyrites are much larger than framboidal pyrites and are identifiable even in a hand specimen. The size of the colloform textures ranges from 200-500 μm but they
exceed the 1 mm when occurring in clusters. They rarely form concentric rings (Fig 6.2G-H). Instead, they have many nuclei forming coalescing botryoidal structures (Fig 6.2D). The colloform textures consist of wide zones of relatively inclusion-free pyrite alternating with zone full of inclusions (i.e., chalcopyrite, Fig. 6.2D; and galena, Fig. 6.2H).

Colloform textures are often found fractured and brecciated, and additionally rimmed by a late generation of fine to medium-grained annealed pyrite. Cataclasis is more often observed when pyrite is associated with silicate or carbonate minerals (Fig. 6.2D), as all the strain is relieved by the brittle fracturing of pyrite. On the contrary, when pyrite is associated with softer sulphide minerals, the strain is taken up by the ductile sulphides. Thus, if in this case pyrite occurs fractured, the ductile sulphide presumably started migrating to that area during or shortly after the cataclasis of pyrite (i.e., sphalerite; Fig. 6.2G). The euhedral pyrite rim (Figs. 6.2F,H) is always present around both fragmented and more preserved colloform textures, indicating that cataclasis took place in advance of the regional metamorphism. Moreover, the presence of the annealed rim corroborates the outward growth of the colloform structure by the accretion of compositionally discrete layers, with the core representing the older pyrite deposited in the structure.

Grain size and width of the individual growth bands vary considerably within the colloform grains. The width of the bands ranges from 10 to 200 μm and tends to become finer towards the rim of the colloform structure. As shown in Figure 6.2H, the wider zones are formed by coarse elongate or acicular pyrite crystals arranged perpendicular to the layering direction, while fine-grained pyrite forms thin layers.

Oscillatory zoning is commonly used to track changes in the composition of the mineralising fluid through time. The major element chemistry of colloform grains is largely
**Figure 6.2:** Photomicrographs (BSE and RL images) of framboidal and colloform pyrite (Py) textures. 

**A)** Pristine framboidal pyrite engulfed by late arsenopyrite (Asp) and remobilised galena (Gn) and sphalerite (Sp). Part of the medium-grade Zn-Pb zone of the systems, this is the only thin section where pristine framboidal pyrite is found; 15-FD-30-P7C. 

**B-C)** Sample (15-FD-32-P8A) from the low-grade Zn-Pb zone with framboidal textures of pyrite up to 20 μm partially replaced by galena and silicate minerals. 

**D)** Coalesced colloform pyrite clusters occurring in the Cu facies (15-FD-19-P9D). Pyrite’s growth zones are interrupted by fine chalcopyrite bands. 

**E-F)** Sample 15-FD-32-P8A from the low Zn-Pb facies with characteristic colloform pyrite grains exhibit rhythmic banding and is rimmed by fine-grained euhedral pyrite. Inclusions of galena and silicates are found along the annealed rim, as well as framboidal pyrite textures fully replaced by galena.
Figure 6. 2 (continued): G-H) Colloform pyrite with concentric rings from the medium-grade Zn-Pb zone (15-FD-30-P9B). Compositional variation illustrated in the BSE image is associated with Sb content. The core and few of the growth bands host galena micro-inclusions. The wider bands are characterised by acicular pyrite growth. I) Large pyrite grain (ca. 600 μm) from the Cu facies (15-FD-20-P24) with inclusions of chalcopyrite and silicate minerals resembling multiple generations of pyrite growth occur while pyrite grains are rotated. J) Fine-grained annealed pyrite occurs within a sphalerite segregation bands. Inclusions of sphalerite are found in pyrite grains. K) Euhedral pyrite occurs within a galena segregation band from the low-grade Zn-Pb zone (15-FD-32-P1C). The pyrite porphyroblasts are partially replaced by galena, as indicated by the rounded inclusions. L) Euhedral pyrite and magnetite overgrown and replaced by sphalerite (sample from the Zn-Pb facies).
stoichiometric, except for the colloform structure shown in Figures 6.2G-H that exhibits notable chemical variation. This sample is derived from the medium-grade Zn-Pb zone and displays varying Sb concentrations with elevated contents closer to the rim of the grain to be captured as brighter zones.

The two primary pyrite textures (colloform and framboidal) are considered coeval and formed by similar mechanisms \(\text{(Chen, 1978)}\). Throughout the petrographic study, the incipient growth of colloform pyrite appears to begin around a framboidal pyrite grain (Fig. 6.2D), indicating that the formation of framboidal pyrite textures predate the colloform growths. However, framboids are often found in the rim of colloform pyrite (Fig. 6.2F), suggesting that some of the colloform grains are formed earlier than the framboidal pyrite. \text{Chen (1978)} found relict framboidal cores in disseminated euhedral pyrite crystals (<15μm), however this texture is not observed in the samples of the current study.

“Porous” pyrite occurs in granular shape forming fine-grained pyrite aggregations that locally coalesce to from 1 to 5 mm thick porous clusters. This texture is often found cataclastically deformed with cracks filled by gangue minerals and other softer sulphide (i.e., galena).

Large pyrite grains up to 600 μm across are found exclusively in the Cu facies. The internal pattern of these grains resembles the inclusion of silicate minerals and chalcopyrite that occur when the growth of pyrite is taking place while the grains are rotated. Similar features are described by \text{Craig et al., (1998)} and \text{Craig (2001)}.

The latest generation of pyrite that occurs in the NLS is the euhedral pyrite associated with the metamorphic overprint of the mineralisation. Coarse-grained annealed pyrite is rarely found in the deposit (Fig. 6.2I), instead, medium to fine-grained euhedral pyrite (Figs. 6.2J-L) is abundant across the sulphide body. When the metablastic growth of
pyrite has occurred in a matrix of ductile sulphide minerals (galena, sphalerite and chalcopyrite), pyrite is observed with its finest grain size (20-50 μm). This texture is commonly associated with the sphalerite and galena segregation bands, which are macroscopically described as galena and sphalerite wispy bands (see Chapter 6.2.2). These fine-grained pyrite porphyroblasts are occasionally associated with relatively rounded inclusions of ductile minerals (e.g., galena and sphalerite; Figs 6.2K-L), and it is regarded as a replacement texture (Craig and Vaughan, 1994).

Compositional data shows that pyrite is arsenian in nature, exhibiting elevated concentrations of As and more rarely Sb. Arsenic contents of pyrite average 1.5 wt. %, and rarely reach up to 5.5 wt. % As; the highest As concentrations were measured on the annealed pyrite grains. When pyrite contains over 3 wt. % As, it also exhibits mild anisotropy. Irregular-shaped inclusions of galena, sphalerite and chalcopyrite are abundant within the pyrite boundaries and when they affected the SEM-EDS measurements on pyrite, EDS spot analyses were rejected.

6.2.1.2 Intra-mineral trace element signatures of pyrite

High resolution “single mineral maps” were generated by LA-ICP-MS in order to study the internal trace element variation of the pyrite. A set of chemical maps from two multi-generation pyrite grains of the Zn-Pb facies are presented here. Compositional variations of As, Sb, Au, Ag, Pb, Hg, Ni and Co were mapped in both grains.

The composite pyrite grain in Figures 6.3A-B, derives from the medium-grade Zn-Pb zone and is characterised by three discreet generations of pyrite (Py1, Py2 and Py3). A BSE image of the same composite grain is presented annotated in the previous section (Figs. 6.2G-H).
Figure 6.3.
Figure 6. 3 (continued): Reflected light image (A), BSE image (B) and semi-quantitative pyrite maps (C-J) illustrates the trace element variations of pyrite in selected elements; 15-FD-30-P9B, medium-grade Zn-Pb zone. Trace element variation along the profile A-B can be seen in Figure 6.4.

Figure 6. 4 (next page): Linear profile illustrates the chemical variation across a composite pyrite grain consisting of three generations. The beginning “A” and end “B” of the profile is situated on sphalerite. Semi-quantitative elemental concentrations are extracted from the LA-ICP-MS maps (see Fig. 6.3) and presented in logarithmic (for Pb, As, Sb, Ag, Au) and linear scale (for Fe) to highlight the compositional variation of pyrite.
The earliest generation of the composite grain (Py1; Fig. 6.3B) was initially formed as framboidal pyrite aggregates. The framboidal texture was later replaced by galena and sphalerite that gave pyrite its porous appearance. The chemistry of Py1 does not vary considerably, having elevated contents of As, Sb, Au, Ag and Pb (Figs. 6.3C-G). High Pb corresponds to galena inclusions that additionally host elevated contents of Ag. Antimony contents are significantly low where galena inclusions are not present (low Pb). Then, Sb distribution is associated with As, Au and Ag, elements that are often found structurally bound in pyrite. Gold distribution in Py1 is more likely an effect of Au remobilisation that took place during the partial replacement of the grain. This hypothesis is supported by the irregular distribution of Au that seems to have no association with any inclusions.

The nucleation of Py2 is initiated around the partially replaced framboidal pyrite. The colloform bands consist of wide zones of relatively inclusion-free pyrite alternating with narrow bands full of galena and sphalerite inclusions. The colloform growth is described by a great variation in pyrite composition. Nevertheless, the small bands of galena inclusions are equally responsible for this chemical variation. The two wider bands of Py2 that consist of long acicular crystals (see Fig. 6.2H) show no variable composition, displaying depletion in As, Sb, Au and to a limited extend in Ag. This suite of four elements consistently co-varies throughout the colloform growth.

The annealed fine-grained pyrite (Py3) is considerably enriched in Ni and Co (Figs. 6.3I-J). Besides the late rim, Ni and Co are consistently below detection limit. The rim is particularly depleted in Au and Sb, while Ag is present in low concentrations. Mercury shows no enrichment in pyrite Py3, instead, the narrow Hg-rich rim around pyrite is an artefact of signal dilution that occurs when the beam intersects both pyrite and the Hg-enriched sphalerite matrix (Fig. 6.3H). Before the formation of the later pyrite generation
(Py3), the Py1-Py2 composite grain endured brittle deformation with only a fraction of the original grain to be found preserved in the thin section. Py3, formed during the regional metamorphism, rims symmetrically the fractured grain.

Figure 6.4 displays the semi-quantitative concentrations of the composite pyrite grain along the A-B section in Figure 6.3A. The elemental concentrations of Pb, Sb, As, Ag and Au are presented in a log scale, while Fe, due to its high concentrations, is presented in a linear scale in order to highlight its variation. The start and the end points of the cross-section are situated on sphalerite, whereas from A to B the profile intersects first the Py3, then Py1 and Py2, and last, Py3 that envelopes the entire grain. The chemical variations within the pyrite are attributed to either trace element substitutions in pyrite, unresolvable nano-inclusions or micro-inclusions of other minerals.

At least five clusters/bands of galena inclusions are intersected as indicated by the highest Pb contents of the profile (>10,000 ppm; Fig. 6.4). Depending on the width of galena band, signal dilution may occur leading to a drop in Fe signal (<45 wt. % Fe). The galena bands on pyrite are visually identifiable in Figures 6.3B,G.

Back to the profile, elevated Ag and Sb contents are detected upon galena intersections. However, Ag and Sb covary even where galena is absent, suggesting that these elements also occur in solid solution within pyrite.

