The trace element chemistry of arsenopyrite and its potential use as an indicator mineral for gold deposit exploration in Australia

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This thesis is presented for the degree of Doctor of Philosophy of the University of Western Australia.

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I declare that this thesis is an account of my own research and contains work that has not previously been submitted for a degree at any other educational institution.

Matthew Edmund Murphy
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Hofstadter’s Law: It always takes longer than you expect, even when you take into account Hofstadter’s Law

-Douglas Hofstadter
ABSTRACT

Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) has been used to determine the relative abundance of specific trace elements in 626 arsenopyrite samples from a selection of 79 different national and international gold and non-gold mineral deposits. From the investigation of these samples it was possible to determine inter-relationships between the relative abundance of specific elements in the arsenopyrite crystal and the geological environment associated with the formation of these crystals. On the basis of these relationships it was possible to determine relationships between the style of mineralization, associated host rocks, distance from significant gold mineralization, and the endowment of the mineralizing system. In addition to using trace element inter-relationships to determine these aspects of the mineralized system, an investigation was also undertaken to establish if the distribution of mercury compounds (HgS, HgCl₂, HgO, and HgSO₄) and the mercury isotope distribution patterns for these compounds can give an indication of the distance from an orebody within the depositional environment.

It was determined that the concentration of iron within the arsenopyrite crystal lattice was essentially consistent. In addition, the relative sensitivities of analyte isotopes were influenced (usually as a result of ICP-MS operating conditions and laser ablation conditions) to the same degree as iron. Therefore, it was possible to use the Counts Per Second (CPS) data for this element to normalize data for all other analytes and to ensure consistency of analytical data throughout the entire study data base of arsenopyrite crystals. This observation was confirmed using solution based analytical data. Consequently, iron-normalized analyte data were used for all interpretational purposes throughout the thesis.
Using Linear Discriminant Analyses (LDA), Principal Component Analysis (PCA), Comparability Index (CI), and analyte ratio protocols it was possible to differentiate arsenopyrite samples which were associated with gold depositional environments from those which were formed under different geological processes. Within the non-gold arsenopyrite sample suite (59 individual samples) it was also possible to differentiate arsenopyrite samples which were associated with different metal assemblages (Pb-Zn, Sn-W, Ag and Cu).

Arsenopyrite samples collected from three significant gold producing provinces in Australia (Yilgarn Craton, Pine Creek Region, and Victorian Goldfields) were investigated. It was determined that the trace element signatures of the relevant samples could be used to unambiguously differentiate samples from each of these provinces. Additionally, it was possible to use the trace element assemblages of arsenopyrite samples to differentiate between gold depositional camps from within the Yilgarn Craton (35 deposits) and the Victorian Goldfields (10 deposits).

The overall host rock type at the site of a mineral deposit (i.e. greenstone or Banded Iron Formation (BIF)) has a significant impact on the trace element chemistry of arsenopyrite. This effect is most significant when comparing samples from the Kambalda region (greenstone hosted) with deposits formed synchronously (and likely of a very similar fluid chemistry) in the Randalls region (BIF). It has also been determined that the differences in lithology within a particular deposit change the localized chemistry of the hydrothermal fluid during the mineralizing process. Within the Mount Porter deposit arsenopyrite formed in BIF has a different chemistry to the arsenopyrite formed in dolerite (a greenstone). Overall it was determined that arsenopyrite samples deposited in, or associated with, greenstones contained significantly more Co, and Ni than their BIF
counterparts which in turn contained significantly more Se, Mo, Te and Bi. An investigation into the trace element assemblages of arsenopyrite from the Boorara deposit indicated that arsenopyrite formed in, or associated with, chlorite altered dolerite contained higher levels of Co and Ni than the arsenopyrite formed in carbonated dolerite (leucodolerite). This implies that as the host rock alters it transfers analytes into the adjacent hydrothermal fluid, thus affecting the arsenopyrite being formed in the vicinity.

Comparison of geologically analogous gold deposits, with endowments at least an order of magnitude apart, indicated that, when ablated, arsenopyrite from deposits with the greater endowment produced higher CPS data for Sn (commonly with increased Se and Hg CPS) compared to arsenopyrite from their less well endowed analogues. In addition, when the chemistry of arsenopyrite from gold deposits within the Yilgarn Craton was compared, it became apparent that Giant and Super-Giant deposits contained arsenopyrite yielding higher CPS data for Co, Sb, and Hg than arsenopyrite from the Intermediate and Small deposits.

Using samples from a number of known locations within the Homestake, Mount Porter, and Boorara deposits, it was possible to investigate the variation of arsenopyrite trace element chemistry within a deposit. This is most apparent in the Homestake deposit where the relative CPS for Ni, Se, Mo, and Sb in arsenopyrite changed systematically with respect to the distance from the main fluid focussing region (inferred to be the Main Ledge conduit).

Mercury has been recognised as a gold pathfinder in many geological environments since the 1970's and the investigation into their isotopes has commonly been theorised as a potential exploration tool. As such, an addendum to the main body of research has been
undertaken. In this investigation specialized instrumentation has been developed to heat a small (<1 g) crushed rock sample for the purpose of volatilizing mercury from naturally occurring mercury compounds trapped within the rock. Two prototypes were developed and a procedure for the determination of mercury released from specific mercury compounds was trialled. However, it was not possible to investigate this part of the research in detail due to time constraints largely caused by breakdown of the heating apparatus during prototype development. However, using the data obtained from preliminary experiments it was possible to confirm that the various mercury compounds could be separated, identified, and determined. It was also observed that there were differences in the concentration and isotopic distributions of the mercury compounds between the samples. However, it was not possible to quantitatively determine the mercury isotopic ratios of the various compounds due to lack of appropriate precision of the quadrupole ICP-MS. Due to the difficulty in determining isotope ratios, together with problems associated with fine tuning the mercury compound release ramps to ensure compete separation of the individual study mercury compounds, it has not been possible at this stage to establish specific relationships between the distribution of these compounds and the proximity of the sample to gold mineralization.

On the basis of the research detailed in this project it is possible to interpret the trace element signatures of arsenopyrite to understand the geological and geochemical processes which formed this mineral under the different geological environments associated with the ore forming process of the main orebodies.
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DEFINITION OF TERMS

Anomaly- A geological feature, especially in the subsurface, distinguished by geological, geophysical, geochemical, and remote sensing means, which is different from the general surroundings and is commonly of potential economic value.

Arsenopyrite- The mineral that fits the formula FeAsS, in the monoclinic crystal system. The arsenopyrite group of mineral includes Sb, Os, Ru, Ir, Co, and Ni rich end-members. For the purpose of this thesis, any mineral with less than 1% of these other elements is considered to be arsenopyrite.

Assay- A chemical analysis with a high degree of accuracy and precision, used extensively in financial evaluation of a deposit or mineralized region. These chemical analyses are performed by agents that usually have national and international accreditation.

Banded Iron Formation (BIF)- Sedimentary or metasedimentary rocks consisting of thin layers of iron-rich minerals (commonly as iron-oxides, silicates, carbonates, or sulfides) alternating with bands of shales and/or chert.

Base Metals- Any of the more common and more chemically reactive metals, e.g. lead, copper.

Basement- the solid rock which underlies the rocks of interest.

Batholith- A large composite intrusion with a surface area >100 km$^2$ made up of multiple plutons of gabbroic to granitic composition.

BIF- Abbreviation for “Banded Iron Formation.”

Brine- A concentrated aqueous solution primarily consisting of sodium chloride, in nature also containing the cations Na$^+$, Ca$^{2+}$, K$^+$ and Mg$^{2+}$, but with Cl$^-$ being the dominant anion, which is capable of leaching metals from the rocks through which it passes.

Centroid- The primary mineral-bearing fluid conduit (commonly a fault) or lode.

Chalcophile- Descriptive of an element with a strong affinity for sulfur.

CI- Abbreviation for “Comparability Index”; the measure of the similarity between a chosen sample and the comparative database as determined using a sorting sub-routine.

Clast- A particle of rock or a single mineral which has been derived by weathering and erosion.

Complexation- The formation of a ligand-metal aqueous complex.
Connate Fluid- An aqueous fluid which is trapped in the pores of rocks, usually being trapped during the formation of the rock.

Country Rock- The rock into which extraneous magma or mineralization is intruded or emplaced.

CPS- Abbreviation for “Counts Per Second”.

Craton- The stable interior of a continental plate, unaffected by plate margin activity since the Precambrian era.

Cross-over sample- A sample which is analysed on more than one period of analysis. This sample is used to measure the drift and tuning differences between analytical runs.

Crust- The outermost layer or shell of the Earth. It represents less than 0.1% of the Earth’s total volume.

Depositional Environment- A generic term referring to a combination of local camp and deposit scaled physical and chemical processes associated with the formation of a gold deposit.

Dimer- A dimer is a chemical structure formed by two sub-units. When a sample is ionized in a plasma two ions or an ion and an element may bond together to form a dimer which has a combined mass to charge ratio.

Disseminated- Said of a mineral deposit in which the desired minerals occur as scattered particles in the rock, sometimes in sufficient quantity to form a low grade mineral deposit and even ore (if the rock is economic to exploit).

Distal- Descriptive of a feature far from its source

Dyke- A tabular, near vertical minor igneous intrusion that cuts across horizontal to gently dipping planar structures in the host rock.

Ejecta- Solid material thrown from an impact crater.

Epigenetic- Mineral combinations that are formed by hot hydrothermal fluids.

Epithermal- Mineral combinations that form in the upper 200 m of the paleo surface, which are generally formed at low temperatures. The upwelling metal bearing fluids are commonly mixed with descending surficial waters.

Exsolution- The process whereby an initial homogenous solution separates into two (or possibly more) distinct liquid, mush, or crystalline phases without addition or removal of material.
**Facies**- Rocks of any origin formed within certain pressure-temperature conditions

**Felsic**- Applied to an igneous rock having abundant silica-rich light coloured minerals (quartz, feldspar, feldspathoids and muscovite).

**Fluid Source**- A deep crustal process (intrusions and/or metamorphism) that leads to the formation of a hydrothermal fluid which is later responsible for the mineralization of gold or base metals. The fluid may originate from an intrusive body, metamorphic dewatering of country rocks, connate fluids, or from a combination of sources.

**Grade**- The concentration of a metal in a metalliferous mineral system.

**Granitic**- A term for any “granitic” rock, ranging from granodiorite through adamellite to granite.

**Greenfields**- A generic term referring to early stage exploration, prior to significant drilling and resource estimations, on a prospect license.

**Greenstone**- A general term for a rock package composed of the green or basic minerals high in magnesium and iron (pyroxene, amphibole, and chlorite) and their altered or metamorphosed equivalents (usually the precursors rock is a basic igneous plutonic, volcanic or tuffaceous material.

**Greenstone Belt**- Zones of greenstone rock packages which are bordered by granitic bodies and sediments (“whitestones”). Usually these belts have been exposed to some degree of metamorphism.

**Hydrothermal**- Of or pertaining to hot water, to the action of hot water, or to the products of this action, such as a mineral deposit precipitated from a hot aqueous solution.

**Intrusion**- The process of emplacement of magma into pre-existing rock.

**Labile**- Constantly undergoing or likely to undergo chemical change.

**LDA**- Abbreviation for “Linear Discriminant Analysis”; a statistical method used to model the extent to which observations belongs to a particular group.

**Lewis Acid**- A compound capable of accepting a pair of electrons to form a (weak) covalent bond. Most commonly; cations in an aqueous solution.

**Lewis Base**- A compound capable of donating a pair of electrons to form a (weak) covalent bond. Most commonly; anions in an aqueous solution.

**Lithophile**- Said of an element that is concentrated in silicate rather than the metal or sulfide phases.
Lithostatic Pressure- The vertical stress due to the weight of overlying rocks

Lode- A mineralized body resulting from the extensive replacement of pre-existing host rock and/or infilling of voids.

Mantle Plume- A persistent column of hot material in the form of a vertical cylinder with a radius of ~150 km rising to the crust from the mantle.

Mafic- An igneous rock, low in silica and composed chiefly of one or more ferromagnesian, dark coloured minerals.

Mantle- The zone of the Earth below the crust and above the core, which is divided into upper mantle and the lower mantle. The mantle is a zone of assimilation of deeply buried crust and of fractionation of core liquid.

Mesothermal- The rock sequence below the epithermal zone, commonly 200 m to hundreds of kilometres below the paleosurface.

Metamorphism- The process by which rocks are changed by the solid-state application of heat, pressure, and fluids.

Metasomatism- A metamorphic, igneous, or diagenetic process in which the chemical composition of a rock is changed significantly, usually as a result of fluid flow.

Mineralize- The term is applied to the process of ore formation.

Moz- An abbreviation for one million troy ounces of gold.

Native- A mineral comprising a metallic element in an uncombined state or as an alloy with another element(s)

Ore- The naturally occurring material from which a mineral or minerals of economic value can be extracted for a reasonable profit.

Orogen- The process involved with the thickening of crust, commonly associated with the process of forming mountain chains. An orogen is characterised by large regions of extensive folding and faulting.

Orogenic- For the purpose of this thesis, the term orogenic refers to a mineral deposit formed within an orogen. This classification covers a range of deposits that may not be strictly related to the formation of orogens, but instead may have been formed by extensive crustal deformation, metamorphism, and/or influenced by a range of igneous events.

Overburden- Loose, unconsolidated, or weathered rock sediments.
**Paragenesis**- In this thesis paragenesis refers to the equilibrium mineral assemblages formed during the process of gold mineralization.

**PCA**- Abbreviation for “Principal Component Analysis”; a statistical means of assessing the variability of the inter-relationships within a data set.

**Phenocryst**- A mineral grain ranging upwards in size from approximately 1 mm in diameter found within the fine-grained matrix of an igneous rock.

**Physicochemical**- The natural physical and chemical parameters of a geological system or of a hydrothermal fluid.

**Pluton**- A large, thick, igneous body with steep lateral contacts which was emplaced and crystallised beneath the crustal surface.

**ppb**- Abbreviation for “parts per billion.” One part analyte in $10^9$ parts of a matrix.

**ppm**- Abbreviation for “parts per million.” One part analyte in $10^6$ parts of a matrix.

**Primary Mineral**- A mineral which grew within an upward and laterally migrating magmatic mass and whose formation and chemical composition is unrelated to post depositional hydrothermal alteration or metamorphic activity.

**Proximal**- Descriptive of a feature close to its source.

**Quaternary**- The second period of the Cenozoic era, following the Tertiary. It begins two to three million years ago and extends to the present.

**Regolith**- The superficial layer of friable to lose unconsolidated material which overlies bedrock.

**Secondary Mineral**- For the purposes of this research, a secondary mineral refers to those minerals that were not normative or part of the original host rock formation but rather evolved following the superimposition of metal-bearing hydrothermal related solutions.

**Siderophile**- Said of an element with a weak affinity for oxygen and sulfur, and readily soluble in molten iron.

**Sideroplesite**- A mineral which is a magnesium rich (FeO/MgO ≈0.75) siderite (FeCO$_3$).

**Stock**- An igneous body smaller than a batholith with a sub circular cross section; and commonly more fractionated and/or volatile-fluid rich than the progenitor batholith.

**Stratigraphic Column**- The vertical or chronologic arrangement or sequence of rock units portrayed in a geologic column.
**Strike**-The direction or trend taken by a structural surface as it intersects the horizontal plane.

**Subaerial**- Said of conditions and processes, such as erosion and volcanism, that exist or operate in the open air or immediately adjacent to the exposed land surface.

**Subcrop**- The minimal expression of a basement rock that is near surface or is proximal to the surface.

**Sulfosalt**- A complex sulfide mineral with the general formula $A_mB_nS_p$; where A represents a metal, B represents a metalloid, and S is sulfur.

**Terrane**- A specific geological term describing a fragment of crustal material having its own distinctive geologic history.

**Tertiary**- The first period of the Cenozoic era, thought to have covered the span of time between 65 and 3-2 million years ago.

**Trace Element**- An element in a solid sample with a concentration of 1-100 ppm. In this thesis the term trace element is applied to any element which is not a major or minor element in the arsenopyrite matrix.