Throughout the profile, elevated Ag contents typically correspond to high Sb, while the converse relation is not always true. In particular, sections of the pyrite where Sb is not coupled with Ag, it correlates with As. This Sb-As covariation is indicative of the substitution of these elements into pyrite.
Figure 6. 5.
Figure 6.5 (continued): Reflected light image (A) and semi-quantitative pyrite maps (B-J) illustrates the trace element variations of pyrite in selected elements; 15-FD-32-P8A, low-grade Zn-Pb zone.
With regards to Au distribution, there is an evident covariation of Au with As. However, several As-enriched and Au-depleted bands are identified. This inconsistency represents the original chemistry of the hydrothermal fluid since the As-enrich fluid is not always Au-bearing.

Along with the pyrite in Figure 6.3, three generations of pyrite are distinguished in the composite pyrite grain shown in Figure 6.5. It is worth mentioning that the annotations given to the pyrite generations (Py1, Py2 and Py3) do not necessarily correspond to common depositional events (Figures 6.3 and 6.5). Besides the regional metamorphic episode resulting in formation of the Py3 that envelopes the composite grains, Py1 and possibly Py2 are likely to have been deposited by different events during the hydrothermal evolution of the deposit.

The core (Py1; Fig 6.5) of the composite grain is characterised by depletion in most of the analytes (As, Au, Ag and Ni), while micro-cracks infilled with galena, sphalerite and silicate minerals are observed in Figures 6.5D,G,H and have also penetrated Py2. Py1 is enriched in Hg and Sb, whereas very high Hg and Pb concentrations are associated with sphalerite and galena inclusions.

The colloform growth (Py2) is developed by successive precipitation cycles of the hydrothermal fluid. There is an evident variation in the Fe composition of the colloform structure. Three distinct Fe-depleted growth rings are identified Py2 and are attributed to fine bands of sphalerite and silicate minerals precipitated at the end of each precipitation cycle. The spotty As and Ni maps (red and yellow colour) indicate randomly distributed sub-microscopic inclusions in both Py1 and Py2.

Euhedral pyrite grains (Py3; Fig. 6.5) surround the Py1-Py2 composite grain and show enrichment in As, Sb, Pb, Hg and Ni. Arsenic and Sb covary within Py3, expect for the
bottom-left section of the structure where Sb distribution is essentially controlled by sphalerite inclusions that are readily identified using Hg distribution map (Fig. 6.2H). Silver follows the distribution of Pb implying that Ag is exclusively bound to galena. Gold is significantly enriched in Py3, following an erratic distribution similar to As and Hg.

6.2.2 Sphalerite

Sphalerite, although less abundant than pyrite, is a principal constituent of the ore. It occurs as distinct wispy bands together with galena and pyrite that are typical within the Zn-Pb facies (Fig. 6.6A). The sphalerite bands are developed by mechanical and chemical remobilisation under increased temperature and differential stress (Cook et al., 1993). Under these conditions, sphalerite behaves plastically and segregates into bands that are typical of the Zn-Pb facies of the system. Cassiterite and pyrite are often accommodated within these bands (Fig. 6.6B).

Under the microscope, sphalerite is observed interstitially between the minerals or filling tension gashes. Rarely, sphalerite exhibits finely dispersed inclusions (blebs) of chalcopyrite (Fig. 6.6C). This texture is often described as chalcopyrite disease and is attributed to replacement of sphalerite by chalcopyrite during zone refining or co-precipitation of the two minerals (Barton and Bethke, 1987; Bortnikov et al., 1991; Kojima, 1992).

The distinct variation in the colour (crimson red-brown-honey yellow) of sphalerite bands, as observed macroscopically, is commonly attributed to a variation in the Fe-contents of sphalerite. Nevertheless, under reflected light, the colour of sphalerite is consistently grey. Compositional data revealed that sphalerite is largely stoichiometric with a limited number of analyses displaying elevated Fe composition up to 6 wt % Fe. However, no
Figure 6.6: Photomicrographs of sphalerite textures along the NLS. A) Interbanded sphalerite (Sp), galena (Gn) and annealed pyrite (Py) from the high-grade Zn-Pb facies (15-FD-22-P4A). Single pyrite grains have grown isolated in the sulphide-sphalerite matrix, while an earlier generation of pyrite consists of massive aggregations displaying cataclastic fracturing with infillings by galena and silicates. B) Sphalerite wispy band with numerous euhedral to subhedral inclusion of pyrite, cassiterite (Cst), arsenopyrite (Asp) and silicates (15-FD-29-P17A; high-grade Zn-Pb facies). C) Chalcopyrite diseased sphalerite from the Zn-Pb facies. Chalcopyrite blebs have variable size, probably due to a low degree of segregation occurred during metamorphism.
Figure 6.7: Photomicrographs (BSE and RL images) illustrate common galena and chalcopyrite textures. A) Tension gashes filled by galena (Gn) within a sphalerite (Sp) segregation band from the medium-grade Zn-Pb facies; 15-FD-30-P9B. B) Remobilised galena and sphalerite penetrates fractures in brittle magnetite (Mag). There are abundant euhedral pyrite grains in the thin section. C) A Galena segregation band with minute annealed pyrite. Minor chalcopyrite (Ccp) and sphalerite also occur between the euhedral pyrite grains. D) Tension gashes on pyrite filled primarily with chalcopyrite, as well as galena and minor sphalerite. E) Large chalcopyrite bleb, typical of the Cu facies with fine-grained pyrite. F) Chalcopyrite has migrated among the late pyrite grains. Pyrite porphyroblasts have grown with curved boundaries to minimise the free energy associated with the phase and grain boundaries. Minor sphalerite is also present.
correlation between the macroscopic colour and the Fe contents was confirmed. Hence, the macroscopic colour variation observed between the different sphalerite bands is more likely associated with the grain size. While from a mineralogical point of view, up to 3 wt. % higher Fe content of sphalerite may seem trivial, Fe content of sphalerite should be taken into account for the design of the ore processing, as increased Fe content of sphalerite adversely affects the flotation of the mineral (Boulton et al., 2005).

In an attempt to study the internal structure of sphalerite, SEM-CL imaging was used, however, sphalerite did not show a cathodoluminescence response. This suggests that sphalerite has been recrystallised during metamorphism.

6.2.3 Galena

Galena is the third most abundant mineral of the deposit after pyrite and sphalerite. Along with sphalerite, galena also segregates into layered bands (Fig. 6.6A), where abundant small inclusions of pyrite, tetrahedrite and cassiterite are accommodated. Deformation of galena predominantly occurs with the coble creep mechanism (Rockingham and Hutchinson, 1980 and references therein) which is associated with the most readily deformed minerals; a fact that can explain its enhanced remobilisation during stress and the resultant erratic distribution. Deformation textures of the segregation bands have been entirely overprinted by metamorphic recrystallisation.

Where galena does not form layered bands, it migrates into the pressure-shadows of harder minerals (pyrite, magnetite, sphalerite; Figs. 6.7A-B). Galena also occurs as fine-grained matrix interstitial to pyrite porphyroblasts (Fig. 6.7C). The ductile flow of galena occurs under relatively the same condition with the brittle fracturing of pyrite, arsenopyrite and magnetite that result in galena infillings between the broken fragments of the
refractory minerals (Craig and Vaughan, 1994). These gash veins are often filled by chalcopyrite (Fig. 6.7D). Minor amounts of galena occur as small (20 - 80 μm), rounded to irregular inclusions within pyrite (Fig. 6.2K) and arsenopyrite (Fig. 6.2A).

6.2.4 Chalcopyrite

Chalcopyrite is identified in a limited number of samples and specifically those that derived from the Cu facies. More rarely, it occurs in samples from the Zn-Pb facies in the form of chalcopyrite disease in sphalerite (Fig 6.6C). For the most part, chalcopyrite replaces and is intergrown with pyrite, healing cataclastically deformed pyrite (Fig 6.7D) or it occurs as small (20 μm; Fig 6.7C) or large blebs (250 μm; Fig 6.7E). In the Cu facies, where chalcopyrite is abundant, pyrite exhibits curved boundaries with chalcopyrite (Fig 6.7E). This geometric constraint is adopted during recrystallisation, in order to minimise the free energy associated with the phase and grain boundaries (Smith, 1948).

Systematic in-situ analyses of chalcopyrite reveal a stoichiometric composition. Cobalt contents of 0.2 wt. % were determined for chalcopyrite, however, this value is placed within the error of the analysis. The composition of chalcopyrite blebs from the chalcopyrite diseased sphalerite texture was not determined due to their limited size (<10 μm).

6.2.5 Arsenopyrite

Arsenopyrite is found in most of the samples studied form the Zn-Pb facies, whereas it is notably absent from the Cu facies of the NLS. The high abundance of arsenopyrite towards the stratigraphic hanging wall of the Zn-Pb facies is in broad agreement with the findings of Roscoe (1969) and Goodfellow (2003). Considered one of the lately
Figure 6.8: SEM-BSE photomicrographs of arsenopyrite within the Zn-Pb facies. A) Massive aggregation of numerous fine-grained arsenopyrite crystals (ca. 8 μm) within a sphalerite segregation band from the medium-grade Zn-Pb facies; 15-FD-30-P7C. B) Aggregation of euhedral arsenopyrite that exhibits a minor chemical zonation; 15-FD-30-P7C. C) A cluster of euhedral arsenopyrite crystals in pyrite and silicate mineral matrix. Arsenopyrite is cataclyastically deformed with galena healing the tension gashes; 15-FD-22-P4A. D-F) Euhedral arsenopyrite crystals of various sizes formed between pyrite and gangue minerals, are found in samples from the low-grade Zn-Pb zone; 15-FD-32-P8A.
formed minerals of the paragenetic sequence, arsenopyrite has a very strong tendency to
develop euhedral to subhedral crystals.

Arsenopyrite is usually fine-grained (5-20 μm; Figs. 6.8A-B), but it reaches up to
100 μm in size (Figs. 6.8C-D). Fine-grained arsenopyrite occurs in aggregations intergrown
with sphalerite and pyrite exhibiting small inclusions of galena (Figs. 6.8A-B). These type
of arsenopyrite grains are often finely zoned (Figs. 6.2A and 6.8B), however, this aspect
was not investigated owing to the small size of the zones and the grains themselves.

Coarse-grained arsenopyrite tends to develop characteristic rhombohedral and
prismatic forms (Figs. 6.8C-F). Rhomb-shaped and prismatic crystals coexist between the
boundaries of pyrite and silicate minerals. Surrounded by equally competent minerals and
having no ductile mineral phase to absorb the stress, these arsenopyrite crystals have un-
dergo cataclastic deformation; remobilised galena fills the fractures within pyrite and ar-
senopyrite (Fig. 6.8C).

The SEM-EDS analyses were limited to coarse-grained arsenopyrite and revealed
Sb-enrichment (up to 1.5 wt. %). However, the analyses acquired are not satisfactory with
the wt. % totals to be considerably low owing to the small size and topography of the
grains.

6.2.6 Tetrahedrite and Sb-Ag sulfosalts

Tetrahedrite occurs as fine-grained inclusions (< 70 μm) within a limited number of
thin sections. It is a minor constituent of the ore, although it is locally abundant especially
in the bands of galena (Figs. 6.9A-B). Beyond galena, tetrahedrite is intergrown with sphal-
erite. Disequilibrium of tetrahedrite with galena and sphalerite, possibly during the meta-
morphism, resulted in partial replacement of tetrahedrite and the irregular embayment
textures (Figs. 6.9A-B). Based on the textural associations, tetrahedrite is considered as pre-metamorphic minerals, however, the timing for its deposition cannot be further constrained.

Across the Zn-Pb facies, elevated Ag contents, revealed from the bulk-rock chemistry, correspond to abundant galena. The host minerals of Ag is not only galena itself; there are numerous small grains of tetrahedrite (ca. 10.5 wt % Ag and 29 wt. % Sb; Figs. 6.9A-B) and rare Sb-Ag sulfosalts (ca. 27 wt. % Ag and 53 wt. % Sb; Fig. 6.9B) that host substantial amounts of Ag.

The tetrahedrite isotypic series is the most complex among sulfosalts as it has the capacity to accommodate multiple substitutions in the mineral lattice (George et al., 2017). Tetrahedrite from the NLS of the Caribou deposit was analysed under the SEM-EDS and found to be argentiferous, without containing any detectable amounts of As. However, the Ag contents measured for tetrahedrite are not high enough to be classified as freibergite or argentotetrahedrite (ca. 40 wt. % Ag). The major element chemistry of Sb-Ag sulfosalts is not determined due to the minute size of the grains (<10 μm; Fig. 6.9B) that would compromise the quality of the spot analyses.

6.2.8 Magnetite and hematite

Iron oxide minerals that occur in the hydrothermal system consist of magnetite and hematite (Figs. 6.9C-F). Hematite is identified only in a single thin section, while magnetite constitutes a major mineral phase of the massive sulphide lenses across the NLS. Magnetite is more abundant in the footwall rather than the hanging wall of the lenses. However, the most pronounced changes in magnetite abundance are lateral (along the lens strike); as magnetite has not been reported in the eastern lenses (Cavelero, 1993; Jambor, 1979).
Figure 6. 9: SEM-BSE photomicrographs (BSE and RL images) display common features of minor mineral phases across the NLS. **A-B)** Typical occurrences of tetrahedrite (Tet) with sphalerite (Sp), euhedral pyrite (Py) and Sb-Ag sulfosalts within a galena segregation band (low-grade Zn-Pb facies; 15-FD-32-P1C). Replacement of tetrahedrite by galena and sphalerite have resulted in embayed boundaries of tetrahedrite. Galena inclusions within the pyrite porphyroblasts are also considered replacement textures. **C)** Magnetite (Mag) replaced by silicate minerals and associated with euhedral pyrite in a sample from the high-grade Zn-Pb facies; 15-FD-29-P17A. **D)** Magnetite and fine-grained pyrite porphyroblasts are partially replaced by sphalerite. **E)** Magnetite and pyrite with inclusions of chalcopyrite (Ccp) in a sample from the Cu facies; 15-FD-20-P24. Magnetite is replaced by silicate minerals. Pyrite and magnetite are depicted with the same colour in the BSE images and they are distinguishable only from the subtle porous texture of pyrite that is not seen in magnetite. **F)** Magnetite, pyrite and hematite associated with silicate minerals; 15-FD-29-P17A, high-grade Zn-Pb facies. Hematite is an oxidation product of pyrite.
Magnetite is replaced by silicate minerals and sphalerite (Figs. 6.9C-E). Magnetite’s replacement by sphalerite (Fig. 6.9D) more likely occurred during metamorphism, as high temperature and tectonic stress induced the remobilisation of sphalerite. These conditions also promoted the formation of pyrite porphyroblasts that grew uninterrupted when occurred in sphalerite matrix.

The backscattered electron contrast among pyrite, magnetite and hematite is low, therefore the areas of interest were marked, and reflected-light images were obtained before the SEM study. Upon closer examination, pyrite exhibits a subtle porous texture that is also distinguishable under the SEM. In-situ spot analyses on magnetite and hematite indicated the stoichiometric composition of both minerals.

Minor hematite is present in a single thin section from the Zn-Pb facies where chalcopyrite is unusually abundant (Fig. 6.9F). The textural association between pyrite and hematite indicates that hematite is possible formed by the oxidation of pyrite. Then, hematite was partially replaced by chalcopyrite, presumably during the regional metamorphic event.

6.2.7 Cassiterite

Cassiterite occurs as anhedral equant inclusion-free grains in close association with the layered segregation bands of galena and sphalerite (Fig. 6.10), representing one of the major hosts of Sn in Caribou deposit. Cassiterite is translucent with weak reflectance. These two characteristics in combination with its very fine-grained nature (<20 μm) easily result in its misidentification as a gangue silicate phase. This is possibly the reason why the presence of cassiterite in Caribou deposit was not documented in any of the early works.
Figure 6. 10
Figure 6. 10 (continued): SEM maps of the sample with the highest Sn bulk-rock composition; 15-FD-25-P5. Late sphalerite vein crosscutting the fabric. Wispy sphalerite layered band with minor galena (Gn) and cassiterite (Cst) inclusions. Pyrite (Py) aggregates are also replaced by galena. Brightness variation of the BSE image reflects different mineralogy, while differences in brightness of the individual chemical maps illustrate differences in the relative abundance of the corresponding element. 

A) BSE image. B) Layered EDS image combining S, Fe, Zn, Pb, Si and Sn spectra. C) S map shows the location of sulphide minerals: pyrite shown with bright yellow, and sphalerite and galena with darker yellow. D) Fe map shows the location of pyrite and other Fe-rich minerals (dark grey). E) Zn map shows the location of sphalerite. F) Pb map shows the location of galena. G) Si map shows the location of silicate minerals that represent most of the gangue minerals occur in the thin section. H) Sn map shows the location of cassiterite.
Figure 6.11: SEM-BSE and SEM-CL images of sample 15-FD-24-P5 from the high-grade Zn-Pb facies illustrate common occurrences of cassiterite within the NLS. **A-B**) Isolated subhedral cassiterite exhibits oscillatory zoning. It is rimmed by an irregularly shaped band possibly formed by fluid-driven dissolution-precipitation. **C-D**) Subhedral cassiterite grains accommodated in sphalerite layered band and exhibit an irregular hourglass growth with a low luminescent core. **E-F**) Coalesced and isolated cassiterite grains along a galena-sphalerite segregation band exhibit zonation and the similar non-luminescent core with cassiterite in 6.11D.
a detailed petrographic study is carried out for the identification of cassiterite.

As part of this study, SEM-EDS mapping was employed to investigate the distribution of Sn-rich mineral phases. Once located, the area was re-examined for SEM imaging and *in-situ* analyses. Spot analyses on the limited number of cassiterite grains showed high Sb contents and slightly elevated concentrations of Fe and Zn. Although Sb and Fe often reside in cassiterite lattice, Zn incorporation into cassiterite is not reported in the literature. This implies that Zn is derived from the surrounding mineralogy - namely sphalerite – owing to the large excitation volume activated when analysis acquired in maximum magnification.

Considering that the grain size of cassiterite did not favour the acquisition of reliable compositional data, SEM-CL imaging was employed to investigate the intermineral chemical variation and structure of the grains. As shown in Figure 6.11, CL photomicrographs revealed the micrometre-scale zoning of cassiterite grains which is not discernible in the BSE images. This zoning is associated with variations of the trace element distribution within the cassiterite (*Wille et al.*, 2018).

Notably, Figure 6.11A-B shows oscillatory zoning of cassiterite grains that is more likely associated with their primary growth. This banding is not continuous around the grains as it is interrupted by an outer band with irregular shape. The regional metamorphic event may result in replacement of cassiterite and sphalerite from galena and it is shown in Figure 6.11A-B.

Similarly, Figures 6.11C-F show cassiterite grains from sphalerite and galena-sphalerite layered bands of the same sample. These grains are characterised by an irregular hourglass growth and a dark (low luminescence) centre. The dark core, that is frequently...
observed with a characteristic euhedral shape (Fig. 6.11F), is regarded as a pre-existing seed crystal of the incipient oscillatory growth.

6.3 Discussion

Growth zones, mineral habit, and textures and mineral associations are used to determine the paragenetic sequence of the mineralisation. Due to metamorphic recrystallisation, the original mineral fabrics have been severely overprinted, posing a major obstacle to reconstructing the mineral paragenesis. Pyrite, sphalerite, galena, chalcopyrite, arsenopyrite, cassiterite, tetrahedrite and magnetite comprise the principal mineral assemblage of the Caribou deposit. Based on the petrographic observation described earlier, the following distinct paragenetic stages are envisaged along the evolution of the hydrothermal system: I) Syngenetic precipitation, II) Zone refining, III) Waning stage and IV) Regional metamorphism and deformation.

I) Syngenetic precipitation

Pyrite is the most abundant sulphide mineral in the Caribou deposit and due to its refractory nature provides the most complete record of hydrothermal evolution across the system. Framboidal and colloform pyrite are considered as the only primary sulphide textures that are preserved within the deposit and thus included in the syngenetic precipitation stage of the mineral paragenesis.

As part of this study, a single intact framboidal grain (Fig. 6.2A) was identified in the NLS, whereas most of the framboids are found partially or fully replaced by galena (Fig. 6.2B). Pyrite framboids are frequently seen in sedimentary environments and are linked to biological activity. However, the work of Butler and Rickard (2000) demonstrates that
such textures can be formed without biological intervention. Textural evidence of the Caribou deposit also suggests the non-biological origin of framboidal pyrite.

Occurrences of framboidal pyrite within the Caribou deposit documented by previous studies are in greater abundance than that observed in this work. In particular, the framboidal-rich samples studied by Dehnavi et al., (2018) were collected from the footwall of the deposit (below the horizon of the massive sulphides), whereas Chen (1978) did not indicate the origin of samples studied. In this regard, the author of this study argues that the identified scarcity of framboidal pyrite within the NLS is a consequence of hydrothermal evolution and lack of preservation rather than a result of sampling bias.

Pyrites with colloform banding are considerably more abundant across the NLS. Colloform pyrite and sphalerite textures occur in both VMS and SMS deposits (Hurley and Croket, 1985; Craig, 1990; Hannington et al., 1995). Colloform sphalerite, if ever formed in the Caribou deposit, has been obliterated and remobilised during syn-metamorphic deformation. In contrast, colloform pyrite is most likely to endure, even after a granulitic facies metamorphism (i.e., Broken Hill-type Pinnacle deposit; Parr, 1987).

Colloform textures are often associated with diagenetic mineral growth, however, this did not occur in the Caribou deposit due to several factors. Firstly, deposition of Au does not occur during biological processes, as Au requires high temperature conditions to become soluble in the hydrothermal fluid where biological activity can be rarely sustained. In addition, the precipitation of galena, sphalerite and chalcopyrite (Fig. 6.2D,H) that had interrupted the continuous development of the pyrite growth is unlikely to be caused by bacteria or micro-organisms. The scenario of a metamorphic origin is also eliminated as there are no defects and domain structures that typically indicate high temperature colloform textures (Murowchick and Barnes, 1987).
For the most part, the colloform growth is initiated around an earlier generation of porous pyrite, as the degree of fluid supersaturation required for growth is much lower than that required for nucleation. Temperature and degree of fluid saturation are the most important parameters that dictate the crystal morphology (Murowchick and Barnes, 1987). Experimental observations by Barrie et al. (2009) showed that deposition of fine-grained pyrite transpires under a high degree of saturation, while lower degrees of saturation favour crystal growth over nucleation and thus large acicular crystals are formed. Besides a few exceptions (see acicular pyrite bands; Figs. 6.2G-H and Fig. 6.3), the crystals that comprise the colloform bands are narrow in width, indicating that precipitation of pyrite occurred under high degree of supersaturation.