**Turbidite**- A geological deposition formed during sediment gravity flow in deep ocean terrains.

**Ultramafic**- Said of an igneous rock composed chiefly of mafic and ultramafic minerals.

**Ultra Trace Element**- An element in a solid sample with a concentration of less than 1 ppm.

**Wall Rock**- The rock adjacent to a mineral deposit or igneous intrusion.
1.0 INTRODUCTION

The primary aim of this thesis is to determine if the inter-element relationships of trace elements present in arsenopyrite crystals may provide information that can be used to determine the style of mineralization, similarity (or otherwise) to analogous deposits in the district, potential endowment of a mineralized system, and the distance between arsenopyrite and any significant gold concentration present in the area. If this information can be provided, it will be of substantial use both in the exploration for buried and blind orebodies that cannot be otherwise detected using current geochemical exploration regimes and in “near-miss” exploration drilling. The relative abundances of the trace elements present in arsenopyrite crystals are determined using Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS).

A secondary aim of this research is to undertake a preliminary investigation to determine if the distribution of mercury compounds in host rock, and the isotopic abundance of mercury in these compounds, may be used to determine the distance between a specific rock sample and a gold orebody. This information could then be used (potentially together with arsenopyrite trace element data) to assist in forming a drilling regime to identify more rapidly and exactly the position and orientation of a potential orebody.

1.1 General Background

For millennia gold has been inextricably entwined with the fate of economies, cultures, and empires (Turner, 1933). Its rarity has led to a widespread desire for its possession and today it is used as a measure of status and as a means of storing value for the future (Mackenzie, 1991, Turner, 1933, Blose, 1995). Beyond its monetary value, gold has major uses in electronics, medicine, dentistry, computers, and technology (Sadler, 1994, Huang et al., 2003). Since the abolition of the “gold standard” in 1971 the nominal gold
price has fluctuated, but in general has climbed over $1800 USD per troy ounce, strengthening its perceived position as a hedge against inflation and a secure repository for future investment. In the financial year 2012-2013 Australia exported over $15 billion of gold (D.F.A.T, 2014). From the 1970’s onwards, as demand for the metal has increased, the rise in the gold price has encouraged mining companies to invest in exploration. However, fewer deposits with some surface expression are being discovered, as many deposits which are easier to discover have already been found. This has led to the need for more sophisticated techniques to be developed in order to identify the existence of buried and blind deposits that can be exploited commercially.

1.1.1 Gold in Australia

Gold was first discovered in Victoria in 1851 as native gold in placer deposits. These large deposits in Victoria eventually led to the Australian gold rush and to the population of Australia tripling in a period of 10 years (Maddock, 1984). During this period Australia was responsible for the production of one third of the total gold produced in the world. In the 1890’s gold was discovered in the Eastern Goldfields in Western Australia leading to a second Australian gold rush (Mudd, 2007).

The majority of gold deposits formed in Australia are orogenic, that is, primary lode-gold deposits formed in accreted terranes or cratons. Many of these deposits were discovered in the period 1850-1930 with several still being mined to this day. Three of the major orogenic gold regions that will be investigated throughout this thesis include: the Yilgarn block, the Pine Creek region, and the Victorian goldfields (Eilu and Groves, 2001, Willman, 2007, Robert et al., 2007). These regions represent significant periods of gold formation during the Archean, Proterozoic, and Phanerozoic eras, respectively.
1.1.2 Gold Mineralization

The gold deposits that are detailed in this thesis are primary in origin and have been formed directly as a result of dissolution, concentration, and subsequent precipitation of gold associated with fluids travelling through the earth’s crust. The popular hypothesis for primary gold formation is that a high temperature and pressure fluid (hydrothermal fluid), resulting from either the emplacement of an intrusive body or as a result of regional metamorphism, leaches gold and other elements from a large reservoir of country rocks. The solubilised elements are subsequently redeposited in greater concentrations in a new location as a result of changes in localized physicochemical conditions (Groves, 1993).

In these areas of precipitation a gold deposit may form should the gold bearing fluids encounter a favourable depositional environment and efficient fluid focussing mechanisms. Many fluid focussing systems, which do not have favourable conditions to lead to the formation of an economic gold deposit, may still concentrate enough gold for the area to be defined as a mineral occurrence. The determination of the favourable factors and methods to detect these conditions is essential in assessing the economic potential of a hydrothermal system.

“A “mineral occurrence” is a concentration of a mineral that is considered valuable by someone somewhere, or that is of scientific or technical interest... A “mineral deposit” is a mineral occurrence of sufficient size and grade that it might, under the most favourable of circumstances, be considered to have economic potential. An “ore deposit” is a mineral deposit that has been tested and is known to be of sufficient size, grade, and accessibility to be producible to yield a profit” (Cox, 1986).

Hydrothermal fluid convection cells that deposit gold may encompass vast areas and may not necessarily deposit gold in a single location. This will lead to the formation of multiple...
ore shoots in an orebody, multiple orebodies in a deposit, multiple deposits in an ore field, multiple ore fields in a district, and multiple districts in a province (Figure 1).

**Figure 1.** A representation of the scale in which deposits and orebodies are located within a regional setting. Edited from Laznicka, 1983.

Gold is deposited in a number of terranes throughout the world and is formed under a range of different conditions where it may be co-precipitated with a variety of other elements. Amongst these elements the most common are: Si, S, Cl, C (as carbonate), Fe, and As, with Pb, Zn, Cu, Mo, Ag, Sb, Te, and Hg ranging from significant to trace and ultratrace quantities. Hydrothermal alteration leaches elements from host rocks and may also precipitate elements from the ore forming solution into the environment. The elements precipitated from the ore forming solution may form new mineral species.
(commonly quartz, carbonates, and sulfides), chemically alter existing minerals, or may be present as trace elements in the newly formed/altered minerals (Reed, 1997).

1.1.3 Deposit Exploration

Exploration for gold deposits requires the identification of a favourable tectonic, structural, and lithological setting. The general principles of the geochemical exploration for gold deposits, when assisted by remote sensing geophysical techniques, are well understood, accepted and commonly implemented. Terrain in developed countries has been extensively geologically mapped and the favourable tectonic and structural settings can be identified.

Following geological, geophysical, and structural targeting at various scales, a geochemical exploration program is undertaken over a prospect licence to identify the presence of “hot spots” that may indicate subcropping mineralization. Current gold exploration geochemical protocols typically involve the identification of gold and associated elements in surface samples. Thousands of samples of rock chips, sediments, and alluvium are collected at regular intervals over a prospect licence and assayed as part of the overall geochemical program. Gold deposits with mineralization close to the surface may be easily discovered by the significantly elevated (above background) concentrations of Au (the prospectors dictum is that gold is the best pathfinder for gold), Pt, and Pd, sometimes with observation of the remaining Platinum Group Element (PGE) suite (Ru, Rh, Os and Ir), and other elements associated with gold mineralization (S, Cu, Ag, Sb, Bi). The concentration of elements Au, Pd and Pt are usually determined in industry by a lead fire assay, whereas the other PGE’s require more specialised and expensive assays (such as NiS assay). However, deeply buried and blind sub cropping orebodies will have a more diluted surface expression of these elements with
concentrations not sufficiently above background to be easily discernible (Eilu and Groves, 2001, Christie, 2003, Reis, 2001). If the initial geochemical assays are able to identify a suitable indicator multi-element halo, and if geophysical signatures are favourable, then drilling is a high priority to confirm the presence of gold.

Exploration for new gold deposits to replace exhausted mines is paramount to maintaining long term profits (Smith, 1996) and may account for hundreds of millions of dollars expenditure in Australia alone (Jaques and Huleatt, 2002, Mudd, 2007). A significant proportion of this capital may be expended on less prospective terrain and on less effective, or outdated, geochemical exploration techniques which ultimately indicate barren ground. Throughout history, numerous gold deposits with mineralization outcropping at the earth’s surface have been discovered (many of which been discovered serendipitously) (Long, 2000). The exploration for, and the discovery of, shallow gold deposits is declining as most of this type of deposit have already been found and mined for decades to progressively lower grades. Approximately two thirds of the gold mined around the world today comes from gold deposits that have been continuously mined for over sixty years (Frimmel, 2008, Long, 2000). It is therefore of concern to those who require gold for commercial purposes that discovery rates of new deposits to replace depleted mines have fallen despite rising exploration expenditure (Jaques and Huleatt, 2002).

Undiscovered gold deposits within 4 km of the surface (the maximum distance in which mining using current techniques can be performed profitably) in the continental crust are believed to be numerous, voluminous, and potentially feasible to mine.

“The overall proportion of gold concentrated in known orebodies is only $7 \times 10^{-7}$ of the estimated total amount of gold available in the continental crust. A high
potential for the existence of voluminous, hitherto undiscovered, gold resources may thus be inferred” (Frimmel, 2008).

Currently these buried deposits will remain undiscovered as there are few geochemical exploration techniques that are suitable and cost-effective at distances greater than tens to hundreds of metres from gold mineralization (Eilu and Groves, 2001). However, even if current geochemical protocols were to be used to explore for these buried or blind gold deposits, the costs would be uneconomically high. Therefore, to find these potentially profitable deposits exploration techniques are required that are cost-effective, precise, and effective at hundreds of metres from mineralization.

Sulfide minerals which are formed by hydrothermal fluids and which are associated with gold mineralization are usually deposited at significant distances (laterally and vertically) from the core of the gold mineralization. The trace elements entrained within these minerals have the potential to reflect the geological processes that have led to the formation of the mineral and of the gold deposit. Therefore, the determination of the trace element composition and inter-relationships in a sulfide mineral has the potential to be used for exploration. Arsenopyrite has been selected in preference to other mineral species for investigation because its crystal structure is known to typically incorporate a large concentration of trace elements which have the potential to represent mineralizing processes (King, 2002, Murphy, 2009). Arsenopyrite is also more intimately related with gold mineralization than many other sulfide minerals (with the exception of pyrite, pyrrhotite, and chalcopyrite) (Cook et al., 2013). Pyrite is more ubiquitous than arsenopyrite, however, pyrite may be related to a myriad of paragenetically diverse loci unrelated to the gold mineralizing event. In addition, arsenopyrite is more easily identified by the exploration geologist than many other sulfide mineral species. It is the central hypothesis of this thesis that the trace elements in arsenopyrite may reflect the style,
depth, and location of gold mineralization and consequently the protocols developed from the understanding of the arsenopyrite trace element assemblages could theoretically be used to explore for buried and blind gold deposits.

### 1.1.4 Mining

Over 190,000 tonnes of gold (6 billion troy ounces) were mined up to 1995 (Singer, 1995), and since then the rate of mining has been steadily increasing. During the 2005/2006 financial year the Australian gold exports were valued at $7.12 billion (Mudd, 2007) and $15.29 billion in 2012/2013 (D.F.A.T, 2014). Gold is mined by fracturing the orebody into rocks of manageable size which are then crushed into a fine powder. This powder is then mixed into a large froth-flotation separator whereby gold particles and sulfide minerals will bind with surfactant agents causing them to become suspended in a froth. This froth is then separated from the slurry (usually skimmed off the top of the solution) containing gangue minerals. In most modern processes the Au-sulfide concentrate is then mixed with an oxidised cyanide solution and gold is dissolved to be subsequently collected using activated charcoal. Gold is subsequently leached from the charcoal, electrochemically precipitated, and then refined to >99.99% purity. The development and implementation of this technology in the 1970’s has lead to a significant increase in Australian gold production (Mudd, 2007).

Profits can only be made on mines where the value of the gold produced exceeds the establishment and operational costs. The price of gold, the geology, geographical position of the deposit, the gold grade, mineralogy and the tonnage of the deposit will dictate the profitability of gold production from the site. The average crustal concentration of gold is in the range 1.5-5 mg per tonne of rock (1.5-5 ppb) (Crocket, 1991, Frimmel, 2008, Marsden and House, 2006). An approximate one thousandfold concentration of the gold
from these crustal levels, to approximately 1 ppm, will be required to produce deposits that can be potentially profitably mined with open-cut mining techniques (underground mining usually requires grades exceeding 10ppm) (Marsden and House, 2006). The average grade of ore mined has been steadily decreasing and has remained under the 5-7 g/t level since 1985. The decrease in grade consequently leads to an increased environmental impact in the form of greater waste rock and tailings per gram of gold produced (Mudd, 2007). The expenses associated with shallow pit mining techniques are comparatively lower than deeper shaft mining techniques and tend to be favoured due to a lower economic risk. However, newly discovered high grade deposits at depth may have their increased cost of deep mining techniques offset by the increasing price of gold and new innovative mining techniques (Mackenzie, 1991, Govett, 1982).

1.2 Theory of Gold Mineralization

1.2.1 Gold Precipitation

Gold deposits are only a small part of a much greater fluid migration and mineralizing system which may be the product of craton-wide fluid convection cells which can span hundreds of kilometres and focus hydrothermal fluids into an area only a few hundred to a few thousand meters across (Ho, 1992). While the tectonic, crustal and geological settings may differ between deposits, all gold deposits require certain components to facilitate their formation (Figure 2). These components are; a heat source, fluid source, fluid pathways, ligand source, metal source, and a trap. Hydrothermal fluids are high temperature (160-600 °C), aqueous solutions that have been generated by the dewatering of a fertile deep (or occasionally shallow specialized) intrusive or metamorphic source (usually both fluid sources are associated with gold mineralization (Ho, 1992)). This hot fluid will migrate towards the surface through faults, rock boundaries, grain boundaries and rocks of various porosity and permeability (Lichtner, 1988). The hydrothermal fluid
travels through large volumes (tens of km$^3$) of rock in the upper region of the Earth’s crust (Phillips, 2004). During this journey certain chemical species will be selectively leached in the solution and ultimately enriched into a final depositional environment (Heinrich, 2007). This gold-rich hydrothermal fluid must be concentrated into an area with favourable host rock and physicochemical conditions that will then lead to the rapid precipitation of gold into a small volume (trap). Within the trap the solubilised gold will be deposited from solution by one of four processes; phase separation, fluid mixing, fluid-rock interactions or adiabatic cooling. The dominant mineralizing process is mostly dependent on the host rock lithology and the crustal depth (Mikucki, 1998).

**Figure 2.** A schematic diagram of the components required for gold deposit formation (Hagemann, 2008).

Solubilised gold may become unstable when the physicochemical conditions of the gold-bearing hydrothermal fluid change. In convection systems, without an efficient fluid focussing mechanism, the gold will be precipitated over a large area and insufficient gold concentration will occur to result in an economic mineral deposit being formed. However, in a number of situations, such fluid focusing structures do exist. For example, fault and fracture zones allow changes in physicochemical conditions to occur repeatedly over
small areas and facilitate the emplacement of a mineralized zone or even economic ore deposit. Changes in the physicochemical conditions of the fluid that may lead to the instability of solubilised gold result from such geological processes as phase separation, fluid-rock interactions, mixing of the hydrothermal fluid with a fluid of dissimilar composition, and adiabatic and conductive cooling of the fluid (Kuehn and Rose, 1995, Lu, 1996, Mikucki, 1998). These physicochemical changes, when imposed on the migrating hydrothermal fluid, may lead to the transporting solution being oversaturated in gold and associated elements. Over many thousands of years this process may result in the progressive build-up of a gold deposit (Roedder, 1960, Seward, 1991).

Phase separation occurs when the ambient geological conditions fall below the liquid-vapour phase boundary for the hydrothermal fluid. This results in a vapour phase being formed as the lithostatic pressure is no longer sufficient to constrain the aqueous solution in only the liquid phase (Clarke et al., 1994, Mikucki, 1998). Phase separation may take place through the advection of the fluid to higher crustal levels (lower lithostatic pressure) caused by either a catastrophic change in pressure (faulting) or by raising of the fluid-vapour phase boundary through changes in the fluid chemistry (Mikucki, 1998). The formation of two fluid phases typically leads to elemental fractionation between the liquid and the gaseous phase and can commonly result in gold mineralization (Wilkinson, 1996, Sibson, 1988). Volatile less polar elements will fractionate into the vapour phase and the more polar elements will be retained in the liquid phase (Heinrich, 1999). In hydrothermal systems, Au, As, Sb (as HS⁻ complexes), S, B, and Li, will selectively fractionate into the vapour phase. The metals with a harder Lewis acidity form Cl⁻ complexes and will be predominantly enriched into the liquid phase, as they are more polar than most other ions in the solution. The vapour phase is typically highly unstable and any pressure changes greatly affect the solubility properties of elements in the vapour. Therefore, small changes
in the pressure of the vapour may rapidly lead to the precipitation of any solubilised species. With the exception of phase separation, pressure has minimal influence on the gold mineralization process. This is because the solubilities of the sulfur and gold complexes (the primary gold transportation mechanism in hydrothermal systems, discussed later in section 1.3.1) are not strongly affected by pressure changes (Figure 3) (Mikucki, 1998, Seward, 1973).

**Figure 3.** The contributions of sulfur complexes to the overall solubility of gold at various temperatures and pressures in a brine buffered solution. Note the logarithmic y-axis. Edited from Loucks, 1999.