Fine banding may also be generated as an effect of rhythmic interruption or slowing of the pyrite growth process. In fact, within the NLS, colloform growth of pyrites is frequently interrupted by precipitating galena, sphalerite and chalcopyrite. This observation suggests that the periodic deposition of colloform structures is synchronous with the main phase of base metal sulphide deposition.

Textures of colloform growth can capture the fluctuating physicochemical conditions of the fluids. This compositional growth banding is a result of either a periodically recharged fluid with consistent composition, or by a fluid that changes composition in an episodic manner (Fleet et al., 1989). The first scenario is closely associated with fine-scale zoning as identified in Caribou deposit, whereas variation in the chemistry of the mineralising fluid usually results in deposition of wider growth bands.

As noted by examining the trace element distribution of colloform pyrite (Py2; Fig. 6.3 and Fig. 6.5), galena and sphalerite micro-inclusions account for most of the discrete
bands of Sb, Ag and Hg. Coupled substitutions (e.g., Ag-Sb, As-Sb, As-Au), although present, have limited contributions to the chemical variability featured within the colloform grains.

As previously mentioned, it can be assumed that the colloform structures are deposited by different fluid pulses of similar if not identical composition. Each fluid pulse results in a single pyrite depositional cycle. Here, the pyrite depositional cycle is defined as a period when uninterrupted precipitation of pyrite occurs resulting in deposition of multiple growth bands. The total width of the precipitated bands within a single depositional cycle can vary considerably.

Disregarding the bands consisting of galena and sphalerite micro-inclusions (Py2; Fig. 6.3 and Fig. 6.4), changes of the pyrite trace element chemistry within each depositional cycle appear to be gradual and systematic, displaying increasing trace element contents. This progressive enrichment in the trace element composition of pyrite reflects the chemistry of the metal-bearing fluid and it is presumably derived by a trace element (e.g., As, Sb, Ag and Au) build up in the residual fluid towards the latest fraction of each depositional cycle. A similar argument was made by Fleet et al., (1989) who suggests that growth banding of As-poor pyrite followed by As-rich pyrite occurs after a specific level of fluid supersaturation in As has been reached.

Based purely on the petrographic data, it is difficult to pinpoint the mechanism resulting in the variable trace element composition of colloform pyrite and the base metal sulphide bands. Therefore, the interpretations of these textures are based on experimental data for the precipitation of the sulphide minerals; Seward (1973) and Helgeson (1969) show that Au is transported predominately as \( \text{AuCl}_2^- \) and \( \text{Au(HS)}_2^- \) complexes. In particular, \( \text{AuCl}_2^- \) is more stable in high temperature (>350°C) and slightly acidic hydrothermal fluids with precipitation triggered by a decrease in temperature. In lower temperature
environments (<300°C), Au(HS)₂⁻ is considered to be the most stable complex and Au precipitates by an increase in fO₂ or pH, possibly via mixing with the seawater. It is worth mentioning that Au precipitation by Au(HS)₂⁻ does not occur due to a temperature decrease, in contrast, a temperature decrease causes an increase of Au solubility in the fluid (Huston and Large, 1989). Additionally, Au(HS)₂⁻ is more soluble in the pyrite field, therefore, in very reduced (pyrrhotite) and very oxidizing (hematite and magnetite) fluid environments, Au must be transported by a different complex (Huston and Large, 1989).

According to Ohmoto (1996), the precipitation of sphalerite and chalcopyrite takes places based on the following reactions:

\[
\text{ZnCl}_2 + \text{H}_2\text{S} \, (\text{aq}) \rightarrow \text{ZnS} \, (s) + 2 \, \text{HCl} \quad (1)
\]
\[
\text{CuCl} + \text{FeCl}_2 + 2\text{H}_2\text{S} \, (\text{aq}) \rightarrow \text{CuFeS}_2 \, (S) + 3 \, \text{HCl} + \frac{1}{2} \, \text{H}_2 \, (\text{aq}) \quad (2)
\]

The deposition of sphalerite, galena and chalcopyrite is considered to occur from the transport of base-metal chloride complexes, since bisulphide complexes of Cu, Pb, Zn and Fe are weakly soluble under these temperatures (>250°C). Reactions 1 and 2 can be triggered by an increase of H₂S or Cl⁻, or by an increase in pH (Crerar, 1974). The composition of the mineral that will precipitate is dependent on the fluid chemistry. Under certain right conditions, a ZnCl₂ rich fluid can precipitate sphalerite, while a CuCl rich fluid would precipitate chalcopyrite. Both reactions (1 and 2) consume H₂S and produce HCl that cause a decrease in pH of the mineralising solution.

Colloform textures are considered to be formed in unrestricted open space close to hydrothermal conduits (Craig, 1990) and they are often used for the regional identification of a system’s vent complex (Parr, 1994). It is argued herein that the precipitation of colloform pyrite in the Caribou deposit transpired close to the main hydrothermal conduits or scattered pathways followed from the ascending and convective fluid. The proximity to
the hydrothermal conduits secures a relatively rapid channelised metal-rich fluid flow, instead of the slow fluid percolation through the massive mound. Also, these colloform pyrites have probably formed in a relatively shallow environment within the mounds to ensuring the Cl complexes from the main transport and deposition mechanism for the base metals. Additionally, colloform pyrites of Caribou deposit may not be associated with exhalative precipitation directly into seawater as this would have been recorded as a single stage continuous and uninterrupted growth of pyrite.

II) Zone Refining

As described in chapter 5, zone refining is the main process resulting in the geochemical and mineralogical zonation of the system. Through this process, sulphides precipitated syngenetically during the formation of the mounds are remobilised and re-precipitated as the mound grows outwards.

The only petrographic texture that may record the zone refining process in the deposit is the chalcopyrite disease in sphalerite (Fig. 6.6C). There are different mechanisms proposed for the formation of this texture such as co-precipitation, exsolution and replacement for temperatures between 200 - 400°C (Barton et al., 1987; Bortnikov et al., 1991) or solid-state diffusion within high temperature environments (Bente and Doering, 1993). Recent studies show that exsolution mechanism require the formation of wurtzite which has potential to host increased concentrations of Cu, however wurtzite is formed under a higher temperature environment that cannot be attained during the formation of a VMS deposit (Zierenberg et al., 1984; Maslennikov et al., 2013; Libbey and Williams-Jones, 2016). Secondary replacement of sphalerite by chalcopyrite is more likely the dominant mechanism for the formation of the chalcopyrite disease textures in the Caribou deposit.
Chalcopyrite disease is more likely associated with the replacement of the bedded sulphides from the chalcopyrite, following the reaction:

\[ 2 \text{CuCl}_0 + 2 \text{ZnS}_\text{(s)} + 2 \text{FeS}_\text{(s)} + 2 \text{H}^+ + \frac{1}{2} \text{O}_2 \text{(aq)} \rightarrow 2 \text{CuFeS}_2 \text{(s)} + 2 \text{ZnCl}^+ + \text{H}_2\text{O} \]

The late metamorphic event has played an important role in the segregation and coarsening of the chalcopyrite occurrences in sphalerite (Barton et al., 1987).

The zone refining stage in the evolution of the system is not constrained from the previous and the following paragenetic stages, instead zone refining and the remobilisation of sulphides may occur from the earliest stages of the hydrothermal mound development until the terminal waning stage of mound growth.

III) Waning stage

The waning stage of the system occurs when the fluid circulation declines and mound growth has slowed down. During this event, the system may incur less reducing conditions. At the beginning of this paragenetic stage, the coupled deposition of arsenopyrite and cassiterite takes place, while towards the end, when the system become considerably less reducing the formation of the magnetite facies may occur.

It is worth mentioning that occurrences of cassiterite have been documented in other deposits of the Bathurst Mining camp such as Brunswick No. 12, Brunswick No.6 and Heath Steele (Lea and Rancourt, 1958; Chen and Petruk, 1980; Petruk and Schnarr, 1981) whereas cassiterite is reported for the first time for the Caribou deposit. Arsenopyrite is present as a minor mineral in almost all deposits in the BMC.

The significance of cassiterite and arsenopyrite coupled precipitation is that this allows the extraction of Sn from the solution over a short cooling interval. This wall rock-independent oxygen-conserving redox reaction has been proposed by Heinrich and
Eadington (1986). Under this reaction, the precipitation of $\text{As}^{3+}$ from the $\text{H}_3\text{AsO}_3^0$ complex occurs consuming the available $\text{H}_2\text{S}^0$, while $\text{Sn}^{2+}$ is deposited as cassiterite from the $\text{SnCl}_2^0$ complex:

$$3 \text{SnCl}_2^0 + 2 \text{H}_3\text{AsO}_3^0 + 2 \text{FeCl}_2^0 + 2 \text{H}_2\text{S}^0 \rightarrow 3 \text{SnO}_2 + 2 \text{FeAsS} + 10 \text{Cl}^- + 10 \text{H}^+ (4)$$

Arsenopyrite and cassiterite are abundant in the upper section of the zoned massive sulphide pile, particularly in the Zn-Pb facies, and are found chemically zoned and enriched in Sb, with their exact chemical composition and variation to have not been determined due to the small size and the topography of the grains.

Interestingly, coarser arsenopyrites that formed on the boundaries with silicate minerals do not show any oscillatory growth in the BSE image (Fig. 6.8); whereas fine-grained arsenopyrite clusters that occur in sphalerite wispy bands are distinctly zoned (Fig. 6.2A). Such textural variations of minerals are often associated with different patterns of growth and deformation depending on the groundmass within which they are surrounded by (Cook et al., 1993).

Similar to fine-grained arsenopyrite, cassiterite grains of equally small grain size are also found to be zoned using SEM-CL imaging. These zones are more likely associated with trace element variation of one or more CL activator elements. The CL response of cassiterite also revealed the presence of a non-luminescent core (Fig. 6.11). The dark colour is attributed to elevated Fe concentration in cassiterite that tends to quench cassiterite luminescence (Farmer et al., 1991), and is often formed from the interaction with relatively oxidised fluids, where Fe occurs in the trivalent state and can be readily incorporated into cassiterite (Cheng et al., 2019). A seeding core exists in the majority - if not all - of the cassiterite grains, but only when the centre of the grains is exposed in cross-section, are the cores are visible.
Cassiterite nucleation around a seeding crystal is documented for Kidd Creek deposit (Hennigh and Hutchinson, 1999). In that case, the core of the grains is an early generation of sphalerite. The cores at Kidd Creek were initially precipitated as sphalerite and later pseudomorphically replaced by cassiterite. Based on the compositional data acquired on cassiterite from the Caribou deposit, there is no evidence that the primary seeding crystals were sphalerite grains. However, experimental data have shown that the presence of pre-existing grains favour nucleation, triggering the mineral deposition before the fluid reaches the critical supersaturation (i.e., pyrite, Murowchick and Barnes, 1987).

Niobium, Ta, Zr, Hf, Ti, W, U, Sc, V, Mn and Al are the activator elements proposed for cassiterite luminescence (Farmer et al., 1991 and reference therein; Lerouge et al., 2017; Wille et al., 2017), with the low-temperature systems found to favour Ti incorporation in cassiterite (Cheng, 2019). The activator elements in the samples could not be identified due to the lack of trace element data of cassiterite.