The convecting gold-bearing hydrothermal fluid is likely to precipitate gold by reaction with a chemically reactive rock and/or by mixing with a fluid with different physicochemical properties. The gold-bearing fluid will attempt to reach chemical equilibrium with the new fluid or rock and this may cause the physicochemical conditions of the hydrothermal fluid to significantly change. Some of these physicochemical changes
may lead the destabilization of soluble gold species and subsequent mineralization. The changes that may lead to the destabilization of the gold complexes are predominantly chemical reactions, and changes in the pH and E$_h$ of the solution. In addition, when the hydrothermal fluid travels upwards and interacts with lower temperature rocks and mixes with a fluid of lower temperature, it will ultimately reduce the temperature of the gold-bearing fluid. This may also lead to the oversaturation of gold in solution and result in gold precipitation.

When the hydrothermal fluid equilibrates with a dissimilar fluid or rock it may react chemically and while some of these reactions will not interfere with the gold-sulfur complexation, many chemical reactions will lead to the precipitation of gold. The most significant chemical reactions leading to mineralization in lode-gold systems involve the depletion of sulfur ligands inevitably leading to gold de-complexation (Mikucki, 1998, Brown et al., 2003, Hofstra, 1991). The number of gold-sulfide complexes may be reduced by the increased concentration of additional chalcophile elements which are dissolved by the fluid from the hydrothermal alteration of rocks or through mixing with other fluids which are enriched in chalcophile elements. Many chalcophile elements (such as Cu, Zn, Sn, Sb, Hg, and Bi) have a greater affinity for sulfur and sulfur complexation than gold (Ahrland et al., 1958) and this may lead to fewer sulfide ions in solution that are able to complex with gold. This ultimately leads to a decrease in complexed gold and will result in gold precipitation.

A change in the pH of the gold-bearing fluid may cause transformations of the sulfur complexing ligand species which may result in a lowered total gold solubility (Seward, 1973, Renders and Seward, 1989). The concentration of the soluble species in a gold-sulfur aqueous system is significantly dependent on the pH of the fluid; as changing the
pH of a system will change the concentrations of the specific gold-sulfur complex species (Figure 4). Not all orogenic deposits will have physical conditions similar to the system presented in Figure 4 and the fluid chemistry may be vastly more complex. However, in most analogous hydrothermal systems, any significant changes from a neutral pH (~7) will typically lead to gold mineralization.

![Figure 4](image)

**Figure 4.** Calculated solubility curves for three thio-gold complexes with varying pH, compared to the experimentally determined solubility isotherm (thick black line), in a gold saturated system with $\Sigma S=0.5M$, at 225 °C and 1000 bar (Seward, 1973).

The total gold solubility of a hydrothermal system may be affected if the oxidation state of the system changes (Groves et al., 2003). Greatly increasing the oxygen fugacity of a hydrothermal fluid usually results in lower total dissolved gold and is the cause of gold precipitation in many deposits (Figure 5). An increase in the oxidation state of the ore-bearing fluid may cause the sulfides complexing gold to react and form sulfate. These
sulfates will have a harder Lewis basicity than the soft sulfide ligands and will have significantly lowered affinity for gold and are less likely to form gold complexes, ultimately leading to gold-sulfur decomplexation (Sillitoe, 1997).

Figure 5. A $f_{O_2}$-$pH$ diagram with gold solubility contours (dashed lines) for a gold-saturated solution with $\Sigma S=0.05$ M, at 300 °C. The areas marked in solid lines represent the stability fields of common secondary iron minerals (Phillips and Groves, 1983).

During fluid advection the temperature of the fluid will decrease as the fluid interacts with cooler rocks and connate fluids. A decrease in the temperature of the fluid will not necessarily destabilise gold complexes, but will result in decreased solubility of bisulfide ligands. An overall decrease in sulfide concentration will reduce the availability of
bisulfide ligands for complexation and will decrease gold solubility (Mikucki, 1998). A reduction in solution temperature does not directly lead to decreases in gold-bisulfide solubilities. For example, \((\text{Au(HS)}_2^-)\) solubilities change negligibly with temperature under geological conditions, but the reduction in temperature will lead to the precipitation of sulfur in the form of iron sulfide minerals (Mikucki, 1998). The decrease in temperature may also alter the nature of the complexing ligands which then do not complex as efficiently with gold and will result in a decrease in total gold solubility (Figure 3) (Phillips and Groves, 1983, Seward, 1973).

1.2.2 Hydrothermal Fluids

Hydrothermal fluids are solutions which usually containing high concentrations of Si, Ca, Na, K, Fe, in addition to ligands, metals, metalloids, and gases that have originated from the fluid source and may have been gathered from the country rocks during the convection cycle. This fluid has been heated by the geothermal gradient, regional metamorphism, and/or the introduction of intrusions. These fluids can be formed as a result of a number of events including:

- released water during a metamorphic event (Groves et al., 2003);
- released water from country rocks during an igneous intrusive event (Sillitoe, 1997);
- released water from the intrusion itself (Wang, 1993) or
- tectonic-scale mantle plumes heating brines or ground-waters (Groves, 1993).

Typically, the hydrothermal fluid at the depositional site may be a fluid that is a combination of multiple sources with the exact source of the fluids being difficult to determine (Ho, 1992). The lability of individual elements in solution are dependent on the availability of the encapsulating mineral (from which the elements may be sourced),
and the physicochemical conditions of the fluid (Brown et al., 2003, Phillips and Groves, 1983, Loucks, 1999). Some of the solutes in the fluid will precipitate during fluid convection to form discrete mineral phases. Other solutes will react with the rocks they travel through, and will cause hydrothermal alteration of the host rocks. Due to thermal expansion, the hydrothermal fluid is more buoyant than the surrounding rocks and migrates towards the surface (lithostatic pressure decreases with decreasing depth), creating fluid convection cells lasting for millennia (Lang, 1979, Cooke et al., 2005).

1.2.2.1 Hydrothermal Alteration

Hydrothermal alteration is the transformation of the chemistry and mineral assemblage of a rock as a result of significant reactions and interactions with hydrothermal fluids (Helgeson, 1968, Anand, 2002). Hydrothermal alteration is one of the more recognisable features of mineralization and it is usually the observation of this alteration that is used in exploration protocols (Kelley, 2006). The hydrothermal fluid acts as the medium which delivers the chemical reactants and removes soluble reaction products; leading to the formation of secondary minerals (Reed, 1997). The secondary minerals will have a greater thermodynamic stability in the hydrothermal environment compared to the replaced primary minerals and the type and volume of secondary minerals formed in this way is dependent on the overall physicochemistry of the system during mineralization (Duuring, 2007, Kelley, 2006). The chemistry of the system is determined by the interaction of the primary minerals present in the country rocks and the hydrothermal fluid composition (Reed, 1997, Eilu and Groves, 2001). The major and minor mineralogical and elemental associations for hydrothermal alteration of country rocks, due to gold-bearing fluids, may be observed in Figures 6 and 7.
Figure 6. A schematic diagram of the hydrothermal alteration of the host rock due to emplacement of gold and sulfide bearing quartz vein at the Hunt Mine, Kambalda. Edited from Neall, 1987.

The fluid chemical composition will vary within a given deposit usually with respect to distance from the area of greatest fluid flux (Robert et al., 1997). The modification of the fluid composition with respect to the distance from greatest fluid flux is a result of chemical reactions that take place during fluid dispersion and diffusion into the wall rock (Ridley and Diamond, 2000). Changes in the country rock mineralogy can be observed radiating outwards from the areas of greatest fluid flow (Lang, 1979), sometimes with
sharp reaction fronts differentiating the zones (Lichtner, 1988). The radiating alteration zones are known as “haloes” (owing to their concentric shape) with each halo having a different mineralogy and chemistry to the other zones (assuming the same host rocks). The alteration haloes are differentiated from each other based on their easily observable mineralogy (major and minor minerals). The mineral and chemical alteration haloes typically extend farther than the obvious limits of the deposit and traces of some hydrothermal minerals (especially sulfides) may extend farther than the most distal observable alteration halo (Kelley, 2006). The degree of alteration is typically influenced by the fluid flux, fluid composition, and the type of host rock (Lichtner, 1988). The mineralogy of the host rocks will determine how the alteration is expressed, while the degree and type of alteration between rocks (assuming equal fluid flow) is dependent on the lability of the elements within the minerals of the host rock. In ideal cases, hydrothermal alteration displays haloes around the areas of greatest fluid flux. However, the shape of alteration zones can easily be changed as a result of asymmetric fluid flow, heterogeneity of host rocks, and complex geological structures (fault and shear zones) (Lichtner, 1988, Eilu and Groves, 2001, Helgeson, 1968). Significant concentrations of gold are typically found proximal to the areas of greatest fluid flux, favouring zones of intermediate to advanced hydrothermal alteration (Kuehn and Rose, 1991). It should be noted that all gold deposits will have alteration haloes that extend further than both the ore zone (Figure 6) and detectable Au anomalies (Figure 7) (Eilu and Groves, 2001). Therefore, by investigating the trace element chemistry of arsenopyrite in regions distal to high fluid flux it may be possible to determine the location of the regions proximal to the high fluid flux, and hence the gold orebody.
Figure 7. A cross-section of the hypothetical primary geochemical dispersion haloes (arrows) and the alteration haloes (shaded areas) around a gold deposit. The solid arrows represent the most common extents and variations in the geochemical dispersion, dashed lines indicate less common cases. Note that Au dispersion does not extend farther than the alteration zones and As (typically present as arsenopyrite) extends farther than alteration. In addition, it should be noted that the alteration and metal introduction may be vertically attenuated. Edited from Eilu and Groves, 2001.

The primary geochemical dispersion of a deposit is the overall concentration and distribution of elements associated with the hydrothermal fluid flow throughout the depositional environment. Only a minor correlation exists between the elemental association of the alteration halo and the host rock type (Eilu and Groves, 2001). Therefore, the zonation of elements is predominantly dependent on the initial physicochemical conditions of the fluid. The observable primary geochemical dispersion ends where elemental anomalies can no longer be detected above background concentrations in whole rock samples using modern analytical techniques. The primary dispersion haloes may extend anywhere between 20-600 m laterally and up to 2 km vertically or along strike (Eilu and Groves, 2001, Stewart, 2013).
produces elemental concentration haloes which are analogous to hydrothermal alteration haloes (Figure 6). In the case of the geochemical haloes, they are based on the relative variation in bulk chemistry and are independent of mineralogy. Typically, the geochemical dispersion will extend further than the observable hydrothermal alteration (compare Figure 6 and Figure 7).

Each deposit type is defined by its generically different fluid sources, its surroundings, and host rock geology. As a result, the hydrothermal fluid chemical composition will typically differ significantly between deposit types (Christie, 2003). The variations in the fluid and country rock chemistry between deposit types will be expressed in the mineral assemblages and trace elements present in the secondary mineral phases of the hydrothermal alteration zones (haloes), (Zoheir and Qaoud, 2008, Christie, 2003, Ridley and Diamond, 2000).

**1.2.3 Gold Deposit Types**

Primary gold deposition is the process whereby hydrothermal fluids precipitate gold under varying geological and physicochemical conditions (Seward, 1991). This process results in sixteen recognised deposit classes based on variations in the nature of country rocks and the variations in fluid source and fluid pathways (Robert et al., 1997). Deposit classes are distinguished by their crustal depth and geological settings (Figure 8) and commonly include a myriad of sub-classes. The hydrothermal alteration and geochemical assemblages for the majority of gold deposit classes are heavily influenced by the physicochemistry of the hydrothermal fluid during deposition. This physicochemistry is in turn heavily influenced by tectonic settings, system scale settings (ligands and metals dissolved) (Phillips and Groves, 1983) and the physical and chemical conditions of the specific gold depositional environment.
Figure 8. A schematic representation of the crustal levels inferred for gold mineralization of the deposit classes. The depth scale is approximate and logarithmic (Robert et al., 2007).

1.3 Orogenic Gold Deposits

The research detailed in this thesis focuses on gold deposits from three significant gold producing regions in Australia. These regions include the greenstone-hosted Yilgarn craton (Archean), the Pine Creek orogen (Proterozoic), and the Victorian Goldfields (Phanerozoic). These gold deposits are classified as orogenic (Robert et al., 2007). However, it should be noted that some gold deposits investigated in this thesis are seen as being atypical (Kanowna Belle, Fimiston) (Robert et al., 2007) or the actual mechanism of their depositional formation may be contentious amongst various authors (Homestake) (Rye, 1974a, Caddey et al., 1991). Nevertheless, these atypical or contentious deposits are classified as being orogenic by Robert et al. 2007 and their definition of deposit types is adopted throughout this thesis.
Orogenic gold deposits are defined by their tectonic setting (accreted terranes) and occur over a range of crustal environments (Figure 8) (Groves, 1998, Ridley and Diamond, 2000, Eilu and Groves, 2001, Robert et al., 2007). These deposits are located in orogens, directly associated with orogenic activity, or are on the margins of impacting crustal plates where the formation of large structural features (shear zones and complicated fault zones) occur. The high regional pressure (and typically elevated temperature) may lead to large fluid circulation events. These fluids may have originated from intrusive bodies or from the dewatering of the country rocks undergoing diagenesis and metamorphism. Hydrothermal fluids will mostly travel through areas of lower mean pressure, (usually through structural features) as the hot fluids ascend towards the crustal surface. During fluid ascent, gold and other elements are leached and subsequently precipitated into traps such as faults and fissures, leading to the concentration of gold into ore zones. Complex networks and lithological contacts allow for the highly pressurised fluid to travel along multiple pathways during the leaching process of country rocks and then for these solutions to be focussed and concentrated into a smaller area which is favourable for the precipitation of gold and other elements (Groves, 1993). Consequently, orogenic gold deposits are highly structurally controlled (over a large range of physical scales) and it is the complexity of these structures that is an important factor in gold mineralization in orogenic terranes (Duuring, 2007).

Orogenic deposits display a number of differences to each other and as such, many orogenic gold deposits may initially seem unrelated. Differences between orogenic gold deposits include; host rock lithology, hydrothermal alteration and structural style of the camp-deposit scale (Witt, 1998). However, all orogenic deposits have been created in the same tectonic and crustal settings and have a broad set of similarities at the deposit scale.
The similarities between these orogenic deposits (as detailed by Groves, 1993, Duuring, 2007, Stewart, 2013) are:

- epigenetic and structurally controlled
- similarities in the hydrothermal alteration (CO$_2$, S, K, Na, Si)
- enrichment of Au together with Ag, As, Fe, Se, Sb, Te, W, and Bi (among others) in the deposit as a whole
- formation late in the history of the orogen

1.3.1 Gold Bearing Hydrothermal Fluids

The fluid source for the majority of the orogenic hydrothermal systems is believed to be magmatically or metamorphically derived, but many fluids at the depositional site may be a mixture of two or more fluids from different sources (Heinrich, 2007, Mikucki, 1998). The growing consensus amongst geologists is that gold bearing hydrothermal fluids originate from deep within the upper mantle to lower crust where they mix with variable amounts of metamorphic fluids (Heinrich, 2007, Groves, 1993, Ho, 1992, Duuring, 2007). The precise source and the extent of fluid mixing of the gold-bearing hydrothermal fluids will not be explored to any great extent, as the source of the fluids is complex, highly contentious, and beyond the scope of this thesis. Instead it is pertinent simply to recognise that the gold-bearing fluid for these deposits displays a range of physical and chemical conditions.

Hydrothermal ore-forming fluids are typically aqueous multi-component electrolyte solutions which will transport gold (and many other elements) to a trap in the Earth’s crust (Seward, 1991). Studies suggest that the fluid sources of many gold deposits were under-saturated with respect to gold. Therefore, the hydrothermal fluid will leach gold (and other elements) from country rocks and will precipitate various elements when the
solution becomes over saturated (Mikucki, 1998). Gold-bearing hydrothermal fluids demonstrate a consistent set of major characteristics for most of the deposit classes, despite differences in geological settings or depositional styles. Gold has the greatest solubility in geological environments in slightly acidic pH (5.2-6.2) solutions which exhibit reducing conditions and have a high sulfur concentration (Mikucki, 1998, Ho, 1992). The average orogenic gold-bearing hydrothermal fluid is aqueous and has;

- a low salinity (0-10 wt% NaCl) (approximately 82-90% of primary gold deposits exhibit this low salinity (Phillips, 1993, Singer, 1995)),
- relatively simple paragenetic history (Stewart, 2013, Ho, 1992)

It can be inferred that the majority of arsenopyrite samples collected from gold deposits which are investigated in this project will have been formed by fluids of broadly similar major component compositions.

In order for a hydrothermal fluid to be considered gold-bearing it must have a set of chemical conditions which allows it to dissolve gold and then to retain it in solution. The dissolution of gold into an aqueous solution requires an abundance of ligands that are able to form weak electrostatic bonds around the Au$^+$ ion. The complex formed has a high stability in aqueous solutions and allows the gold to remain in solution until such time as the physicochemical conditions of the fluid change and render the complex unstable. There are two potential ligands that may assist in the dissolution and transport of gold; these ligands are sulfide and chloride based. Aqueous gold-bisulfide and gold-chloride complexes are considered the most likely species for gold transport in hydrothermal systems due to the availability of reduced Cl\(^-\) and S\(^{2-}\) species and the stability of these complexes (Seward, 1991, Groves, 1993, Mikucki, 1998). The moderately reducing
conditions of most hydrothermal fluids favour the Au\(^+\) ionic state for solubilised gold. This cation is a soft Lewis acid and predominantly complexes, with partial covalent bonding, to a soft Lewis base such as HS\(^-\) (Phillip, 2004). Due to the relatively high concentration of bisulfide and its soft Lewis basicity, it is considered to be the dominant gold transportation ligand in most hydrothermal systems (Phillips, 2004, Seward, 1991). In most of these fluids gold is transported as Au(HS)_2\(^-\), while in lower temperature orogenic fluids (<270 °C) gold is transported as Au(HS)_0 (Figure 9A). In many gold-bearing hydrothermal fluids the concentration of the bisulfide ion is within the range of 10\(^{-3}\) to 5x10\(^{-2}\) molL\(^{-1}\) (approximately 200-1,000 ppm) which is significantly higher than gold concentrations in solution (1 to 100 ppb) (Mikucki, 1998, Seward, 1973, Skinner, 1973). Chloride ions are the most abundant ligands in hydrothermal solutions. However, these ligands are less significant in Au transportation due to the superior thermodynamic stability of gold-sulfide complexes under most hydrothermal conditions (Hayashi, 1991, Mikucki, 1998, Shenberger and Barnes, 1989, Seward, 1973). Due to the hard Lewis base nature of Cl\(^-\) ligands, gold-chloride complexes play only a minor role in Au transportation (except under extreme chemical, pH or f\(_{O2}\) conditions (Figure 9B)) (Mikucki, 1998, Seward, 1973, Phillips and Groves, 1983, Loucks, 1999). In Archean orogenic gold deposits, chloride complexes are the dominant gold transporting ligand in fluid temperatures over 550°C (Mikucki, 1998). Over all the possible temperature ranges the chloride ions display a greater affinity for bonding to the harder Lewis Acids (Ahrland et al., 1958).
Figure 9. A) The stability fields for gold-bisulfide complexes for hydrothermal fluids as a function of temperature and concentrations of bisulfide ions. The thin lines represent the relative ratio of \( \text{Au(HS)}^2^- \) to \( \text{Au(HS)}^0 \). The shaded area represents the most common hydrothermal fluid temperature and bisulfide concentrations (Mikucki, 1998). B) Solubility contours (thin black lines) for gold in a solution of \( T = 300 \, ^\circ\text{C}, \Sigma S = 0.01 \, \text{molL}^{-1} \), and \( \Sigma Cl = 1.0 \, \text{molL}^{-1} \), displayed as a function of \( f_{O_2} \) and \( \text{pH} \). The thick black lines delineate the stability boundaries for common iron oxide and iron sulfide minerals. The minerals are as follows: \( \text{bn} \)-bornite, \( \text{py} \)-pyrite, \( \text{cp} \)-chalcopyrite, \( \text{po} \)-pyrrhotite, \( \text{mt} \)-magnetite, \( \text{hm} \)-hematite (Hayashi, 1991).

Certain physical conditions must be met in order for the gold-bisulfide complexes to remain stable in the fluid. As previously discussed, pressure has a minimal effect on the stability of sulfide complexes. However, the temperature of the fluid has a strong sympathetic relationship to sulfide solubility. Most gold-bearing hydrothermal fluids exist within the temperature range 160-600 °C and pressures of approximately 1-3 kbar (Seward, 1973, Ho, 1992, Duuring, 2007, Mikucki, 1998). Within this range of physical conditions sulfide ligands are highly soluble in solution and will be present in concentrations sufficiently high for gold-sulfide complexation.
1.3.2 Gold Mineralizing Processes

As a group, orogenic gold deposits display a number of characteristics and mineralizing processes that are somewhat different from those discussed in section 1.2. Within this group, lithology, temperature, and pressure of the depositional environment dictate which mineralizing process will be dominant for a particular deposit (Figure 10).

As previously discussed (section 1.3), orogenic gold deposits are structurally controlled and the dominant fluid focusing structures are the regions of major shear zones, usually formed at the intersection of major tectonic boundaries. The hydrothermal fluid that has sequestered gold is able to flow upwards through these shear zones and is subsequently focussed within these areas. It is as a result of this focusing and concentration of the ore fluids that the gold is significantly concentrated into a finite area that can be classified as a deposit. Areas of intense foliation, faulting, and fracturing (and hence hydrothermal alteration resulting from the fluid flow) exist within these shear zones (Groves, 1993). The changes in the shear zone orientation, as a response to changing regional-scale pressure regimes, result in the shear zones dilating and forming faults, fractures, and
breccias (Eisenlohr, 1989). A higher density and increase in the complexity of faults and fractures increases the potential for fluid flow which in turn has the potential to lead to greater gold endowment. In addition, the increased complexity of lithological contacts has the potential to increase rock permeability and chemical gradients within an area; resulting in an increased favourability for gold deposition (Hodkiewicz, 2003). The majority of the gold deposits from the Yilgarn (and hence the majority of deposits discussed in this study) are formed in areas of low stress during regional compression. Evidence may be found for this high fluid pressure and rock dilation from the presence of hydraulically formed breccias and quartz veining (Witt, 1998).

The majority of host rocks of the gold deposits from the Yilgarn Craton which are investigated in this study are mafic rocks with low porosity and permeability; and as such the fluid requires faults, fractures, breccias, and shear zones to travel to the depositional site (Manning, 1999). The host rocks are typically metamorphosed (greenschist and amphibolite facies) and are of basaltic to komatiitic composition with gold mineralization rarely forming in granitoids. At the site of each deposit the host rocks are reasonably reactive. Conversely, the host rocks for the majority of deposits in this study from the Pine Creek Geosyncline and the Victorian goldfields are sedimentary turbidites (weakly reactive in the lithified state at the deposit site) and black shales. The lack of permeability in host rock typically causes gold deposits to be formed in highly deformed terranes that have experienced extensive folding and faulting prior to gold mineralization. Most of the deposits investigated in this study (with the exception of the Victorian goldfields deposits) are located within, or proximal to, cratons and their margins. These terranes are usually tectonically stable and have not experienced significant additional deformational or alteration events. Therefore, the geology must be considered as being a strong reflection of the ore depositional environment during mineralization.
The basic chemical changes imposed on a gold bearing hydrothermal fluid that will lead to mineralization are detailed in section 1.2.1, with the most important change being the removal of bisulfide ligands from the solution, with pH and fO2 dictating the nature of the sulfide ligand in solution. A chemical or physical change in the gold bearing fluid is likely to reduce the concentration of bisulfide ligands in solution and has the potential to lead to gold mineralization (section 1.2.1). In orogenic systems the gold bearing hydrothermal fluid may encounter and react with rocks that change the pH and redox potential of the fluid. These rocks must be quite reactive in order to decrease the H+ concentration or increase the fO2 of the fluid. Highly reactive rocks ((ultra)mafics and BIF) are present in most orogenic deposits and, as such, pH, and Eh changes are commonly the result of the interaction of the hydrothermal fluid with the host rocks. In addition, the mineralization of gold in orogenic deposits may be initiated by the removal of dissolved sulfur in the gold-bearing solution. For example, bisulfide ligands are easily removed from the solution by reaction with iron in the host rock to form pyrite (and other iron sulfides) by the following reaction (Hodkiewicz, 2003):

\[
2 \text{Fe}_3\text{O}_4(s) + 6 \text{HAu(HS)}_2(aq) + 0.5 \text{O}_2(aq) \rightarrow 6 \text{Au}(s) + 6 \text{FeS}_2(s) + 9 \text{H}_2\text{O}(l)
\]

In addition, the dissolved carbonate in the fluid may react with the host rock to form dolomite and lead to a decrease in the pH in the fluid. One such example from Mikucki, 1998, includes:

\[
\text{MgO}(s) + \text{Ca}^{2+}(aq) + 2\text{H}_2\text{CO}_3^0(aq) \rightarrow \text{CaMg(CO}_3)_2(s) + 2\text{H}^+(aq) + \text{H}_2\text{O}(l)
\]

A decrease in the fluid pH will lead to a decrease in the solubility of sulfide ligands which will result in a decrease in gold solubility.

1.3.3 Orogenic Gold Deposit Morphology

Deposits are usually morphologically complicated as multiple overlapping fluid pulses and fluid pathways can be superimposed on the simple alteration patterns described
previously in section 1.2.2. However, a basic set of characteristics can be applied to each deposit type to broadly describe the morphology of each fluid pathway or orebody within a typical orogenic gold deposit. Usually orebodies are formed in areas of significant fluid focussing and high fluid flux. In these situations the chemical and mineralogical alteration zones associated with a specific orebody are usually symmetrically disposed around the orebody in a pseudo-spherical concentric shape and are referred to as haloes (Bierlein, 2000). The disposition of the haloes around an orebody can be used to identify the centre of the fluid focussing event that emplaced it. Consequently, greenfields exploration for gold commonly focuses on the interpretation of geochemical data to identify haloes that may be used to isolate the centroid of the mineralizing event and consequently the most appropriate area for subsequent exploratory drilling. The concentration of gold will drop to background levels tens of meters from this centroid (Figure 7 and Figure 11). The chemical haloes of gold deposits usually describe changes in the relative abundance of certain elements that are associated with both hydrothermal alteration and gold mineralization (Eilu and Groves, 2001) (Figure 7).

Figure 11. Schematic cross section through a porphyry deposit showing the primary features that may represent the obvious limits of the deposits and the theoretic zone in which the mineral chemistry may be used to detect the deposit. Edited from Kelley, 2006. Note that in orogenic deposits the hypogene zone is subdivided into epithermal and mesothermal zones with increasing depth.
Unlike the chemical haloes, the mineralogical haloes for gold deposits are highly dependent on the lithology and precursor mineralogy of the host and country rocks. In addition, changes in the mineral assemblage, as a result of hydrothermal alteration, will vary with the metamorphic grade; as both the temperature and pressure of the system will determine the thermodynamic stability of the final mineral assemblage (Duuring, 2007). The hydrothermal fluid will transport a large number of elements to the depositional site and these elements will be deposited there. Some elements will form new mineral phases and some other elements will react with the minerals present in the existing host rock creating new minerals. Mineral assemblages distal to the centroid of the ore fluids will change to reflect the relatively cooler conditions occurring in these areas as the hydrothermal fluids cool in response to their interaction with the host rock (Kelley, 2006).

The shape of the deposits and the orientation of orebodies within a given deposit is considerably more complicated than the basic cases mentioned previously in this subsection. The shape and positioning of orogenic gold deposits is highly influenced by the crustal depth of the deposit (Figure 12) (note that these are only deposits with granitoid association). The chemical and mineralogical haloes radiating out from a gold deposit may be confounded and overprinted by the presence and orientation of multiple orebodies, emplacement events and fluid focussing structures. Thus, it is difficult to represent a generic gold deposit morphology that is applicable to all orogenic gold deposits.
Figure 12. A schematic cross-section that shows the crustal distribution of orogenic gold deposits with spatial and generic relationships with granitoids within the Yilgarn craton. Abbreviations: ab, albite; ank, ankerite; bt, biotite; calcic am, calcic amphibole; cc, calcite; chl, chlorite; cpx, clinopyroxene; kf, alkali feldspar; pc, plagioclase; po, pyrrhotite; py, pyrite; tn, titanite; wm, white mica (Duuring, 2007).

1.3.4 Gold Deposit Endowment

Not all gold deposits are created equal; some deposits have world-class amounts of gold while others are less well endowed. The endowment of a gold deposit is the total amount of gold (commonly measured in troy ounces) in a given system. It is calculated from the amount of gold historically mined and the mineral resources and gold reserves of a system. The mineral resources of a gold deposit include the measured, indicated and inferred resources in a deposit (J.O.R.C., 2012). The measured, indicated, and inferred resources are the reserves of gold in a deposit and are based on exploration results in
decreasing order of confidence. One such measurement of the amount of gold in a deposit is the Tonnage Accumulation Index (TAI) proposed by Laznicka, 1983, and is a method of objectively determining the total amount of metal accumulated in a deposit. The TAI is the economic metal tonnage in a deposit divided by the average crustal concentration of the metal in question. The economic metal tonnage is an arbitrary unit and may suffer from fluctuating markets and incomplete mining data. Additionally, incomplete exploration of the system and unrecognised disembodied orebodies may distort the true endowment of a deposit. In the same manner, the measurement of gold endowment suffers from a number of setbacks, similar to the TAI, in accurately assessing the amount of gold in a given system (Laznicka, 1983). It is likely that the accuracy of the endowment, calculated using J.O.R.C criteria, will be similar or greater than the TAI. Therefore, endowment will be used in this thesis as the measurement of the gold in a depositional system.

The factors leading to increased gold endowment are; the chemical composition, mechanical properties and thickness of the host rock, geometry of terrain, pressure and temperature conditions, and proximity to regional-scale shear zones (Hodkiewicz, 2003). In addition, longer periods of deposition and multiple fluid focussing and mineralizing events are potentially responsible for increasing the endowment of a deposit. A super-giant deposit will typically exhibit all six of these factors while a giant deposit may have four to five and a smaller deposit only two to three of these factors (Hodkiewicz, 2003). Overall, deposits with high gold endowment are the product of efficient fluid focussing mechanics and the influence of many physical and chemical processes at the deposit scale.

The total mass of mined gold is a term which is currently used to classify a deposit in terms of how much gold in contained within the system. Gold deposits may be ordered in
terms of historically mined gold and are subsequently ranked in the following order based upon the mass of gold mined in terms of millions of troy ounces (Moz) (Singer, 1995):

- The bottom 50% of deposits are defined as small deposits (<0.19 Moz)
- The top 50% of the deposits are defined as intermediate (>0.19 Moz)
- The top 10% of the gold deposits are defined giants (>3.2 Moz),
- The top 1% of gold deposits are defined as super-giant deposits (>39 Moz),

This method of gold deposit assessment does not take into account the mass of gold that may exist in the system but has yet to be mined (mineral reserves). Deposits that have not been mined for a significant period of time, but have a large mineral reserve are not accurately represented by this system.

The mineral reserves of a deposit system are calculated to a specific economical gold grade cut-off with reference to the geological exploration undertaken on the given deposit. The indicated and inferred reserves are the probable and possible grades and tonnages of gold ore that have been estimated by exploration of the existing orebody or nearby orebodies. The cut-off grades are based on the grade of the potential ore and the cost of mining the potential orebody. Information on indicated and inferred reserves is gathered from publicly accessible annual or surrender reports generated by the operating mining company. Potentially, incomplete exploration and economic factors affect the calculated, indicated, and inferred reserves and hence affect the reserves of the gold deposit (Laznicka, 1983). In addition, gold present in low grade rocks, underground pillars, and lost by erosion are rarely included in endowment studies. Therefore, assessing the total mass of gold in terms of endowment is not a highly accurate measurement. However, this remains the only viable method for estimating the total gold deposited in a given system.

Overall, the endowment of a system should be seen as a reflection of the amount of gold
in the deposit and used for comparisons between deposits that have endowments of an order of magnitude apart.

The early assessment of a deposit endowment is desirable for mining companies as they can determine the life expectancy, grade, and tonnage of the system as early as possible allowing the company to assess the feasibility of mining that deposit. Many mining companies will not develop and mine a deposit if it does not appear to display sufficient endowment. The importance in assessing the endowment of a deposit also lies in the fact that the top 10% of primary gold deposits (in terms of gold produced) account for 86% of the total global gold production (Singer, 1995). Thus, the discovery of new giant deposits is significant to exploration and mining companies.