The paragenesis of cassiterite is not well understood for the Caribou deposit as well as other deposits in the Bathurst Mining Camp. A relatively elevated $fO_2$ during the formation of the ores could account for the presence of cassiterite rather than stannite (Petersen, 1986). The relatively less reducing (oxidising?) fluid conditions may also explain the depletion of base and transitional metals in cassiterite (Hennigh and Hutchinson, 1999), with the exception of Sb (approx. 2 wt. % Sb) that is consistently detected in all of the cassiterite grains. According to Cheng et al., (2019), low Sb is associated with high Fe and vice versa, thus, if our assumption for the Fe-rich core is correct, elevated Sb contents should derive from the late overgrowth of cassiterite and not the core.
Considering the limited abundance and grain size of cassiterite, there is no potential for its recovery as a separate concentrate. Since cassiterite is not expected to be liberated from its groundmass, it follows the course of the mineral that is interlocked with, in particular sphalerite and galena, reported in the Zn and Pb concentrate, respectively.

Magnetite is the most abundant oxide mineral occurring in the Caribou deposit. It is associated with the lower hydrothermal stratigraphic section of the system and is considered as part of the pre-metamorphic mineral sequence. Magnetite is found intergrown with sphalerite, a texture that would require the recrystallisation of sphalerite during regional metamorphism, whereas magnetite as a refractory mineral is cataclastically deformed. Such a texture is also documented by Makvandi et al., (2016) across the mineralised zone of the Halfmile Lake deposit and implies that magnetite is pre-metamorphic. Furthermore, the textural association of magnetite with pyrite indicates that magnetite formed during a late stage of hydrothermal evolution, prior to metamorphism, most likely involving less reducing fluids.

In the Halfmile Lake deposit, two generations of magnetite were identified (Makvandi et al., 2016). The primary magnetite (Mag1) is pre-metamorphic, while Mag2 is formed during low-grade metamorphism, exhibiting typically low trace element concentrations. The trace element chemistry of magnetite was not examined in the study. However, based on the textural evidence, only one generation of magnetite has been identified with pre-metamorphic characteristics. Additionally, magnetite of the Caribou deposit did not syn-genetically precipitate as this occurs under oxidizing hydrothermal conditions that would inhibit the precipitation of pyrite.
III) Metamorphism and Deformation

The most prominent feature within the ore body and specifically the Zn-Pb facies is the alternating layered bands of the main ore minerals (sphalerite and galena) that are formed during syngenetic deposition and subsequently overprinted during the regional metamorphic (greenschist facies) event and defferention. As the most readily recrystalised sulphide minerals, sphalerite, galena and chalcopyrite have maintained a record of only the post-metamorphic history of the deposit, healing tension gashes formed within more refractory minerals present in the system (i.e., pyrite, arsenopyrite and magnetite).

Tetrahedrite and other Ag-Sb sulfosalts are concentrated along the sphalerite and galena wispy bands. These sulfosalts show no genetic association with cassiterite although they are often accommodated in the same bands. Textural evidence shows that tetrahedrite has crystallised in equilibrium with galena and sphalerite. It is not clear in which stage of paragenetic sequence the deposition of tetrahedrite occurred. However, it has certainly co-crystalised with sphalerite and galena during the greenschist facies metamorphic overprint. Hence, tetrahedrite could either pre-exist metamorphism or precipitate from an exsolved phase of the metamorphic fluid.

Chalcopyrite is the principal carrier of Cu in the deposit and is more abundant in the Cu facies and the lower section of the Zn-Pb facies. For the most part, where chalcopyrite is more abundant, it occurs as large blebs, otherwise it forms tension gashes along refractory minerals. When it is exposed in high temperature deferential stress, chalcopyrite follows the intergranular slop deformation mechanism (Roscoe, 1975).

Metamorphic pyrite is predominant in massive sulphides of the Caribou deposit. It occurs as fine euhedral grains or is an overgrowth on earlier generations of pyrite. In particularly, the trace element chemistry of metamorphic rims (Py3) in Figures 6.3 and 6.5

136
shows Ni enrichment. Besides Ni, the suites of elements that are present in the metamorphic rims of the individual composite grains are not identical. The metamorphic rim of the first grain (Py3; Fig. 6.3) was found to be enriched in Co, while it was depleted in Au, As and Ag. In the second composite grain (Fig. 6.5), the rim was found to be enriched in Hg, As, Sb and Ag. Hence, from the two set of maps generated, it is concluded that the overall chemistry of metamorphic pyrite of the Caribou deposit is locally controlled by the availability of elements scavenged from pre-existing sulphide minerals. Notably, As is present in the metamorphic rim of both pyrite grains creating a great potential for incorporation of Au into pyrite, however only one of the grains (Py3; Fig 6.5) was found to have a Au-rich metamorphic rim.

The four paragenetic stages that were recognised through petrographic examination, are not successive. Beyond the regional metamorphism and deformation, the timing of the earlier paragenetic stages cannot be constrained, as temporal overlaps between different stages have likely occurred. For instance, during mound development (syngenetic phase of mineralisation; stage I), the zone refining processes had likely already started within the deeper sections of the mound. Textural evidence of the early stages of the paragenetic sequence (e.g., precipitation of the main ore minerals) had been overprinted by the successive stages, with framboidal and colloform pyrite to comprise the only textures preserved across the NLS of Caribou deposit.
CHAPTER 7
Mineral Chemistry

7.1 Introduction

The trace element budget of pyrite, sphalerite and chalcopyrite was determined across 11 representative sample of the Caribou ore. Seven of them were collected from the NLS, whereas the remaining three originate from eastern lenses and are part of Sean McClenaghan’s collection. In addition to the trace element mineral composition of the common ore minerals - that is vital for assessing the recovery potential of credit elements as byproducts - the LA-ICP-MS work revealed a large-scales vertical and lateral geochemical trends in the composition of these minerals. Similar to the geochemical zonation identified by the lithogeochemistry study, the trends associated with the mineral composition are likely driven from the same hydrothermal processes whereby the distance from the active feeder zone was the controlling factor which determined the chemistry of the precipitating sulphides. Consistent geochemical trends associated with the mineral composition are often used as proxies in mineral exploration.

7.2 Trace element distribution

Trace element distribution within the main ore minerals of the Caribou deposits was determined by LA-ICP-MS mapping and spot analysis. Since this technique cannot distinguish between nano-inclusion and lattice-bound hosted elements, the interpretation of mineral composition is based on experimental data from the literature. Description of the settings and data reduction protocol followed for the LA-ICP-MS experiments is included in chapter 4.2.2.3.
7.2.1 Qualitative intra-mineral trace element variations

Trace element distribution maps were generated in regions of interest across different grains and mineral phases. These “large scale maps” were produced as a mean to illustrate the relative trace elemental abundances among pyrite, sphalerite, galena, chalcopyrite, tetrahedrite and cassiterite. This visual representation is used to gain insight into trace element substitutions and highlight the major carriers of valuable and deleterious elements present in the deposits.

The relative trace element abundances between pyrite and arsenopyrite are of particular interest for the Caribou deposit, as there is controversy on which mineral is the principal Au carrier in the systems (McClenaghan et al., 2009; Wright et al., 2016). Due to their similar crystallographic structure, pyrite and arsenopyrite can incorporate a similar suite of trace elements. Nevertheless, in this deposit there are no evidence of co-precipitation of the two minerals, therefore their compositions are possible indicative of the fluid chemistry during their precipitation.

Figure 7.1 illustrates the distribution of selected elements across pyrite and arsenopyrite, with minor sphalerite, galena and chalcopyrite. The ablation conducted with horizontal lines along the x axis. The maps are displayed with 90° rotation to better fit the figure template, thus, the vertical smearing of the maps of Figure 7.1 is an artefact of the ablation.

As shown on the maps, pyrite is the Fe-dominant mineral (Fig. 7.1B) and arsenopyrite is the As-dominant mineral (Fig. 7.1C). There is As detected in pyrite, however this is concealed from the coarse scale of the map, likewise the Fe contents in arsenopyrite. Antimony (Fig. 7.1D) is incorporated in both minerals, however, arsenopyrite shows higher Sb contents.
As shown on the Au distribution map (Fig. 7.1E), arsenopyrite is relatively depleted in Au, whereas fine-grained anhedral masses of pyrite are the main Au-carriers. Notably, the four coarse euhedral grains, possibly annealed during the greenschist facies metamorphic overprint, are evidently poor in As. In the left side of the map, fine-grained masses of pyrite and arsenopyrite are intergrown and aggregate together. The individual grains of the two mineral phases cannot be resolved, hence the signal received from Au-rich pyrite is mixed with the signal acquired from the Au-depleted arsenopyrite giving the impression of an overall low Au abundance. The map of Ag show somewhat similar distribution pattern with Au, suggesting that the two elements have the same mineral host, namely pyrite. The highest Ag contents are attributed to galena.

Due to the absence of tetrahedrite from the sample, the Cu map (Fig. 7.1G) follows the chalcopyrite distribution. Figure 7.1H indicates that chalcopyrite is one of the mineral carriers of In, however, the In contents of sphalerite (Zn distribution map; Fig. 7.1I) are distantly higher. Substitution of In in sphalerite often take place as: $2\text{Zn}^{2+} \rightarrow \text{Cu}^{+}\text{In}^{3+}$ (Cook, 2009). This also explains the limited Cu association with sphalerite. Sphalerite is also Sn-poor (Fig. 7.1J) and Hg-rich (Fig. 7.1K). Low contents of Hg are also hosted by chalcopyrite. Few scattered Sn-rich pixels in Figure 7.1J is attributed to cassiterite as they correlate with elevated In contents. Although cassiterite is not identifiable from the BSE images, it is the only ore mineral of Sn found in the samples collected from the NLS.

Elevated Pb occurrence in Figure 7.1L are exclusively associated with galena - the Pb carrier in the mineralisation. Small blebs (5 μm) of galena occur in the fine arsenopyrite-pyrite aggregation on the left section of the mapped area that is characterised by low Pb abundance.
Figure 7.1.
Figure 7.1 (continued): BSE image (A) and semi-quantitative large-scale maps (B-L) illustrates the distribution and relative abundances of selected elements among the main sulphide minerals: pyrite (Py), arsenopyrite (Asp), sphalerite (Sp), galena (Gn) and chalcopyrite (Ccp); 15-FD-32-P1A, low-grade Zn-Pb facies. Antimony (D) resides in both pyrite (B) and arsenopyrite (C), whereas the highest contents are found in arsenopyrite. Gold is exclusively associated with early (no-annealed) pyrite generation (E). Silver (F) is also hosted by pre-metamorphic pyrite, but its highest contents are attributed to galena. Chalcopyrite (G) hosts a limited amount of In (H) and Hg (K). Elevated concentrations of In are predominately found in solid solution within sphalerite (I). Sphalerite is also Sn-depleted (J) and Hg-rich (K). Cassiterite (yellow and red dots in J) is somewhat associated with In. Scattered galena grains (L) are found throughout the mapped area.
High Pb contents (Fig. 7.2L) extends beyond the grain boundaries of galena. This artefact is linked to the excessive amount of Pb introduced to the system during the ablation of galena. A longer wash-out time is generally required for the Pb signal to drop down to background level counts. The same artefacts are found, to a lesser extent, on Cu and As distribution maps.

The second “large scale map” (Fig. 7.2) presented in this chapter is associated with a galena-pyrite wispy band. Besides the aforementioned minerals, sphalerite, tetrahedrite, cassiterite and silicate minerals were also intersected from the laser rasters (Fig. 7.2A). The silicate minerals are depleted in all elements analysed. Here, pyrite is the only mineral enriched in As (Figs. 7.2B-C), with As abundance varying across the map. Relative abundances between the different pyrite generations are difficult to assess from this low-resolution map, since the varying composition might be an effect of signal dilution when beam intersects two mineral phases of contrasting chemistry.