Attempting to determine a causal link between an observable or measureable phenomena and a deposit endowment has been the subject of a number of research papers and PhD theses (Hodkiewicz, 2003, Weinberg et al., 2004, Bierlein et al., 2006). The ultimate objective of these investigations is to determine if this observable trait can be used in early deposit exploration to minimise costs and increase the accuracy of the exploration. Some of these publications focus on measuring some physical and geological factors and relating them to total endowment:

- determining if the complexity and orientation of geological structures may be related to gold endowment (Hodkiewicz, 2003, Weinberg, 2004).
- determining if the lithology of a deposit has any significant impact on the endowment of a deposit (Bierlein, 2006).
- some correlations can relate the geological structures and the lithology, in terms of complexity, of gold deposits in the Yilgarn to gold endowment (Hodkiewicz, 2003).
• rapid changes in the redox potential of the gold bearing fluid is likely to lead to higher gold grades as the gold is removed from the fluid more rapidly, however, the discovery of a causal link between the redox potential of a fluid and the endowment of a deposit has not been achieved (Duuring, 2007).

1.4 Arsenopyrite in Gold Deposits

The three most common sulfide minerals that are associated with orogenic gold deposits are pyrite, pyrrhotite, and arsenopyrite, with other sulfide minerals (galena, chalcopyrite, and sphalerite) commonly being present as trace occurrences (Cook et al., 2013). Usually gold depositional environments will contain multiple generations of pyrite, many of which are related to hydrothermal events which are not associated with the emplacement of gold. Arsenopyrite is often more easily related to specific gold depositional events than pyrite and pyrrhotite, and usually the presence of arsenopyrite in a prospect licence is an indication of gold mineralization (Cook et al., 2013). Arsenopyrite and pyrite are present at minor and major mineral quantities in the majority of orogenic gold deposits irrespective of crustal depth, pressure, and temperature (Mikucki, 1998). In addition, arsenopyrite has been demonstrated to incorporate observable levels of a wide variety of elements into the its crystal lattice (Murphy, 2009, King, 2002). Arsenopyrite is reasonably easy to identify in a hand specimen with the aid of a magnifying lens, and it may also be identified using a dedicated reflective light microscope operating under plane and cross polarised light conditions (Figure 13). Arsenopyrite crystals are commonly observed proximal to mineralization (within a few hundred metres); and although their frequency decreases progressively distal to mineralization, they can still be detected using reflected light microscopy at distances several kilometres away.
Figure 13. Polished sections of rock samples (58B and P4) displaying crystal of arsenopyrite (circled in red).

The presence of arsenopyrite at significant distances from an orebody attests to the presence of a wide arsenic dispersion halo as detailed in Figure 7. The presence of arsenopyrite crystals at a wide range of distances from mineralization is due in part to the wide range of pressure and temperature stabilities of the arsenopyrite crystal (Figure 14). Consequently, the crystal will commonly be formed and preserved under a wide variety of geological conditions. Therefore, the use of arsenopyrite as a mineral of choice for the investigation of hydrothermal fluid physiochemical conditions associated with gold mineralization is extremely appropriate.

Arsenopyrite is a secondary mineral formed when significant concentrations of soluble As and Fe (transported in hydrothermal systems as H$_3$AsO$_5$\(^{(aq)}\) and FeS$_2$\(^{(aq)}\)) (Heinrich, 1986) become oversaturated, or when soluble arsenic and sulfur react with magnetite (Junqueira et al., 2007), or hematite (Brown et al., 2003). Arsenopyrite is one member of the Fe-S-As mineral group and it should be noted that arsenopyrite may undergo solid solution with other mineral members in this group, ultimately leading to a slight deviation from the ideal stoichiometry (Kretscmar and Scott, 1976). The physical constraints for the stability of arsenopyrite in a Fe-As-S saturated system (which is analogous to orogenic hydrothermal systems) is presented in Figure 15. It may be observed from this figure that
arsenopyrite is stable under a number of chemical conditions, most of which are suitable for maintaining gold in solutions that have a neutral pH and low \( \text{f}_2\text{O} \) (Heinrich, 1986).

**Figure 14.** The pressure and temperature stability fields of common sulfide minerals. The diagonal dashed line represents the average increase in both temperature and pressure with increasing depth in the crust. The red line represents the limit of stability for arsenopyrite and pyrite. Edited from Vaughan, 1978.

**Figure 15.** The stability field of arsenopyrite and the solubility of gold with respect to pH and oxygen fugacity in an Au-Fe-As-S saturated system at 250°C. The green lines are the solubility contours of Au as a bisulfide complex (measured in ppb) and the shaded red area is the stability field for arsenopyrite. Gold solubility data are taken from Shenberger and Barnes (1988) and the Fe-As-S stability field is edited from Heinrich (1986).
Arsenopyrite is a monoclinic sulfide mineral with a marcasite-like unit cell configuration (Figure 16). The crystal structure of arsenopyrite can deviate significantly from the ideal structure presented in Figure 16 as a result of pressure constraints or isomorphous impurity substitutions (Hem, 2001, King, 2002). In many orogenic systems arsenopyrite has been formed under high pressures, resulting in significant strain being imposed onto the crystal lattice. An increase in the concentrations of substituent elements (including Au) into the arsenopyrite lattice results in greater distortion of this lattice and further increases the potential for the distorted crystal to incorporate even more of these elements (Cook et al., 2013). Crystal distortion can often result in the formation of heterogeneous crystal planes allowing for greater incorporation of hydrothermally transported trace elements during crystal growth (Rakovan, 1994). Therefore, it is unsurprising that in some geological systems arsenopyrite may contain concentrations of Co, Ni, Se, In, Sn, Sb, Te, Pb, and Bi greater than 1% (King, 2002). These elements are present in arsenopyrite as either lattice substituents or encapsulated as inclusions into the arsenopyrite crystal during mineralization (King, 2002, Wu et al., 1990, Cabri et al., 2000, Morey et al., 2008). Additionally, substitution may also occur between As and S at the As or S sites and in many situations the As/S ratio varies from core to rim within a given crystal (Lowell, 1982). The concentrations and interrelationships of the trace elements in arsenopyrite have the potential to reflect the physicochemical conditions of the hydrothermal fluid during arsenopyrite formation and gold mineralization (Heinrich, 1986). Arsenopyrite is a stable mineral that will not readily alter in response to changing geological conditions and events, thereby retaining its trace element chemistry from the time of formation (Kretscmar and Scott, 1976, Nickel, 1968) and making the mineral a “time capsule” whereby geological events which have taken place over 2 billion years ago may be observed.
Figure 16. A) The ideal crystal structure of arsenopyrite: each Fe centre is coordinated to 3 As and 3 S atoms, with each As or S atom coordinated to 3 Fe centres (Ribbe, 1974). B) A two-dimensional unit cell of arsenopyrite focusing on the Fe-sites. Adjacent Fe octahedra (filled circle) share two non-metal atoms (empty circles) and an alternating weak metal-metal interaction (dotted line) (Nickel, 1968).

1.4.1 Trace Elements

The strict definition of a trace element is an element that occurs within a matrix at a concentration of between 1 to 100 ppm (Morrison et al., 1979). Although for the purpose of this thesis, which is specifically related to arsenopyrite analysis and data interpretation, all elements in the arsenopyrite lattice with the exception of Fe, As, and S are referred to as trace elements irrespective of their actual concentration. In general, trace elements that are present in minerals occupy locations within the crystal lattice. This substitution requires a variation in the stoichiometry of the effected mineral and results in atomic imperfections being introduced. Atomic imperfections typically occur as one of three different types (Kroger, 1973):

1. Voids within the crystal structure that would typically be occupied in an ideal crystal are known as vacancies.
2. An atom within a site in the crystal structure that should be empty in an ideal crystal is known as an *interstitial* atom.

3. An atom which has occupied a site that would be occupied by one of the crystal forming elements is known as a *substituted* atom.

Trace elements are typically present in the arsenopyrite crystal as substitution or interstitial atomic imperfections. Vacancies in a mineral will distort the crystal structure and may indirectly lead to greater trace element incorporation. Interstitial atoms and substituted atoms may also distort the structure of a crystal as the atomic radii may be too large or too small to fit precisely into the lattice.

Sulfide minerals deposited during ore formational processes may contain trace element chemical signatures that are indicative of the ore forming process (Kelley, 2006). Therefore, the analysis and interpretation of trace element chemistry of arsenopyrite may be used to determine certain geological parameters and conditions of the mineralizing process. Sulfide mineral phases are strongly associated with gold deposit formation and these minerals typically contain significant concentrations of siderophilic and chalcophilic elements. Lithophilic elements are associated with most forms of hydrothermal alteration and many lithophilic elements present in a deposit will be enriched in hydrothermal processes unrelated to gold mineralization. In addition, these elements usually do not substitute into the sulfide lattices to an appreciable extent. Therefore, the determination of lithophilic elements in arsenopyrite is of less importance than the determination of siderophile and chalcophile elements. Siderophile and chalcophile elements require sulfide complexation in order to be dissolved into a hydrothermal solution. Therefore, gold transportation (and subsequent deposition) is strongly associated with sulfur, chalcophilic and siderophilic elements.
During the hydrothermal mineralizing process sulfide minerals may grow and incorporate a large concentration of elements which were previously dissolved in solution. This is due, in part, to the sulfide minerals displaying an affinity to bind metals (mostly siderophile and chalcophile elements) to their surface, many of which are pH and fluid chemistry dependant (Jean, 1986). Secondary minerals contain the greatest concentration of hydrothermally transported trace elements, due to specific mineral formation mechanisms; with the elemental assemblages in these minerals reflecting the physical and chemical conditions of the fluid (Chenery et al., 1995). The degree to which trace elements are incorporated and the ratios between the elements in these minerals is determined by the physicochemical conditions of the fluid. The process of forming minerals during hydrothermal alteration will result in a change in the chemistry of the fluid. Most specifically, the abundance and type of transporting ligands will dictate the concentration of trace elements available at the mineral formation site. As sulfide minerals are formed, sulfur is removed from the system which may lead to the destabilization of bisulfide complexes. This process ultimately leads to the further precipitation of dissolved species, resulting in trace elements displaying different concentrations with respect to distance from mineralization and the imposition of elemental zoning within a deposit (Figure 7).

The understanding of the arsenopyrite lattice stability may be rationalized by the use of two “end-member” models: the ionic model and the molecular orbital model. These two models describe chemical bonds in terms of purely ionic and covalent bonds, respectively. These models may be implemented to understand the degree of trace element incorporation in the arsenopyrite lattice.
The ionic model describes a mineral lattice of cations and anions rigidly bound by electrostatic attraction with no sharing of electrons. The likelihood of an element substituting into one of the lattice sites may be assessed by comparison of the charge and ionic radius between the substituent and the element it replaces. The substituent should have the same charge as the lattice ion that it is replacing in order to stabilize the overall charge of the lattice. Additionally, the substituent ion should also have a similar or smaller ionic radius than the ion which it is substituting for in order to be able to fit into the lattice.

There is only a small difference between the electronegativities of sulfur, arsenic, and iron. Consequently, bonding within arsenopyrite is predominantly covalent and therefore the ionic model is incapable of fully explaining the crystal structure of, and the nature of substitution in, sulfide minerals (Pauling, 1960). The molecular orbital model describes the covalent bonding of the components in arsenopyrite and the various energy levels of the valence electrons. The energy levels of the valence orbitals for Fe, S, and As in arsenopyrite are detailed in Figure 17. This image describes the energy levels of electrons involved in the covalent bonds (shaded boxes) and the non bonding orbitals (empty boxes). Using the molecular orbital model as a guide, a trace element may readily replace a lattice element if it has the same (or similar) number of valence electrons and a similar electron cloud radius to the element it is replacing (such elements include; Ru, Os, Co, Rh, Ir). In this manner the total number of electrons involved in bonding is maintained; and all electrons are at a low energy level (which is thermodynamically favourable).
Figure 17. A schematic electron energy band diagram for arsenopyrite. The numbers in square brackets represent the total number of electrons that can fill the orbital. The shaded orbitals represent orbitals that are fully filled. Note that one of the Fe d orbitals parallel to the c-axis (a\|) is split into a metallic Fe-Fe bonding (lower energy) and non-bonding orbital (higher energy) (Goodenough, 1972).

1.5 Gold Deposit Exploration

The discovery of new orebodies is essential in maintaining the mining industry and to increase profits for mining companies. Therefore, it is no surprise that mining companies will invest millions of dollars in exploration to ensure their long term profitability (Mudd, 2007). The exploration for new gold orebodies or deposits involves elucidation of the tectonic, structural, and geological settings by geophysical and remote sensing means. The prospective area then undergoes either initial geochemical, geophysical, or shallow drilling exploration protocols. If these results continue to be positive then an intensive drilling regime may be justified in order to confirm mineralization. The exploration for new orebodies may take several months to several years depending on individual circumstances and this may involve extensive sampling and drilling of many kilometres of rock, costing millions of dollars. It is therefore of significant interest to mining
companies to reduce exploration costs and to increase the accuracy and efficiency of the exploration protocols. Consequently, numerous research projects have been undertaken in order to develop new methods and technologies focused on the exploration for gold deposits (Paterson and Hallof, 1991, Der Meer and Bakker, 1998, Kelley, 2006).

In the exploration for orogenic gold deposits the initial geophysical data is analysed to determine if the tectonic, structural, and geological settings are potentially suitable for gold mineralization (Duuring, 2007). The large scale geophysical exploration techniques may involve traverses using a plane or a helicopter which measure the gravity, residual magnetism, induced polarity, and/or electromagnetic properties of a large area (Paterson and Hallof, 1991). Analysis of the geophysical data reduces the area in which the gold deposit may exist to a “camp” up to several tens of square kilometres in surface area.

Surface geochemical exploration protocols are implemented after geophysical techniques have indicated the potential for gold mineralization in target areas (Reis, 2001). Surface geochemistry typically involves the analysis of surface material for the presence of gold and associated indicator elements (Zeegers and Leduc, 1991). Following this exploration phase, targeted drilling may be recommended to test an anomaly and to define any possible orebodies (Assibey-Bonsu and Krige, 2003). Bulk samples (100-2000 g) of rock chips, sediments or alluvial material are collected at regular intervals over a prospect licence and are assayed using one or more of the following common geochemical analytical techniques: lead fire assay (Au), bulk leach extraction of gold (Au), bulk leach aqua regia (Au), partial leach (elements in sulfide minerals), and/or full dissolution (all elements) (Zeegers and Leduc, 1991). These geochemical protocols require the gold mineralization to be close to the surface to provide analytical data with high enough analyte concentrations to be distinguishable from the regional background for the specific
element or elements of interest. If mineralization is buried beyond a few tens of metres (occasionally up to 100 m) then it is rare that analyte concentrations will be present above background (Eilu and Groves, 2001, Christie, 2003, Reis, 2001). Under these conditions, deeply buried orebodies can be missed as they have no significant surface expression in terms of elevated trace element concentrations.

Approximately three quarters of Australia is sterile to conventional geochemical exploration techniques as the Tertiary or Quaternary sedimentary units mask the \textit{in situ} rocks below, making it difficult to use current geochemical techniques to explore for gold deposits buried beneath the regolith (Anand, 2002). The majority of the Yilgarn Craton is covered with regolith (Eilu and Groves, 2001) averaging in the tens of metres in thickness and may be up to kilometres deep in some parts of Western Australia (Smith, 1996). In the last few decades more obscured gold deposits are being discovered, especially with alternative exploration techniques (Kelley, 2006). The imposition of geochemical sterility by regolith in Western Australia limits exploration initiatives largely to areas of exposed \textit{in-situ} rocks and to areas where selective leaching techniques may be applied (Chao, 1984). However, this latter methodology is prone to producing ambiguous or difficult to interpret data. Consequently, Western Australia is a prime target for finding new gold deposits with geochemical exploration protocols that are not dependant on obvious surface expression and are effective at distances beyond the obvious mineral and chemical limits of an orebody.

1.6 Research Objectives

The project detailed in this thesis seeks to investigate if the unique chemical signatures of arsenopyrite samples, present in the primary depositional environment, may be used to develop a new geochemical exploration protocol which may discover buried and blind
lode-gold orebodies. If successful, this research will facilitate exploration initiatives to assist in the discovery of buried and blind gold deposits that are currently difficult or impossible to locate using current exploration protocols. The exploration protocols developed in this research will focus on analyzing the trace element assemblages in arsenopyrite with a secondary emphasis on the analysis of mercury isotopes in whole rock samples in order to determine if any correlations can be made to geological features. This is based on the initial findings of the unpublished research from Stewart and Watling, 2009 and the earlier work of Watling (Watling, 1972, Watling et al., 1972, Watling, 1974).