Gold is associated with arsenian pyrite. Antimony is also present in arsenian pyrite, but this is barely discernible on the map, concealed from the wt. % Sb contents of tetrahedrite. Tetrahedrite is characterised by elevated Ag contents, while Hg and Zn are also part of the mineral composition (Figs. 7.2D,F-I). Sphalerite host trace quantities of Cu and Hg (Figs. 7.2G-I), while In (Fig. 7.2J) perfectly follows sphalerite distribution. Figure 7.2H shows that Hg contents found in tetrahedrite are higher than in sphalerite, while Hg is also present in pyrite; similar observation was made by Dutrizac and Chen (1979). Nevertheless, sphalerite is considered the principal Hg-carrier in the systems owing to its relatively high Hg contents that hosts and its high abundance.

Rare cassiterite grains (Fig. 7.2l) are somewhat associated with elevated In contents (Fig. 7.2J). Detectable Fe contents in cassiterite supports the argument of the Fe-rich
Figure 7.2
Figure 7. 2 (continued): Reflected light image (A) and semi-quantitative large-scale maps (B-L) illustrates the distribution and relative abundances of selected elements among pyrite (Py), galena (Gn), sphalerite (Sp), tetrahedrite (Tet) and cassiterite (Cst); 15-FD-32-P1A, low-grade Zn-Pb facies. The arsenian pyrite is the exclusive host of Au (B-D). The similar distribution of Sb (D), Ag (F), Cu (G) and Hg (H) shows that these elements are associated with tetrahedrite. Sphalerite is a carrier of In, Cu and Hg (G-J), while In is somewhat associated with the few cassiterite grains (L). Galena (K) is carrier of Sb and Ag.
chemistry of the low luminescent core of cassiterite (see chapter 6.2.7). Galena that covers the two third of the map has invariable composition in the analysed elements showing elevated Sb and Ag contents.

7.2.2 Quantitative trace element variation

Trace element compositions of pyrite, sphalerite and chalcopyrite were quantitatively determined by spot analysis. Inclusion-free single mineral phases were selected for the analyses. Nevertheless, mineral inclusions lying beneath the surface of the target grains were inevitably ablated. While micro-inclusions can be easily identified in the ablation profile by their spiky appearance, nano-inclusions are not detectable and appear the same way as the lattice bound elements. Small micro-inclusions integrated in the measured spots are not excluded from the dataset, since their liberation during the ore processing is unlikely and the presence of these inclusions needs to be acknowledged for the benefit of the ore processing design. When large inclusions are ablated together with the target mineral, the corresponding spot data are entirely discarded. The rejection of these analyses is applied as the total CPS of the major element that is used as internal element standard is significantly reduced during the ablation of the larger inclusions, a fact that leads to an erroneous calculation of the trace element contents for the specific spot analyses. The data reduction protocol followed can be found in chapter 4.2.2.3.3.

To minimise bias, 50 to 55 regularly spaced spot were acquired following a linear traverse across the length of the thin section. These traverses are always in angle or perpendicular to pseudo-bedding when present. Two mineral phases were analysed per sample depending on the sulphide facies they derived from (pyrite and sphalerite, or pyrite and chalcopyrite). For each thin section, the two traverses were placed further apart from
each other to avoid resampling of the ablated material re-deposited over the earlier experiment. With respect to the spot analyses on pyrite, multiple spots were ablated on the composite grains - including core and rim of the grains - aiming to obtain representative analyses from the entire compositional range of the mineral.

7.2.2.1 Vertical zonation

The trace element compositions of pyrite, sphalerite and chalcopyrite (Table 7.1-7.2) were determined in an effort to delineate vertical geochemical trends within the sulphide mineral chemistry of the deposit. The samples derive from the Zn-Pb (15-FD-29-17A and 15-FD-30-P7C) and the Cu facies (15-FD-30-P20B and 15-FD-30-P31B). Sphalerite and galena abundancies decrease dramatically towards the stratigraphic footwall of the deposit; hence sphalerite analyses were carried out only on samples from the Zn-Pb facies. Likewise, chalcopyrite composition was measured exclusively on samples from the Cu facies.

A total of 150 pyrite measurements (out of 200 spots analysed; 50 spots per thin section) retained in the final dataset and are presented in the Table 7.1 and Figure 7.3. The analyte list of the pyrite analysis includes \(^{34}\text{S}, \(^{59}\text{Co}, \(^{60}\text{Ni}, \(^{63}\text{Cu}, \(^{66}\text{Zn}, \(^{75}\text{As}, \(^{107}\text{Ag}, \(^{112}\text{Cd}, \(^{121}\text{Sb}, \(^{124}\text{Sn}, \(^{197}\text{Au}, \(^{199}\text{Hg}, \(^{208}\text{Pb}\) and \(^{209}\text{Bi}. Most measurements returned values below detection limit for Ni and Cd. Distinct trace element signatures are identified in the chemistry of pyrite between the two dominant sulphide facies.

Elevated Zn, As, Sb, Au and Pb contents characterise the composition of pyrite from the Zn-Pb facies. Zn contents are influenced by the number of inclusions incorporated into the ablated profiles. Although sphalerite is overall more abundant in the high-grade Zn-Pb facies, pyrite from the medium-grade Zn-Pb facies host more sphalerite inclusions.
<table>
<thead>
<tr>
<th>Samples</th>
<th>Sulphide Facies</th>
<th>Co</th>
<th>Cu</th>
<th>Zn</th>
<th>As</th>
<th>Ag</th>
<th>Sb</th>
<th>Sn</th>
<th>Au</th>
<th>Pb</th>
<th>Bi</th>
</tr>
</thead>
<tbody>
<tr>
<td>15-FD-30-P7C</td>
<td>Medium Grade Zn-Pb facies</td>
<td>M</td>
<td>8</td>
<td>288.3</td>
<td>2,033</td>
<td>5,927</td>
<td>7.3</td>
<td>196</td>
<td>4.8</td>
<td>0.866</td>
<td>3,156</td>
</tr>
<tr>
<td>LOD</td>
<td>0.1</td>
<td>1.1</td>
<td>9</td>
<td>5</td>
<td>0.0</td>
<td>0.1</td>
<td>0.9</td>
<td>0.013</td>
<td>0.1</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>15-FD-29-17A</td>
<td>High Grade Zn-Pb facies</td>
<td>M</td>
<td>44</td>
<td>382.8</td>
<td>1,075</td>
<td>2,107</td>
<td>13.1</td>
<td>241</td>
<td>9.0</td>
<td>0.675</td>
<td>1,704</td>
</tr>
<tr>
<td>LOD</td>
<td>0.1</td>
<td>1.3</td>
<td>10</td>
<td>3</td>
<td>0.1</td>
<td>0.2</td>
<td>0.9</td>
<td>0.015</td>
<td>0.1</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>15-FD-30-P20B</td>
<td>Cu facies</td>
<td>M</td>
<td>819</td>
<td>362.4</td>
<td>25</td>
<td>292</td>
<td>1.9</td>
<td>93</td>
<td>1.4</td>
<td>0.173</td>
<td>46</td>
</tr>
<tr>
<td>LOD</td>
<td>0.2</td>
<td>1.1</td>
<td>10</td>
<td>4</td>
<td>0.1</td>
<td>0.1</td>
<td>0.9</td>
<td>0.017</td>
<td>0.1</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>15-FD-30-P31C</td>
<td>Cu facies</td>
<td>M</td>
<td>473</td>
<td>570.6</td>
<td>34</td>
<td>111</td>
<td>4.1</td>
<td>18</td>
<td>1.9</td>
<td>0.100</td>
<td>232</td>
</tr>
<tr>
<td>LOD</td>
<td>0.2</td>
<td>1.3</td>
<td>10</td>
<td>3</td>
<td>0.1</td>
<td>0.1</td>
<td>1.0</td>
<td>0.015</td>
<td>0.1</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>62-123-138</td>
<td>High Grade Zn-Pb facies</td>
<td>M</td>
<td>18</td>
<td>690.5</td>
<td>886</td>
<td>2,154</td>
<td>30.4</td>
<td>616</td>
<td>25.2</td>
<td>0.840</td>
<td>2,319</td>
</tr>
<tr>
<td>LOD</td>
<td>0.2</td>
<td>0.9</td>
<td>23</td>
<td>5</td>
<td>0.1</td>
<td>0.1</td>
<td>1.4</td>
<td>0.023</td>
<td>0.2</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>62-81-262</td>
<td>High Grade Zn-Pb facies</td>
<td>M</td>
<td>2.5</td>
<td>581.1</td>
<td>439</td>
<td>1,907</td>
<td>36.4</td>
<td>430</td>
<td>12.9</td>
<td>1.205</td>
<td>3,128</td>
</tr>
<tr>
<td>LOD</td>
<td>0.1</td>
<td>0.6</td>
<td>2</td>
<td>4</td>
<td>0.2</td>
<td>0.2</td>
<td>1.3</td>
<td>0.028</td>
<td>4.1</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>62-42-1476</td>
<td>High Grade Zn-Pb facies</td>
<td>M</td>
<td>46</td>
<td>824.6</td>
<td>816</td>
<td>3,321</td>
<td>8.3</td>
<td>194</td>
<td>24.1</td>
<td>0.166</td>
<td>2,962</td>
</tr>
<tr>
<td>LOD</td>
<td>0.2</td>
<td>0.9</td>
<td>2</td>
<td>5</td>
<td>0.1</td>
<td>0.1</td>
<td>1.3</td>
<td>0.027</td>
<td>0.2</td>
<td>0.02</td>
<td></td>
</tr>
</tbody>
</table>