1.6.1 Arsenopyrite LA-ICP-MS

Arsenopyrite is one of the most appropriate minerals for the trace element analysis of a mineral associated with orogenic (and other styles) gold mineralization (section 1.4). This mineral has been documented to contain significant concentrations of trace elements (King, 2002) and therefore has the potential to be used to assess the physicochemical conditions of the arsenopyrite-forming fluid during the period of gold deposition. Laser Ablation-Inductively Coupled-Plasma-Mass Spectrometry (LA-ICP-MS) was used to determine the trace element assemblages present within arsenopyrite crystals.

The development of exploration protocols using arsenopyrite trace element analysis focused on developing correlations between the arsenopyrite trace element assemblages and five geological phenomena. The analysis and interpretation of arsenopyrite trace element data was undertaken to link the resource and deposit type, together with the camp endowment and the morphology of the deposit. It was envisaged that this research would potentially lead to the development of a suite of arsenopyrite assemblages that could be used for:

1. Identifying the resource type
2. Identifying the gold deposit type or style
3. Identifying the deposit camp signature
4. Predicting the deposit gold endowment
5. Determining variations in the mineral chemistry within a deposit

1. Identifying the resource type

The protocols developed during this research can be used for identifying the difference in arsenopyrite trace element assemblages between systems that precipitate gold and other systems which are unrelated to gold mineralization. The significant chemical differences in the arsenopyrite forming fluids should theoretically result in a significant difference in trace elemental assemblages in arsenopyrite formed in either of the systems (Huston et al., 1995). Consequently, interpretation of the trace element assemblages of an unknown arsenopyrite sample should be able to be used to confirm or refute the probability of existence of nearby gold mineralization. It is also envisaged that the analysis and interpretation of arsenopyrite trace element assemblage data from arsenopyrite samples from non-gold deposits may be used to determine the ore resource type.

2. Identifying deposit type

Deposit types differ in terms of geology and fluid chemistry resulting in differences in the whole rock elemental assemblages (Robert et al., 1997). Theoretically this difference will be reflected by the differences in trace element chemistry of arsenopyrite between classes. It has been suggested in previous work that the nature of the ore fluid may be used as a discriminator between deposit types (Groves, 1998). Consequently, it is theoretically possible that identification and interpretation of the trace element association patterns present in arsenopyrite can be used to identify the nature of the ore fluid and hence may subsequently be used to determine the deposit type.
3. Identifying the deposit camp signature

Within an orogen a number of separate areas, typically defined by geological structure and lithology, may be amenable to gold mineralization. The lithology of the host rock and the hydrothermal fluid source will differ physicochemically between the different deposit camps present within the same orogen. The difference in physicochemistry may lead to slight differences in the arsenopyrite trace element assemblage that may be used to define different gold deposit camps.

4. Predicting the endowment of a deposit

Gold deposits have significantly varying endowments and the early prediction of the potential gold endowment in a hydrothermal system is of significant value in early exploration regimes as this information is essential in improving exploration and development stage decision making. The more well endowed deposits are believed to be the product of a number of conditions that are highly favorable to gold concentration and precipitation and/or the product of multiple fluid depositional events (Hodkiewicz, 2003). It is likely that multiple mineralizing events and/or the coincidence of geochemically favorable conditions for gold mineralization, may affect the trace element chemistry of arsenopyrite forming synchronously with gold deposition. A relationship may be observed between deposit endowment and arsenopyrite trace element assemblages. If such a relationship exists then the analysis and interpretation of trace element assemblages in arsenopyrite samples may be used to predict, with a higher degree of certainty, the endowment of a gold deposit.

5. Determining the chemical morphology of the deposit

Alteration of the country rock by the ore forming process varies with distance from mineralization. The changes in the mineralogy and chemistry of the rock are caused by
changes in the physicochemical conditions of the fluid in contact with it during mineral precipitation or dissolution (Ridley and Diamond, 2000, Lowell, 1970, Zoheir and Qaoud, 2008). Physicochemical changes in the ore fluids may therefore translate into changes in the arsenopyrite trace element assemblage. Sulfides associated with lode-gold deposits have been previously investigated and the results demonstrate evidence for fluid chemistry variation as a function of distance from mineralization (Belcher, 2004). Therefore, analysis of trace element assemblages in an unknown arsenopyrite sample may be used to predict the proximity of the analysed arsenopyrite to gold mineralization and indeed the highly sought after primary mineralising conduit.

1.6.1.1 Analytical Techniques

The trace element assemblages of arsenopyrite will be determined using LA-ICP-MS in order to obtain the best accuracy, precision, and sampling efficiency possible. Laser ablation was selected over dissolution as the sample introduction method, due to the ability to better assess the homogeneity and the representativeness of the sample material prior to introduction into the ICP-MS. This is a result of being able to sample micrograms of material with a high degree of sampling control and precision using laser ablation, compared to milligrams of material being required for dissolution (commonly with significant amounts of this sample being contaminated by other nearby minerals or inclusions).

Multiple rock samples containing arsenopyrite crystals were selectively removed from diamond drill cores, ore facings, or samples from museum collections which were taken from a wide variety of deposits around Australia and the world. These samples were identified and catalogued prior to being cut and polished in order to present arsenopyrite crystals which were then analysed using Laser Ablation-Inductively Coupled Plasma-
Mass Spectrometry (LA-ICP-MS). A “Neodymium doped Yttrium Aluminium Garnet” (Nd:YAG) laser operating at the fifth harmonic wavelength of 213 nm was used to ablate the samples. The ablated debris was carried into a plasma torch where the sample material was ionized and the resulting ions were transported into a quadrupole mass spectrometer where separation and detection of the ions was achieved based on variations in their mass to charge ratio, and the abundance of each analyte was recorded in terms of counts per second. Sampling protocols and laser ablation methodology are described in Chapter 2.

The direct multi-element analysis of sub-millimetre solid materials can be undertaken using laser ablation coupled to a mass spectrometer (Fryer, et al., 1995, Mason, 2001). This analytical technique was first developed in 1985 (Gray, 1985) and is now an accepted and preferred analytical technique for the rapid determination of elemental concentrations in a wide variety of sample materials (Becker, 2002, Gaspar et al., 2008). This system is capable of producing data with extremely high sensitivity, precision, and accuracy. LA-ICP-MS analysis is used in preference to a Sensitive High Resolution Ion Micro Probe (SHRIMP) system due to faster sampling and data collections times. Additionally, LA-ICP-MS is used in preference to an Energy Dispersive X-Ray Fluorescence (EDXRF) system because of significantly improved detection limits and the significantly lower sample masses required.

The “Counts Per Second” (CPS) trace element data collected from the analysis of arsenopyrite will not be converted into concentrations of elements within the arsenopyrite lattice as there is no matrix matched standard (which can account for the ablation of different mineral faces and inhomogeneities) available for arsenopyrite which retains an acceptable level of accuracy and precision and may be considered “fit for purpose”. Additionally, multiple crystal phases and slight differences in crystal hardness will
ultimately affect the amount of material being ablated and hence elemental response and it is not possible to account for these variations in transport mass. Instead the CPS data generated from the LA-ICP-MS has been normalized by comparison of the elemental response to Fe which is used as an internal standard for arsenopyrite. In this manner, samples of arsenopyrite with an approximately stoichiometric concentration of Fe may be compared to each another in the absence of fully quantitative data.

1.6.2 Mercury Isotope Analysis

It has been observed from previous studies that elemental mercury isotopically fractionates within an ore depositional environment, an effect which occurs in response to changes in various physical conditions within the environment (Ozerova, 1971, Lentz, 2005). Additionally, mercury-containing compounds have been proven to vary in concentration within a base metal deposit as a result of various physiochemical conditions within that deposit (Watling, 1974). Therefore, the possibility exists that there will be variations in mercury isotope ratios in the compounds with respect to the distance of the occurrence of the compound from the centroid of an orebody. By analysing and identifying compound specific isotopic patterns within a deposit it may be possible to use this technique in greenfields exploration to better understand the morphology of a deposit and to potentially ascertain the location of the main areas of gold mineralization within a defined area. Consequently, a secondary objective of this thesis was designed as an attempt to determine “proof of concept” of this hypothesis.
2.0 EXPERIMENTAL

2.1 Samples

2.1.1 Sample Collection

Unless otherwise stated, the arsenopyrite samples were collected from rock material which was removed from diamond drill cores in regions that had intersected an orebody or from rocks collected from ore facings in existing orebodies. These samples were collected by Mr. James I. Stewart during site visits (Stewart, 2009). Some of the samples were collected from other areas within a deposit and they are defined by specific coordinates as detailed in section 2.1 and in Appendix A-1 and E-2. It should be noted that the samples investigated in this thesis are limited to those from the personal collection of Mr. J. I. Stewart and those requisitioned from various other archives. Therefore, it was difficult to retrieve additional samples as many of the mines are no longer in operation.

2.1.2 Sample Information

2.1.2.1 Gold Deposits

The majority of the arsenopyrite samples that have been investigated in this project were collected from gold deposits within Australia. The majority of these deposits are Archean greenstone-hosted systems from Western Australia. Other samples have been collected from Proterozoic gold deposits in the Northern Territory and Phanerozoic deposits from Victoria. In addition, several dozen samples were also collected from the Homestake (USA) and Hemlo (Canada) deposits. A brief description of the deposits that were investigated in this thesis are summarised in Table 1.
Table 1. *A brief description of the gold deposits investigated in this project. Information includes; the number of arsenopyrite samples (#), the location, and the age of the deposit (which is indicated as either Archean (A), Proterozoic (Pr), or Phanerozoic (Ph)).*

<table>
<thead>
<tr>
<th>Deposit</th>
<th>#</th>
<th>Location</th>
<th>Age</th>
<th>Deposit</th>
<th>#</th>
<th>Location</th>
<th>Age</th>
</tr>
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<td>A</td>
<td>Harbor Lights</td>
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<td>Leonora</td>
<td>A</td>
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<tr>
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<td>Pr</td>
<td>Harlequin</td>
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<td>Norseman</td>
<td>A</td>
</tr>
<tr>
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<td>A</td>
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<td>A</td>
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<td>A</td>
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<td>A</td>
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<td>Ph</td>
<td>Mount Martin</td>
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<td>Kambalda</td>
<td>A</td>
</tr>
<tr>
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<td>Victoria</td>
<td>Ph</td>
<td>Mount Monger-</td>
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<td>A</td>
</tr>
<tr>
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<td>Ph</td>
<td>Mount Monger-</td>
<td>7</td>
<td>Kalgoorlie</td>
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<td>Pr</td>
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<td>Pr</td>
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<td>A</td>
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<td>Pr</td>
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<td>A</td>
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<tr>
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<td>Ph</td>
<td>Randalls-Anomaly</td>
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<td>Randalls</td>
<td>A</td>
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<td>Pr</td>
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<td>A</td>
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<td>Pr</td>
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<td>4</td>
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<td>A</td>
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<td>Pr</td>
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<td>SW Gneiss</td>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The Archean deposits from Western Australia were formed in the Yilgarn craton between 2.64-2.63 Ga ago, the majority of these deposits being formed within a period of 30 Ma (Groves, 1993). The geology of the Yilgarn craton mostly consists of greenstone belts displaying evidence of sub-greenschist to amphibolite facies metamorphism. These greenstone belts are typically folded, faulted, and are flanked by Archean granitic batholiths. Mineralization within the Yilgarn craton occurs syn- to post- peak
metamorphism with metamorphic dewatering and the sweating of magmatic intrusions being the source of fluids most likely to be responsible for gold transportation and subsequent mineralization (Mikucki, 1998).

The majority of study gold deposits formed during the Proterozoic period are deposits from the Pine Creek region, Northern Territory. The Pine Creek region consists of Proterozoic sediments and volcanics deposited onto an Archean granitic basement which was then subjected to low-medium grade metamorphism (Needham et al., 1988). In addition to the Pine Creek deposits, several dozen arsenopyrite samples from the Proterozoic Homestake deposit were also collected and investigated. All samples from the Proterozoic gold deposits analysed in this thesis were deposited in silicate-sulfide facies Banded Iron Formations (BIF) which are mostly composed of metamorphosed iron-rich sediments banded with shale, tuffaceous, and turbiditic sediments. The majority of the Proterozoic deposits investigated in this thesis were formed in regions of extensive folding and shearing, with gold being mostly hosted within sediments and the BIF.

The Phanerozoic gold deposits which were investigated in this thesis are from the central Victorian goldfields and are hosted in greenschist facies Ordovician to Early Devonian turbidites within the Lachlan Fold belt. The majority of mineralization occurred 440 Ma ago with lesser regional mineralizing events occurring between 420-400 and 385-365 Ma ago (Willman, 2007). Gold mineralization is predominantly associated with quartz veining and extensive arsenic enrichment (Gao and Kwak, 1997). The hydrothermal fluids responsible for mineralization have been interpreted to be generated in association with the devolatilization of Cambrian greenstones during greenschist facies regional metamorphism (Gao and Kwak, 1997).
Deposits where multiple arsenopyrite samples have been collected from numerous locations within a deposit or exploration licence are described briefly in the following sub-sections and in Appendix A-1.1. The descriptive detail given to these deposits in this section is essential for understanding how the arsenopyrite chemistry reflects the changes in the physicochemical conditions of the fluid as it travels within a depositional environment.

2.1.2.1.1 Homestake

The Homestake deposit is located at the northern end of the Black Hills, proximal to the town of Lead in South Dakota, USA (Appendix A-1.1.2.A). This super-giant deposit was discovered in 1876 and was continually mined up to 2002, producing a total of approximately 42 Moz of gold during its lifetime. This deposit lies within the transcontinental structural zone referred to as the Walker Lane Lineament. This structural zone is positioned at the intersection of the Superior Craton, Wyoming Craton, and the Central Plains Orogen (A-1.1.2.B). The orebodies of the Homestake deposit are located within tight anticlinal folds within the Homestake formation and are referred to as ledges. Each ledge is numbered sequentially in increasing order with respect to the distance south west from Main Ledge (Figure 18).
The mine stratigraphy of the Homestake gold deposit consists primarily of three geological formations deposited during the Proterozoic (Caddey et al., 1991). In chronological order these three formations are; Poorman (footwall), Homestake (preferred gold host), and Ellison (hangingwall). The Poorman formation is approximately 600 m thick and consists of phyllitic black shale, mudstone, and cherty layers (in addition to the poorly exposed Yates tholeiitic basalts). The Poorman formation is overlain by the Homestake formation which is 60-100 m thick and consists of quartz-
sideroplesite and/or chlorite schist altered to a cummingtonite-garnet schist in areas of higher metamorphic grade with ubiquitous pyrrhotite and intensely folded and cherty nodule beds. Overlying the Homestake Formation is the Ellison Formation which is approximately 900 m thick and consists of mostly quartzite and interbedded quartz-mica phyllites. The mine sequence was intruded during the Tertiary by a series of sub-alkaline trachytic volcanic dykes, sills, and laccoliths. These tertiary intrusions are also associated with epithermal style Au-Ag-Hg veins and manto-like deposits in Cambrian calcareous rocks.

Rock samples containing arsenopyrite were collected from various ledges (and the open-cut pit) within the Homestake mine and the location of these samples is described in Table 2. For the purposes of understanding the three dimensional positioning of each sample, they are given x, y, and z coordinates. The x, and y coordinates are the distance in terms of north-south and west-east (respectively) from an arbitrary point selected towards the outskirts of the deposit by the mine surveyors, and the z coordinates represents the height above sea level. Additionally, the nature, size, morphology, and abundance of arsenopyrite from the Homestake deposits are detailed in Appendix A-1.1.2.E.