**Table 7.1**: Summary table of the trace element composition of pyrite acquired by LA-ICP-MS. The mean (M) and the detection limit (LOD) in ppm is presented individually for each sample. The pyrite composition of the first four samples is discussed in this section (7.2.2.1), while the remaining three samples are part of the lateral zonation found in chapter 7.2.2.2.
<table>
<thead>
<tr>
<th></th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Cu</th>
<th>Zn</th>
<th>Se</th>
<th>Ga</th>
<th>Ge</th>
<th>Ag</th>
<th>Cd</th>
<th>In</th>
<th>Sb</th>
<th>Sn</th>
<th>Hg</th>
<th>Tl</th>
<th>Pb</th>
<th>Bi</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sphalerite</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15-FD-30-P7C</td>
<td>M</td>
<td>110</td>
<td>44,684</td>
<td>-</td>
<td>317.40</td>
<td>-</td>
<td>-</td>
<td>1.04</td>
<td>0.35</td>
<td>26.5</td>
<td>998</td>
<td>30</td>
<td>49</td>
<td>33.5</td>
<td>30.7</td>
<td>0.24</td>
<td>1,380</td>
</tr>
<tr>
<td>LOD</td>
<td>6</td>
<td>35</td>
<td>1.47</td>
<td>0.07</td>
<td>0.30</td>
<td>0.1</td>
<td>1</td>
<td>0.05</td>
<td>0.1</td>
<td>0.6</td>
<td>0.8</td>
<td>0.4</td>
<td>0.1</td>
<td>0.04</td>
<td>0.1</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>15-FD-29-17A</td>
<td>M</td>
<td>58</td>
<td>57,911</td>
<td>-</td>
<td>723.64</td>
<td>-</td>
<td>-</td>
<td>1.17</td>
<td>3.85</td>
<td>18.4</td>
<td>1,569</td>
<td>124</td>
<td>28</td>
<td>703.7</td>
<td>49.8</td>
<td>0.22</td>
<td>24</td>
</tr>
<tr>
<td>LOD</td>
<td>7</td>
<td>35</td>
<td>1.31</td>
<td>0.08</td>
<td>0.44</td>
<td>0.1</td>
<td>1</td>
<td>0.07</td>
<td>0.1</td>
<td>0.6</td>
<td>1.0</td>
<td>0.4</td>
<td>0.1</td>
<td>0.04</td>
<td>0.1</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td><strong>Chalcopyrite</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15-FD-30-P20B</td>
<td>M</td>
<td>-</td>
<td>-</td>
<td>109</td>
<td>-</td>
<td>189</td>
<td>85</td>
<td>-</td>
<td>-</td>
<td>4.1</td>
<td>5.6</td>
<td>26</td>
<td>28</td>
<td>34.7</td>
<td>6.5</td>
<td>-</td>
<td>34</td>
</tr>
<tr>
<td>LOD</td>
<td>0.6</td>
<td>39</td>
<td>10</td>
<td>0.3</td>
<td>4.2</td>
<td>0.08</td>
<td>1.1</td>
<td>3.4</td>
<td>2.9</td>
<td>0.4</td>
<td>0.13</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15-FD-30-P31C</td>
<td>M</td>
<td>-</td>
<td>-</td>
<td>29</td>
<td>-</td>
<td>293</td>
<td>61</td>
<td>-</td>
<td>-</td>
<td>64.6</td>
<td>8.6</td>
<td>75</td>
<td>30</td>
<td>85.8</td>
<td>9.6</td>
<td>-</td>
<td>25</td>
</tr>
<tr>
<td>LOD</td>
<td>0.8</td>
<td>44</td>
<td>11</td>
<td>0.3</td>
<td>4.2</td>
<td>0.12</td>
<td>1.2</td>
<td>3.9</td>
<td>3.2</td>
<td>0.5</td>
<td>0.16</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 7.2:** Summary table shows the trace element composition of sphalerite and chalcopyrite from the NLS of Caribou deposit. Mean (M) and LOD are presented in ppm.
Within the Zn-Pb facies, elevated Pb and Ag contents are attributed to galena inclusions. Galena is also a common host of Bi. However, the elevated Ag and Bi contents measured in the high-grade Zn-Pb facies pyrite are associated with inclusions of Ag-Bi sulphosalts. Marginally higher Sn contents describe the pyrite form the Zn-Pb facies. In the NLS, Sn is associated with cassiterite, however during the thorough examination on the individual spot profiles of the spot analyses, none of the analyses found to intersect cassiterite inclusions, thus sphalerite inclusions possibly account for the Sn contents.

The pyrite from the Cu facies is relatively depleted in most of the analysed elements primarily due to the lack of sphalerite and galena inclusions and their associated trace element budget. Elevated contents of Cu are ascribed to small chalcopyrite inclusions. Cobalt, which is typically lattice-bound in pyrite, exhibits one to two orders of magnitude higher concentration in pyrite from Cu facies compared to Zn-Pb facies (Table 7.1).

Gold, As and Sb also substitute within the pyrite lattice of the NLS following a contracting distribution to Co. Pyrite of the Cu facies is characterised by the lowest Au, As and Sb contents, while they are measured in elevated contents towards the stratigraphic hanging wall (Zn-Pb facies). The contracting geochemical trends in the pyrite chemistry is consistent for the four samples that were analysed.

A total of 110 spots (55 per sample) were analysed on sphalerite from the Zn-Pb facies (Table 7.2; Fig. 7.4). After the data processing, 91 spots were maintained in the data set. Sphalerite was analysed for $^{34}$S, $^{55}$Mn, $^{57}$Fe, $^{59}$Co, $^{60}$Ni, $^{63}$Cu, $^{66}$Zn, $^{69}$Ga, $^{73}$Ge, $^{75}$As, $^{107}$Ag, $^{112}$Cd, $^{115}$In, $^{121}$Sb, $^{124}$Sn, $^{197}$Au, $^{199}$Hg, $^{205}$Tl, $^{208}$Pb and $^{209}$Bi; Co, Ni, As and Au contents were mostly below detection limit.

Cadmium, In, Sn and Hg contents of sphalerite shows a distinct distribution; the sphalerite from the high-grade zone shows high content in these elements. Silver, Sb and
Figure 7.3: Box plots illustrating the trace element chemistry of pyrite within the Zn-Pb (15-FD-30-P7C, 15-FD-29-P17A) and Cu facies (15-FD-30-P20B, 15-FD-30-P31C) of the NLS of Caribou deposit
Figure 7.4: Box plots illustrating the trace element chemistry of sphalerite within the Zn-Pb facies (15-FD-30-P7C, 15-FD-29-P17A) of the NLS of Caribou deposit.
Figure 7.5: Box plots illustrating the trace element chemistry of chalcopyrite within the Cu facies (15-FD-30-P20B, 15-FD-30-P31C) of the NLS of Caribou deposit.
Figure 7.6: Binary plots of the trace element contents of sphalerite (15-FD-30-P7C, 15-FD-29-P17A) and chalcopyrite (15-FD-30-P20B, 15-FD-30-P31C) from the NLS of Caribou deposit.
Tl occurs is similar content in both samples (Table 7.2; Fig.7.4) and exhibit positive correlation (Figs 7.6A,B), implying a common mechanism controlling the distribution of the three elements within sphalerite. Silver and Sb covariation has been explained by Cook et al., (2009) as nano-scale inclusions of Ag-Sb-bearing minerals and as coupled substitution for Zn in sphalerite lattice. According to the same study Cu and In are also incorporation into sphalerite via coupled substitution for Zn.

Frenzel et al., (2016) argues that the most prominent effect of metamorphic recrystallisation of sphalerite is the decrease in Ga and Ge contents that are subsequently incorporated into other sulphide minerals such as chalcopyrite. However, in Caribou deposit, chalcopyrite is equally depleted in both Ga and Ge, indicating that the low contents reflect the chemistry of the mineralising fluid.

Chalcopyrite chemistry was determined based on 66 spot analyses (out of 105 spots acquired). The two samples analysed part of the same drill hole. Chalcopyrite was analysed for $^{34}$S, $^{57}$Fe, $^{59}$Co, $^{60}$Ni, $^{63}$Cu, $^{66}$Zn, $^{69}$Ga, $^{73}$Ge, $^{77}$Se, $^{95}$Mo, $^{107}$Ag, $^{112}$Cd, $^{115}$In, $^{121}$Sb, $^{124}$Sn, $^{125}$Te, $^{197}$Au, $^{199}$Hg, $^{205}$Tl, $^{208}$Pb and $^{209}$Bi. Nickel, Ga, Ge, Mo, Te, Au and Tl contents of are below detection limit.

The thin section 15-FD-30-P20B, derives from stratigraphically higher section of the drill hole and is characterised by a low overall bulk-rock Cu content (0.49 wt. % Cu). This is noticeable also macroscopically as chalcopyrite of this sample appears disseminated and more fine-grained compared to the second sample. From a total of 50 chalcopyrite spots on this sample only 19 of them were included in the dataset (Table 7.2; Fig 7.5) due to the presence of multiple inclusions that effected the morphology of the ablated profile.
The second sample (15-FD-30-P31C) is proximal to the feeder zone of the system and corresponds to a bulk-rock composition of 3.06 wt. % Cu. Forty-six out of 55 spot analyses were maintained in the dataset with results presented in Table 7.2 and Figure 7.5.

For the most part, the trace element composition of chalcopyrite does not exhibit a distinct variability. Nevertheless, chalcopyrite from the stratigraphic lower section is relatively enriched in Zn, Ag, Cd, In, Sn, Hg contents and depleted in Co, Se, Pb and Bi. Overall, Pb, Sb and Bi contents of chalcopyrite co-vary for both samples. In addition, as shown in Figure 7.6C,D, Cd, In and Sn concentrations of chalcopyrite also positively correlates, implying the substitution of these element in solid solution within chalcopyrite. Few high Sn and In outliers are attributed to sphalerite inclusions incorporated in chalcopyrite.

Intuitively, the reader may suspect that the chemical composition of chalcopyrite represents the chemistry of the fluid or the later zone-refining process of the hydrothermal system. However, the chemistry of chalcopyrite rarely maintains primary chemical signatures, as it is prone to recrystallisation. The chemistry of the recrystallising chalcopyrite is dependent on sphalerite and galena when present, as it incorporates the trace element budget not taken by the co-recrystallising sulphides (George et al., 2016). To that extent, chalcopyrite from the stratigraphically higher Cu facies is expected to contain significant proportion of the available trace element budget on the grounds that sphalerite and galena are absent from the sample (whole-rock composition: 0.06 wt.% Zn and 0.04 wt.% Pb). This readily explains the depletion of 15-FD-30-P31C in Co, Se, and Bi, since chalcopyrite co-crystallised with sphalerite and galena that preferentially incorporate these elements in their chemistry. However, this rule does not rule the partitioning of Sn into chalcopyrite. Tin is typically incorporated into chalcopyrite even in presence of sphalerite (George et al., 2018).
7.2.2.2 Lateral zonation

Pyrite composition was measured on three shallow drill core samples from the Zn-Pb facies across the Caribou synform extending beyond the NLS. This work aims to illustrate the lateral variation of the system between the proximal and the distal facies of the system.

Jambor (1979) used the term proximal facies to describe samples derived from the stringer zone, while the banded Zn-Pb-rich ore is characterised as distal. In this study, these terms are used differently without referring to a specific sulphide facies, but describing the horizontal distance from the principal stringer zone that is located at the west of the deposit below the lenses 2 and 3.

All three thin sections analysed derive from high-grade Zn-Pb facies with similar bulk-rock geochemical signatures. The samples are distributed from the northwest to the east as follow:

a) 62-123-138 (9.2 wt.% Zn, 2.96 wt.% Pb, 0.4 wt.% Cu and 106 g/tn Ag),

b) 62-81-262 (11.6 wt.% Zn, 7 wt.% Pb, 0.26 wt.% Cu and 220 g/tn Ag) and

c) 62-42-1476 (11.52 wt.% Zn, 5.6 wt.% Pb and 90 g/tn Ag).

The location of the samples is indicated in Figure 3.2.

Overall, the trace element signatures of pyrite within the three samples are similar to that measured in the two samples from the Zn-Pb facies of the NLS and described previously (chapter 7.2.2.1). The pyrite chemistry of the sample 62-81-262 found relatively depleted in Co, Zn, Sn and Bi. While Sn and Zn contents covaries implying the present of sphalerite inclusions within pyrite, their association with Cu and Bi is not clear.

Silver abundance follows a district trend (Fig 7.7). In particularly, pyrite composition from the two more proximal samples is characterised by similar Ag contents, while
Figure 7.7: Box plots illustrating the trace element chemistry of pyrite on the Zn-Pb facies across the synform of Caribou orebody. Samples presented from the left to the right as from the northwest to the east (62-123-138, 62-81-262, 62-42-1476).
the easternmost sample shows significantly lower Ag contents. This is consistent with the lower Ag concentrations of the corresponding bulk-rock sample. The same trend is identified for Au, suggesting Ag and Au substitute in the same mineral.