Each of the ledges within the Homestake deposits were mined until the grade fell below approximately 5 g/t rendering it economically unfeasible to mine that particular ledge further. The ledges were explored to the fullest possible extent such that the grade and tonnage of the deposit could not be improved beyond that extent (Stewart, 2009). Therefore, an endowment has been calculated for each ledge based on the grade and tonnage of the ore extracted from the ledges as published (Table 3).
Table 2. Arsenopyrite samples collected from the Homestake deposit. The number of samples (# Aspy) from a particular location are recorded in terms of the ledge, the positioning within the ledge, and the x, y, z coordinates (Stewart, 2009).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th># Aspy</th>
<th>Ledge</th>
<th>x (m)</th>
<th>y (m)</th>
<th>z (m)</th>
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<td>ML</td>
<td>423</td>
<td>-571</td>
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<tr>
<td>N17B</td>
<td>5</td>
<td>15L</td>
<td>946</td>
<td>-2598</td>
<td>-262</td>
</tr>
<tr>
<td>N18B</td>
<td>3</td>
<td>15L</td>
<td>911</td>
<td>-2541</td>
<td>-264</td>
</tr>
<tr>
<td>14B</td>
<td>5</td>
<td>19L</td>
<td>650</td>
<td>-2851</td>
<td>-363</td>
</tr>
<tr>
<td>14Y</td>
<td>4</td>
<td>19L</td>
<td>657</td>
<td>-2859</td>
<td>-364</td>
</tr>
<tr>
<td>23-26F</td>
<td>1</td>
<td>19L</td>
<td>280</td>
<td>-2204</td>
<td>-88</td>
</tr>
<tr>
<td>56B</td>
<td>5</td>
<td>19L</td>
<td>55</td>
<td>-1716</td>
<td>-63</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>19L</td>
<td>310</td>
<td>-2748</td>
<td>-213</td>
</tr>
<tr>
<td>36BC</td>
<td>4</td>
<td>21L</td>
<td>498</td>
<td>-2143</td>
<td>-495</td>
</tr>
<tr>
<td>45-46WB</td>
<td>2</td>
<td>21L</td>
<td>503</td>
<td>-1761</td>
<td>-670</td>
</tr>
</tbody>
</table>

Table 3. The ore tonnage, average ore grade, and endowment of the Ledges in the Homestake deposit (Caddey et al., 1991, and Stewart, 2009).

<table>
<thead>
<tr>
<th>Ledge</th>
<th>Ore Tonnage (x10⁶)</th>
<th>Average Grade (g/t)</th>
<th>Endowment (Moz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Main Ledge</td>
<td>75</td>
<td>8.37</td>
<td>21</td>
</tr>
<tr>
<td>11 Ledge</td>
<td>8.8</td>
<td>7.87</td>
<td>2.3</td>
</tr>
<tr>
<td>15 Ledge</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
</tr>
<tr>
<td>19 Ledge</td>
<td>6.0</td>
<td>7.03</td>
<td>1.4</td>
</tr>
<tr>
<td>21 Ledge</td>
<td>8.9</td>
<td>8.34</td>
<td>2.4</td>
</tr>
</tbody>
</table>

2.1.2.1.2 Mount Porter

The Mount Porter prospect is located at approximately 175 km South-South East of Darwin in the Northern Territory, Australia (Figure 19). This system is located east of the Pine Creek shear system and is present at the border between Proterozoic mafic units (including the Koolpin Formation) and the Cullen granitic stock (Appendix E-2.1 and A-1.1.2.A). The deposit consists of three major formations present in ascending
stratigraphical order: Koolpin (BIF), Gerowie Tuff (siliceous tuffs), and the Mt Bonnie Formation (the latter being a mix of the previous two stratigraphic units inter-bedded with greywackes and sediments from the overlying Burrell Creek formation) (Appendix A-1.1.2.A). The Koolpin formation is characterised by alternating layers of carbonaceous shales, mafic sills (dolerite), and iron-silicates associated with sulfides. The Gerowie Tuff consists of white to black siliceous tuffs and tuffaceous siltstones. The folded stratigraphy was intruded by a granitic sub-stock of the Cullen batholith which has imposed a contact hornfels aureole of cordierite-kyanite-graphite-actinolite-chlorite. Gold mineralization is primarily hosted in the Koolpin formation with some minor gold anomalies detected in later cross-cutting dolerites and siliclastic sediments. The Mount Porter prospect was discovered in 1984 and extensive ore development work and feasibility studies were undertaken from 1992 to 1995. To date no mining has been carried out at this location, however, the project is estimated to have between 100,000 to 400,000 oz of contained gold in the system.

Figure 19. The regional setting of the Mount Porter Deposit in relation to the Pine Creek region, Northern Territory, Australia (Stewart, 1996).
The samples from the Mount Porter prospect license were collected from exploratory diamond drill cores (labelled MP 225, 227, 228, 230, and 231) within the deposit and from nearby orebody exploration drilling (Figure 20). The drilling targets and the depth that the samples were collected from were marked on the sample and the sample positioning and the equivalent gold assay results are described in Table 4. The drill core logs and assays are detailed in Appendix E-2.1.

Table 4. The locations of the arsenopyrite samples taken from the Mount Porter prospect. The Cartesian x and y coordinates are relative to the MP 225 diamond drill hole. The assayed gold concentration of the 1 m core log sections are measured in g/t, when detected.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>x(m)</th>
<th>y(m)</th>
<th>Depth (m)</th>
<th>Host rock</th>
<th>Au (g/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP 225 458.7m</td>
<td>0</td>
<td>0</td>
<td>458.7</td>
<td>Quartz Vein</td>
<td>0.31</td>
</tr>
<tr>
<td>MP 225 533.0m</td>
<td>0</td>
<td>0</td>
<td>533.0</td>
<td>Garnet Skarn</td>
<td>1.59</td>
</tr>
<tr>
<td>MP 227 163.8m</td>
<td>1040</td>
<td>251</td>
<td>163.8</td>
<td>Chlorite</td>
<td>0.00</td>
</tr>
<tr>
<td>MP 227 177.8m</td>
<td>1040</td>
<td>251</td>
<td>177.8</td>
<td>Dolerite</td>
<td>0.44</td>
</tr>
<tr>
<td>MP 227 178.5m</td>
<td>1040</td>
<td>251</td>
<td>178.5</td>
<td>Dolerite</td>
<td>0.375</td>
</tr>
<tr>
<td>MP 227 229.5m</td>
<td>1040</td>
<td>251</td>
<td>229.5</td>
<td>Dolerite</td>
<td>0.34</td>
</tr>
<tr>
<td>MP 227 252.0m</td>
<td>1040</td>
<td>251</td>
<td>252.0</td>
<td>Dolerite</td>
<td>0.00</td>
</tr>
<tr>
<td>MP 228 150.3m</td>
<td>436</td>
<td>404</td>
<td>150.3</td>
<td>Dolerite</td>
<td>0.00</td>
</tr>
<tr>
<td>MP 228 150.5m</td>
<td>436</td>
<td>404</td>
<td>150.5</td>
<td>Dolerite</td>
<td>0.00</td>
</tr>
<tr>
<td>MP 228 209.0m</td>
<td>436</td>
<td>404</td>
<td>209.0</td>
<td>Quartz Vein</td>
<td>0.58</td>
</tr>
<tr>
<td>MP 228 222.5m</td>
<td>436</td>
<td>404</td>
<td>222.5</td>
<td>BIF</td>
<td>0.00</td>
</tr>
<tr>
<td>MP 228 244.0m</td>
<td>436</td>
<td>404</td>
<td>244.0</td>
<td>Chlorite</td>
<td>0.96</td>
</tr>
<tr>
<td>MP 228 250.1m</td>
<td>436</td>
<td>404</td>
<td>250.1</td>
<td>BIF</td>
<td>0.29</td>
</tr>
<tr>
<td>MP 228 252.5m</td>
<td>436</td>
<td>404</td>
<td>252.5</td>
<td>BIF</td>
<td>0.29</td>
</tr>
<tr>
<td>MP 228 259.4m</td>
<td>436</td>
<td>404</td>
<td>259.4</td>
<td>BIF</td>
<td>0.28</td>
</tr>
<tr>
<td>MP 228 337.1m</td>
<td>436</td>
<td>404</td>
<td>337.1</td>
<td>Chlorite</td>
<td>0.00</td>
</tr>
<tr>
<td>MP 230 98.4m</td>
<td>261</td>
<td>379</td>
<td>90.4</td>
<td>-</td>
<td>2.23</td>
</tr>
<tr>
<td>MP 230 125.1m</td>
<td>261</td>
<td>379</td>
<td>125.1</td>
<td>BIF</td>
<td>0.99</td>
</tr>
<tr>
<td>MP 230 192.2m</td>
<td>261</td>
<td>379</td>
<td>192.2</td>
<td>-</td>
<td>0.46</td>
</tr>
<tr>
<td>MP 230 197.0m</td>
<td>261</td>
<td>379</td>
<td>197.0</td>
<td>-</td>
<td>0.46</td>
</tr>
<tr>
<td>MP 231 163.5m</td>
<td>1111</td>
<td>21</td>
<td>163.5</td>
<td>Quartz Vein</td>
<td>0.12</td>
</tr>
<tr>
<td>MP 231 215.5m</td>
<td>1111</td>
<td>21</td>
<td>215.5</td>
<td>Quartz Vein</td>
<td>0.00</td>
</tr>
<tr>
<td>MP 231 320.2m</td>
<td>1111</td>
<td>21</td>
<td>320.2</td>
<td>-</td>
<td>0.00</td>
</tr>
</tbody>
</table>
Figure 20. A map depicting the locations of the diamond drill sites in the Mount Porter prospect license. Assays for Au and As have been included along with significant gold intercepts and areas of significant gold mineralization (Stewart, 1996).

2.1.2.1.3 Boorara

The Boorara deposit is located in the Golden Ridge greenstone belt approximately 15 km East-South East of Kalgoorlie in Western Australia. The deposit was briefly mined and yielded approximately 30,700 oz of gold. Subsequently the deposit has undergone extensive economic appraisals and it has been calculated that this deposit has a sub-economic reserve of approximately 90,000 oz of gold. This gives the deposit a total endowment of 120,700 oz of contained gold.
The Boorara deposit consist of massively carbonated, layered, and fractured dolerite, with the vein to alteration ratio of 1:100 (being similar in lithostructural setting to Paddington except the latter has an endowment approaching 5 Moz gold). Gold mineralization is contained within quartz vein stock works within the host rock greenstone sequence (Appendix A-1.1.3). The location, associated lithology, and gold assay of the nearby lithology of the arsenopyrite samples (donated by Fimiston Mining Ltd) which were collected from the Boorara deposit are detailed in Table 5. The arsenopyrite samples are predominately hosted in dolerite (grading upward from ultramafic composition to quartz leucodolerite) of varying grain sizes, which is indicated in Table 5. Three arsenopyrite samples were collected from more intensely altered vein-proximal dolerites which are dominant in chlorite with minor carbonate-sericite. Rock samples have been collected from the B7 and B10 diamond drill core, and portions of these samples were fire assayed to measure the concentration of gold (g/t) in 1 or 2 m intervals (Appendix E-2.1).

**Table 5.** The location of the arsenopyrite samples collected from the B5, B7, and B10 diamond drill cores from the Boorara deposit.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Hole</th>
<th>Depth (m)</th>
<th>Host rock</th>
<th>Au (g/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B5 (a) 117.5m</td>
<td>B5</td>
<td>117.5</td>
<td>Coarse Grained Dolerite</td>
<td>-</td>
</tr>
<tr>
<td>B5 (b) 117.5m</td>
<td>B5</td>
<td>117.5</td>
<td>Coarse Grained Dolerite</td>
<td>-</td>
</tr>
<tr>
<td>B5 122.4m</td>
<td>B5</td>
<td>122.4</td>
<td>Coarse Grained Dolerite</td>
<td>-</td>
</tr>
<tr>
<td>B5 124.3m</td>
<td>B5</td>
<td>124.3</td>
<td>Medium Grained Dolerite</td>
<td>-</td>
</tr>
<tr>
<td>B5 129.5m</td>
<td>B5</td>
<td>129.5</td>
<td>Fine Grained Dolerite</td>
<td>-</td>
</tr>
<tr>
<td>B5 130.0m</td>
<td>B5</td>
<td>130.0</td>
<td>Fine Grained Dolerite</td>
<td>-</td>
</tr>
<tr>
<td>B5 135.4m</td>
<td>B5</td>
<td>135.4</td>
<td>Fine Grained Dolerite</td>
<td>-</td>
</tr>
<tr>
<td>B7 150.8m</td>
<td>B7</td>
<td>150.8</td>
<td>Medium Grained Dolerite</td>
<td>1.45</td>
</tr>
<tr>
<td>B7 164.0m</td>
<td>B7</td>
<td>164.0</td>
<td>Coarse Grained Dolerite</td>
<td>3.84</td>
</tr>
<tr>
<td>B7 173.8m</td>
<td>B7</td>
<td>173.8</td>
<td>Fine Grained Chloritic Dolerite</td>
<td>3.79</td>
</tr>
<tr>
<td>B7 180.2m</td>
<td>B7</td>
<td>180.2</td>
<td>Fine Grained Chloritic Dolerite</td>
<td>0.76</td>
</tr>
<tr>
<td>B10 83.05m</td>
<td>B10</td>
<td>83.05</td>
<td>Medium Grained Dolerite</td>
<td>1.26</td>
</tr>
<tr>
<td>B10 104.2m</td>
<td>B10</td>
<td>104.2</td>
<td>Fine Grained Dolerite</td>
<td>0.81</td>
</tr>
<tr>
<td>B10 105.5m</td>
<td>B10</td>
<td>105.5</td>
<td>Fine Grained Dolerite</td>
<td>0.59</td>
</tr>
<tr>
<td>B10 108.8m</td>
<td>B10</td>
<td>108.8</td>
<td>Fine Grained Dolerite</td>
<td>1.04</td>
</tr>
<tr>
<td>B10 117.8m</td>
<td>B10</td>
<td>117.8</td>
<td>Fine Grained Chloritic Dolerite</td>
<td>0.03</td>
</tr>
</tbody>
</table>
2.1.2.2 Non-Gold

Arsenopyrite samples collected from regions of hydrothermal activity which were unrelated to gold mineralization are detailed in Table 6. A significant portion of these arsenopyrite samples were collected by J. I. Stewart from several magmatic hydrothermal deposits within the New England region, New South Wales, Australia. These samples were collected from orebodies at these deposits. Although many of the mines were closed over 80 years ago, the ore related arsenopyrites are easily reconciled as being associated with ore-stage mineralization due to the other sulphide ore stage minerals (eg. argentiferous galena, sphalerite, and cassiterite). In addition, single crystals of arsenopyrite have been provided by Peter Downes from the Western Australian Museum and Allan Pring from the South Australian Museum which were collected from orebodies of primary economic ore deposits unrelated to gold mineralization.

Table 6. A brief description of the non-gold deposits analysed in this project. Information includes the number of arsenopyrite samples, the deposit location, and the primary ore assemblage.

<table>
<thead>
<tr>
<th>Deposit</th>
<th># Asp</th>
<th>Location</th>
<th>Primary Ore</th>
</tr>
</thead>
<tbody>
<tr>
<td>Broken Hill</td>
<td>1</td>
<td>New South Wales, Australia</td>
<td>Pb-Zn</td>
</tr>
<tr>
<td>Callington</td>
<td>1</td>
<td>South Australia, Australia</td>
<td>Cu</td>
</tr>
<tr>
<td>Colebrook Hill</td>
<td>1</td>
<td>Tasmania, Australia</td>
<td>Cu</td>
</tr>
<tr>
<td>Collisions</td>
<td>9</td>
<td>New South Wales, Australia</td>
<td>Ag</td>
</tr>
<tr>
<td>Giants Den</td>
<td>1</td>
<td>New South Wales, Australia</td>
<td>Sn-W</td>
</tr>
<tr>
<td>King Conrad</td>
<td>5</td>
<td>New South Wales, Australia</td>
<td>Ag</td>
</tr>
<tr>
<td>Ottery</td>
<td>9</td>
<td>New South Wales, Australia</td>
<td>Sn-W</td>
</tr>
<tr>
<td>Panasquera</td>
<td>1</td>
<td>Castelo Branco, Portugal.</td>
<td>Sn-W</td>
</tr>
<tr>
<td>Renison Bell</td>
<td>2</td>
<td>Tasmania, Australia</td>
<td>Sn-W</td>
</tr>
<tr>
<td>Rivertree</td>
<td>13</td>
<td>New South Wales, Australia</td>
<td>Ag</td>
</tr>
<tr>
<td>Talisker</td>
<td>1</td>
<td>South Australia, Australia</td>
<td>Ag</td>
</tr>
<tr>
<td>Trepcia</td>
<td>1</td>
<td>Mitrovica, Kosovo</td>
<td>Pb-Zn</td>
</tr>
<tr>
<td>Tulloch</td>
<td>8</td>
<td>New South Wales, Australia</td>
<td>Ag</td>
</tr>
<tr>
<td>Webbs Consuls</td>
<td>5</td>
<td>New South Wales, Australia</td>
<td>Ag</td>
</tr>
<tr>
<td>Yaoganxian</td>
<td>1</td>
<td>Hunan Province, China</td>
<td>Sn-W</td>
</tr>
</tbody>
</table>

Professor John Watling has personally collected two rocks samples containing arsenopyrite from regions unrelated to any form of ore mineralization. The first sample (labelled JW) was collected from a metamorphic province in Kyrgyzstan, approximately
200 km South West of Bishkek. The second sample (labelled JC) was collected from a metamorphic terrane located in the south of Arizona, USA.