Besides As and Sb, there is no consistent tendency on how the chemistry of pyrite varies in relation to the distance from the feeder zone. Arsenic concentration increases moving to the east (away from the central feeder zone) while the reverse trend was identified for Sb. Similar increase in As contents on pyrite are identified in the samples from the NLS while, however the Sb distribution does not share a common trend with the pyrite within the NLS.

The individual trends identified across the three samples are relatively weak and beyond As, they don’t show a consistent trend. The small data set generated due to the limited number of available samples is a factor contributing to the uncertainty for the result interpretation. Additionally, the numerous inclusions present in the ablated profiles has possibly concealed chemical trends to some extent. Lastly, the hydrothermal systems formed the deposit might include several feeder zones that have influence the chemistry of pyrite in a more complex way that cannot be resolved due to the small number of samples.

7.3 Discussion

During the course of syngenetic precipitation, mineral composition is controlled by a number of factors that primarily concern the physicochemical conditions of the ore-forming fluid. However, only a limited number of ore minerals eventually preserve tex-
tures and chemistry of their original precipitation since later metamorphic or hydrothermal events resulting in recrystallisation of the minerals have the potential to extensively modify their composition.

Pyrite is one of the sulphide minerals that is most likely to preserve primary geochemical signatures during recrystallisation. On the contrary, sphalerite, galena and chalcopyrite can readily recrystalise and re-equilibrate under the new conditions of the metamorphic or hydrothermal fluid (Cook et al. 1993; Craig and Vaughan, 1994). In the Caribou deposit, sphalerite, chalcopyrite and galena have extensively recrystalised during zone refining processes and late overprinting greenschist facies metamorphism. Hence, the chemistry of these minerals provides limited information on variations in ore-forming fluid conditions, since their chemistry has been strongly modified during recrystallisation.

This study presents the trace element deportment of the sulphide mineralogy. Firstly, the relative element abundances were identified from large scale LA-ICP-MS maps using a qualitative approach. These elemental maps display the major mineral carriers of the deleterious, precious and energy critical elements for Zn-Pb mineralisation.

This study found that Au resides principally within pyrite. This is an important finding since there is some controversy on which is the principal Au carrier for the Caribou deposit (McClenaghan et al., 2009; Wright et al., 2016). The map of Au shows clearly that Au is not associated with the arsenopyrite and it is rather hosted by pyrite. Due to the low map resolution, the different generations of pyrite cannot be distinguished with certainty, aside from the late metamorphic pyrite that forms euhedral grains. Therefore, it is simply stated that the Au-bearing pyrite is pre-metamorphic.

Moreover, this work confirmed the coupled Au-Ag association within pyrite. Nevertheless, pyrite is characterised by overall low Ag contents, while galena is the principal
Ag carrier for the deposit. Antimony is incorporated in several mineral phases of the deposit. Tetrahedrite exhibits the highest Sb contents found at mineral stoichiometric levels. Comparing the relative abundances from the LA-ICP-MS maps, the mineral carriers of Sb are listed below in order of decreasing Sb budget:

- tetrahedrite > arsenopyrite > galena > pyrite > sphalerite.

Indium is hosted primarily in sphalerite, while cassiterite and chalcopyrite carry only limited In. Sphalerite also contained elevated concentration of Hg and Cu. Although tetrahedrite host the highest concentrations of Hg in the system, sphalerite is considered the principal mineral carrier of Hg in the system due to its high abundance.

Pyrite shows variable trace element composition. In particular, pyrite of the Zn-Pb facies is characterised by elevated Zn, As, Sb, Au and Pb contents. Micro-inclusions of sphalerite, galena and Ag-Bi sulphosalts are associated with the majority of the elevated contents. However, elevated contents of Au, As and to less extent Sb are associated with solid solution substitution in pyrite.

In the Caribou deposit, Co, Au and As contents in pyrite can be used as proxy to the feeder zone regarding the vertical zonation/stratigraphy of the system. In particularly, Co contents in pyrite composition increases towards the footwall of the system, while Au and As increases towards the hanging wall.

Apart from As, no other trace element was found to exhibit a distinct chemical trend in pyrite chemistry along strike from the feeder zone (lateral zonation). This is more likely associated with the fact that the three analysed samples derived from the Zn-Pb facies of the system shows a negligible variation in the pyrite chemistry possibly because they are part of the same facies within the hydrothermal system. Moreover, several feeder zones may exist in the system generating multiple pathways of the upwellin...
result in a more complex hydrothermal system. From the suite of elements that were proposed as a vertical proxy to the feeder zone, only As seems to follow an identical vertical and lateral trend, showing notable decrease towards the feeder zone.

Sphalerite is the principal carrier of In and contains elevated contents of Hg and Cu. The trace element chemistry of the samples from the Zn-Pb facies show two contrasting signatures in terms of Cd, In, Sn and Hg contents, with the high-grade facies sphalerite significantly depleted in these elements. Cadmium and In are elements that preferentially partition into sphalerite, with this variation to be attributed to the available trace element budget and the physicochemical conditions during the precipitation and recrystallization of sphalerite. Tin tends to incorporate into the chalcopyrite lattice when sphalerite and chalcopyrite co-crystalise (George et al., 2016). Therefore, Sn deportment of sphalerite is elevated in the absence of chalcopyrite. The high concentration of Hg within the medium-grade Zn-Pb facies sphalerite is more likely linked to micro-inclusions of tetrahedrite rather than Hg within sphalerite structure.

The quantitative trace element chemistry of galena was not studied in this project. However, based on the large area mapping, it is concluded that galena accommodates detectable trace element concentrations of Ag and Sb. Jambor (1979) argues that Ag, Sb and Bi contents of galena vary within the mineralisation, decreasing from the West (NLS) to East lenses.

It is worth noting that the anomalously high Ag concentrations in the bulk-rock geochemistry samples are believed to be associated with galena, but are not directly ascribed to this mineral. Galena segregation bands are a great carrier of argentiferous tetrahedrite that contain about ca. 10 wt. % Ag, whereas galena only hosts trace quantities of Ag. When
both minerals are present and co-crystallise, the largest amount of Ag is preferentially partitioned into tetrahedrite lattice \cite{George et al., 2017}. On the contrary, under the same conditions Bi partitioning into galena is preferred; tetrahedrite can be an important host of Bi only when it precipitates in absence of galena and chalcopyrite.

Overall, chalcopyrite exhibits limited chemical variation. Chalcopyrite forms within the lower stratigraphic section, as exhibited in downhole geochemical profiles, it is relatively enriched in Zn, Ag, Cd, In, Sn, Hg contents and depleted in Co, Se, Pb and Bi. This variation is associated with micro-inclusions or the presence other base metal mineral carrier during the recrystallisation of chalcopyrite. Most of the trace elements incorporated into chalcopyrite- such as Co, Se and Bi - prefer to enter the structure of other mineral phases rather than chalcopyrite. However, when chalcopyrite recrystalises in absence of sphalerite and galena, these elements are bound to the structure of chalcopyrite \cite{George et al., 2016}. An exception to this is Sn, which prefers chalcopyrite to sphalerite \cite{George et al., 2018}. Thus, the rich trace element budget of the stratigraphically higher Cu facies is attributed to the absence of sphalerite and galena, whilst, elements enriched in the chalcopyrite of the stratigraphically lower Cu facies are largely micro inclusions.

Similar to the trace element chemistry of sphalerite, chalcopyrite has not preserved primary chemical signature since it is significantly influenced by metamorphic and chemical variations are localised depending on the trace element contents of the surrounding sulphide minerals. Thus, the chemical signatures of sphalerite and chalcopyrite are localised and are not likely associated with broader trends at the deposit scale.
CHAPTER 8

Conclusion

The Caribou deposit and particularly the NLS is a highly zoned system consisting of three distinct sulphide facies. Its stratigraphic top is characterised by a Zn-Pb facies that has the most economic interest. In the base of the stratigraphic column, the Cu facies represents the feeder zone of the system. A pyrite facies and magnetite zone rarely occur in the system but when present they are found between the Zn-Pb and the Cu facies.

The geochemical correlations identified through the bulk-rock lithogeochemistry study are associated with the trace element substitution and co-existence of sulphide minerals. These groups are: A) Zn-Pb-Cd-Sn-As-Hg-Sb-Tl-Mo-Au-Ag and B) Cu-Co-Se. These two element groups, in effect, represent the chemical signatures within Zn-Pb and the Cu facies, respectively.

The genesis and evolution of Caribou deposit can be described by the following four paragenetic stages: I) Syngenetic precipitation, II) Zone refining, III) Waning stage and IV) Regional metamorphism and deformation. During syngenetic precipitation, deposition of early generations of pyrite (framboidal and colloform) takes place as well as the deposition of early sphalerite, galena and chalcopyrite. The zone refining process is initiated immediately upon hydrothermal mound development. Throughout this process, early precipitated sulphides within the base of the mound are dissolved, and metals remobilised, migrating towards the top of the mound (seawater interface). This process is characterised by a strong temperature gradient and resulted in the deposit scale geochemical and mineralogical zonation observed. The only textural evidence that may be associated with this second paragenetic stage is the chalcopyrite disease of sphalerite. The waning stage commenced late in the development of the mound. During this stage, there
is a gradual introduction of less reducing fluids that triggers the coupled deposition of arsenopyrite and cassiterite. At a later stage, when the $fO_2$ of the fluid decreases further, the precipitation of magnetite occurs. Lastly, metamorphism and deformation overprinted primary textures and modified mineral compositions in ductile phases. The most prominent features of the Caribou ore such as the sphalerite and galena segregation bands are formed during this process. Together with sphalerite and galena, chalcopyrite and tetrahedrite have been extensively recrystallised. During this process, early pyrite generations may behave cataclastically and form a substrate for further metamorphic pyrite growth accompanied by discrete metamorphic pyrite growths.

Pyrite, sphalerite, and chalcopyrite trace element mineral chemistry was determined as part of this study. This work supports the use of As, Au, Sb and Co signatures for systematic variations in pyrite composition. Arsenic contents in pyrite show a gradually increase with distance from the feeder zone both vertically and laterally zone. However, the trends based on Au, Sb and Co are not valid to indicate the vertical and lateral distance from the central feeder zone.

Sphalerite, galena and chalcopyrite are significant carriers of several trace elements found in the system. In particularly, sphalerite exhibits elevated concentrations of Cu, Cd, In, Sb, Hg and Pb of varying concentrations depending on the ore grade of the facies. Chalcopyrite contains Co, Se, Ag, Sn, Pb with its trace element concentrations depending significantly on the presence of other base metal sulphides.
CHAPTER 9

References


https://doi.org/10.1016/j.gca.2009.05.045

https://doi.org/10.1180/minmag.1993.057.386.07

https://doi.org/10.1016/0012-821X(78)90070-5


https://doi.org/10.2475/ajs.267.7.729


Deposits. Rare Earth and Critical Elements in Ore Deposits.
https://doi.org/10.5382/REV.18.07


https://doi.org/10.2113/gsecongeo.72.4.549


https://doi.org/10.1127/ejm/2017/0029-2673

https://doi.org/10.1016/j.jvolgeores.2015.12.011

Makvandi, S., Ghasemzadeh-Barvarz, M., Beaudoin, G., Grunsky, E. C., Beth Mcclenaghan, M., & Duchesne, C. (2016). Principal component analysis of magnetite composition from volcanogenic massive sulfide deposits: Case studies from the Izok Lake (Nunavut, Canada) and Halfmile Lake (New Brunswick, Canada) deposits. Ore Geology Reviews, 72(P1), 60–85.

172


https://doi.org/10.3102/10769986014003245