2.2 Instrumentation

2.2.1 Inductively Coupled Plasma-Mass Spectrometer

*Name:* 7500cs Inductively Coupled Plasma Mass Spectrometer

*Manufactured by:* Agilent Technologies Pty Ltd

*Address:* 5301 Stevens Creek Boulevard, Santa Clara, CA 95051, USA

*Figure 21. Agilent 7500 inductively coupled plasma mass spectrometer.*
2.2.2 Laser Ablation System

*Name:* NEW WAVE UP-213 Laser Ablation System

*Manufactured by:* Electro Scientific Industries, Inc.

*Address:* 13900 NW Science Park Drive, Portland, OR 97229-5497, USA

![Figure 22. A) An image of the laser ablation system. B) A close up of the ablation cell with the laser (encased in orange plastic) above it.](image)

2.2.3 Scanning Electron Microscope (SEM)

*Name:* 1555 VP-FESEM

*Manufactured by:* Carl Zeiss

*Address:* Carl-Zeiss-Strasse 22, 73447 Oberkochen, Germany

2.2.4 Electron Probe Micro-analyser (EPMA)

*Name:* 8530F Microprobe

*Manufactured by:* JEOL Ltd.

*Address:* 1-2, Musashino 3-chome Akishima, Tokyo 196-8558, Japan
2.3 Experimental Procedure

2.3.1 Sample Preparation

Many of the samples collected by J. I. Stewart (section 2.1.1) were already mounted in resin and prepared for LA-ICP-MS analysis, prior to them being received. These prepared samples only required polishing with silicon carbide lapping paper. The majority of these prepared samples had previously been analysed in an unpublished experiment (Stewart and Watling, 2009). Arsenopyrite samples collected from drill core and rock material required significantly more preparation, and the preparatory steps are detailed in this section.

The samples prepared for LA-ICP-MS analysis were later used for electron probe analysis after some additional preparation (detailed in section 2.3.1.2).

2.3.1.1 Arsenopyrite Sample Mounts

Samples already prepared by J.I. Stewart were labelled rock chips mounted in resin with one surface polished flat. The samples had oxidised during their storage and required polishing. These samples were first rinsed in MilliQ™ (18 MΩ) water and allowed to air dry. The flat surface displaying the arsenopyrite crystals were ground with 500, 1000, 1200 and then, 4000 Struers™ silicon carbide lapping paper using a South Bay Technology model 900 lapping machine. The samples were then placed in a beaker of MilliQ™ water and were then ultrasonicated for ten minutes using a Digitech Ultrasonic Cleaner, model YH-5410. The water was then drained from the beakers and fresh MilliQ™ water added. The sample mounts were ultrasonicated for a further 10 minutes. The samples were rinsed with MilliQ™ water and air dried on paper towel. The sample mounts were placed and sealed in labelled plastic bags.
The unmounted rock samples were prepared by cutting the rock using a diamond saw to produce rock portions with a useable face area no larger than 2 cm$^2$, with at least one arsenopyrite crystal exposed on the surface. The samples were then stored to be later mounted in resin. A 5 mm thick panel of glass approximately 1 m by 0.4 m was used as the base for the resin mounting. A coating of petroleum jelly at least 1 mm thick was distributed onto the surface of the glass. Up to 52 copper rings with a 3 cm diameter and 2.5 cm depth were lightly coated with petroleum jelly on the inner surface and then placed onto the jelly-covered glass panel. The rock samples which were cut by the diamond saw were then placed inside the copper ring so that the arsenopyrite surface was facing down towards the glass panel. A solution of 20 mL PVC resin and 0.4 mL peroxide catalyst were mixed together. This solution was then poured into the copper rings to approximately halfway up the mount. The resin was allowed to set for one hour and a small piece of paper detailing the sample number was then placed on top of the setting resin. An additional volume of resin solution was then added to the copper rings to bring the solution to the top of the ring. The resin was allowed to set for a period of 24 hours. The resin mounts were then removed from the copper rings and placed into a large plastic snap lock bag with 5 g of powdered pyroneg detergent solution and filled with tap water. The bag was vigorously shaken for at least 5 minutes and the solution was drained. Each sample mount was then cleaned with a paper towel soaked in a detergent solution to remove any petroleum jelly on the surface. The sample mounts were then allowed to dry. The flat surface displaying the arsenopyrite crystals was successively ground with 180, 360, 500, 1000, 1200, and then 4000 Struers™ silicon carbide sanding paper. The samples were placed in a beaker of MilliQ™ water and ultrasonicated for 10 minutes. The water was drained from the beakers and fresh MilliQ™ water added and the sample mounts were placed in the ultrasonic bath again for another 10 minutes followed by rinsing in
MilliQ™ water. The sample mounts were then left to air dry on a paper towel and subsequently placed and sealed in labelled plastic bags.

2.3.1.2 Electron Probe Sample Preparation

The polished arsenopyrite samples only required carbon coating to improve their electronic conductivity for electron probe analyses. Carbon coating was performed by the Centre for Microscopy Characterisation and Analysis at the University of Western Australia.

2.3.2 LA-ICP-MS Analysis

The ICP-MS instrument was tuned at the beginning of each analytical run in order to achieve optimum operating conditions. Tuning was performed by continually ablating a NIST 612 glass standard. During this period the ion beam was focused by adjusting the ion lenses. After this the analogue and pulse detectors were adjusted to ensure a semi-linear relationship between instrument response and isotopic concentration. Isotopic ratios for barium, cerium and thorium (together with their equivalent oxide and doubly ionized equivalent m/z ratios) were investigated in real time to optimize the system and overcome interferences from oxides and from doubly-ionized elements. The gas flow speed and gas composition were adjusted to reduce oxide interferences. Response ratios between high and low mass isotopes were investigated to observe potential mass bias. The voltages to the quadrupole and the ion lenses were adjusted to reduce any mass bias.

2.3.2.1 Spot Ablation Method

After instrument tuning, the samples were placed into the laser cell and held in place using Blutac™. The distance between the top of the sample and the base of the laser cell were adjusted to a consistent distance for all of the samples and all samples were levelled to
ensure that the sample surface was at right angles to the direction of the laser beam. The cell was purged with an Ar/He carrier gas for a period of 90 seconds prior to analysis commencing. The area of ablation on the sample was manually selected using the laser ablation software and data collection was initiated for 5 seconds with the laser switched off to obtain a background signal. This procedure also allows a baseline to be determined as a reference point for the subsequent analytical run. After the five seconds had elapsed, the laser was switched on and sample ablation commenced. After the 30 seconds of ablation the next sample location was selected and the procedure was repeated until all analytical sites on the sample had been ablated.

A set of standards were run regularly throughout a typical LA-ICP-MS analytical period of approximately eight hours. The NIST 610 standard was used to establish the optimum ablation conditions at the beginning of a sample run and then reanalysed every 45 minutes to facilitate drift correction throughout the day. A set of cross-over samples (samples that had been analysed in a previous run and were re-analysed in each current run) were analysed at the beginning, middle, and end of the analysis period. These samples were analysed in every analytical period throughout this study and their frequent analysis facilitated achieving reproducibility of data between runs. The ordering of the standards and cross-over samples was as follows:

- NIST 610 (3 ablation sites)
- Cross–over Samples (2 sites each)
- 3 Samples (10 ablation sites each)
- NIST 610 (3 ablation sites)
- 3 Samples (10 ablation sites each)

The sequence was repeated with the NIST 610 standard being re-analysed between each set of 3 samples.
2.3.2.2 Traverse Ablation Method

Initial setup for this procedure was identical to that described in Section 2.3.2.1. Following initial setup, the analytical sequence incorporated a 10 second Ar/He purge prior to an ablation period of 60 seconds. After the ablation of a single traverse line, the process was repeated for an additional 5-10 lines on each sample. After this the sample was removed from the laser cell and a new sample was placed into the cell. The cell was purged for 90 seconds and the procedure was repeated until all of the samples had been analysed.

2.3.3 Electron Probe Analysis

2.3.3.1 SEM

The carbon coated sample was placed onto the sample stage of the SEM. Two small strips of electrically conductive adhesive tape were used to attach the sample mount onto the stage. The chamber was evacuated to create a vacuum and the stage moved until an arsenopyrite crystal could be observed in the field of view. Visual assessment using backscattered electron detection determined the location of arsenopyrite crystals. The raster rate of the electron beam was reduced to produce a higher definition image, which was then saved onto the computer.

When using the Energy Dispersive X-ray (EDX) spectrometer, for either a spot analysis or for an elemental map of the arsenopyrite crystal, the stage was adjusted to create a flat surface with the relevant locations in focus. The spot analysis procedure was undertaken for a period of 60 seconds to generate a spectrum of the major and minor element assemblages of the selected arsenopyrite crystal.
2.3.3.2 EPMA

The carbon coated samples were placed into the sample stage of the EPMA. Each sample was secured to the sample stage and two small strips of conductive adhesive tape connected and secured the sample to the EPMA sample holder. The sample stage was moved in order to position a specific sample directly under the beam. Visual assessment using backscattered electron detection determined the locations of the arsenopyrite crystals. The elemental map function was selected and the map size and map positioning were determined by selecting a specific pixel size and number of pixels. The elements and their specific pixel dwell time were selected for each of the Wavelength Dispersive X-ray Spectroscopy (WDS) detectors. After data acquisition, the elemental maps were generated and could be manipulated to set the upper and lower response limit for the analysed elements.

2.3.4 Arsenopyrite Acid Digestion

A drill press equipped with a 1.4 mm diameter tungsten carbide drill bit was used to remove material from the arsenopyrite. The material collected was at least 20 mg in mass (with a desirable mass of 100 mg). This material was added to pre-weighed 50 mL polytetrafluoroethylene (PTFE) beakers. The mass of the beaker and material were recorded. Approximately 50 mg of an in-house reference material of crushed chalcopyrite, accurately weighed to four decimal places, was added to another two pre-weighed beakers.

Beakers were placed on a hotplate (at room temperature) together with three empty PTFE beakers to be used as blanks. Two millilitres of redistilled nitric acid were added to each beaker and PTFE watch glasses were placed on top of each beaker (convex side down). The hotplate was switched on and set to 175 ºC. The samples were allowed to digest for
a minimum of 3 hours, after which time 2 mL of distilled hydrochloric acid were added to each of the beakers. The samples were allowed to digest for a further two hours, after which time the watch glasses were removed and their convex surface washed into the beaker using deionised water. The samples were then evaporated until the contents reached a volume of approximately 1 mL. Approximately 100 µL re-distilled hydrochloric acid were then added to each beaker and the solutions were quantitatively transferred into pre-weighed 15 mL plastic centrifuge tubes using MilliQ™ water until a volume of approximately 10 mL had been reached. Each centrifuge tube was weighed and the mass of solution calculated.

2.3.5 Solution ICP-MS Analysis

Samples were diluted tenfold using MilliQ™ water prior to analysis. The analytical solutions were ordered so that calibration standards were placed first followed by three 2% nitric acid solutions, three deionised water blanks, analytical blanks, the chalcopyrite standard, and finally the sample solutions. Isotope concentrations were calculated by comparison to the standards run at the beginning of the data acquisition procedure.

2.4 Analytical Methodology

Normally ICP-MS is operated in solution mode where a sample solution is nebulised into a fine mist and is subsequently ionised by an argon plasma. However, in this thesis the ICP-MS instrumentation is used primarily in conjunction with a laser ablation unit. In this mode of operation, a frequency quadrupled Nd:YAG laser (operating at 213 nm) is used to directly ablate a solid sample (Figure 23). The resulting mist of sample debris (ejecta) created by the laser ablation is transported by an Ar:He (54:46%) carrier gas stream into the central channel of a “torch” assembly that contains and maintains an argon plasma. The helium leads to ablation with a smaller average particle size of ejecta and these
particles are more readily ionised in the plasma and also tend not to experience as significant fractionation effects in the plasma compared to larger particles (Horn, 2003). As a result, an Ar-He carrier gas was used in this thesis to provide superior sensitivity in the ablation of the arsenopyrite compared to lower concentration He mixtures, or pure Ar gas (Mason, 2001, Gunther, 1999). The torch consists of three annular quartz tubes: outer, intermediate, and injector. The main plasma is contained within the outer quartz tube and is supported by an argon flow of up to 13 L per minute, while an intermediate flow of argon, directed at the base of the plasma, ensures that there is no coupling of the plasma with the nebulizer capillary which is used to introduce the ablated sample debris into the plasma. The plasma is maintained using a water-cooled Radio-Frequency (RF) induction coil. Ionisation of the argon is initiated by a spark from a Tesla coil, and the resulting ions (and their electrons) interact with the fluctuating magnetic field created by the RF coil. This interaction creates a closed annular flow of ions and electrons, thus creating a semi-stable plasma that achieves a temperature of approximately 7100-8150 K in the plasma core (Houk, 2001). The sample is introduced into the base of the plasma through the injector tube and passes through the core of the plasma where the sample is heated and ionized by the plasma. The stream of ions produced from the plasma are passed through a series of sampling cones and ion lenses to create a tight and focused beam of ions. A collision cell was not used during this thesis and therefore the resulting beam of ions are introduced straight into the quadrupole mass filter. The quadrupole mass filter consists of four molybdenum rods held parallel in a vacuum with opposing pairs of rods having either a Direct Current (DC) or Radio Frequency (RF) voltage applied to them which are independently ramped to both sets of rods. This results in a situation where, at any given point during the quadrupole cycle, an ion with a specific mass to charge ratio has a resonance frequency which is stable within the central core of the quadrupole, and will pass directly into the detector. At this particular relationship between the voltages applied
to the DC and RF rods, all other ions of a different mass to charge ratio (m/z) have unstable resonance frequencies, consequently, they will cascade outwards from the central channel of the quadrupole and be pumped to waste. By varying the RF and DC voltages in a controlled sequence, the specific m/z ratio ions of all elements can be sequentially “filtered”; potentially allowing for the entire periodic table to be sequentially separated by the quadrupole. Once the ion beam has passed through the quadrupole, it passes into a discrete dynode electron multiplier which translates the number of ions into an electrical signal. The electron multiplier will count each electron it encounters as a "pulse" and requires a short period of time (17.5 ns) to return back to the original passive state (this is known as dead time) (Held, 1999). The analogue counter will start to measure the electron responses when the number of electrons (and the associated recovery time) becomes too large for the pulse analyser to count. Calibration of the equipment is therefore required to convert the signal produced from the analogue counting mode into a CPS equivalent.

**Figure 23.** Schematic diagram of the component of a laser ablation sampling device connected to and inductively coupled plasma mass spectrometer (Fryer, et al., 1995).
The technique of LA-ICP-MS is a modification of the solution based system where a laser replaces the nebulizer of the solution mode (Figure 24). This enables solid samples to be analyzed directly with minimal or no sample preparation, thus facilitating micro-spatial analysis. The Ultra-Violet (UV) light produced by the laser ablation system is the fifth harmonic (213 nm) of a 1064 nm Nd:YAG laser. The sample is placed in an air tight cell which is purged with the carrier gas prior to ablation. The 213 nm light pulsed (at 10Hz) and is focused through a series of lenses and ionizes the Ar-He carrier gas above the surface of the sample creating a micro-plasma which is then lowered until the plasma is directly interacting with the surface of the sample. The micro-plasma rapidly heats the surface of the sample resulting in ablation with relatively low elemental fractionation (compared to longer wavelength ablation systems) between the bulk sample matrix and the volatilized surface material (Motelica-Heino, 2001, Durrant, 1999). The rapid heating creates a plume of volatilized sample debris which is evacuated out of the sample cell and carried into the ICP.

Figure 24. Schematic diagram of a laser ablation system (Chenery, et, al., 1995).
The extreme difficulty and practical unfeasibility of developing matrix matched standards for arsenopyrite (see section 1.6.1.1) dictates that a set of standards for laser ablation work cannot be produced and used for elemental concentration quantification. Therefore an internal standard is necessary in order to normalize the elemental CPS to be independent of operating conditions and any matrix effects. The standardization of the elemental CPS cannot be used to determine the accurate concentrations of elements in arsenopyrite, however, the normalized CPS may be used to compare CPS data between samples.

2.4.1 Spot Ablation LA-ICP-MS

2.4.1.1 ICP-MS

The majority of LA-ICP-MS analyses were performed with laser ablation taking place at a single site on the arsenopyrite sample. This so called spot ablation methodology is the default method for the determination of trace elements in arsenopyrite in this thesis and as such arsenopyrite trace element analysis is considered to have been performed using the spot ablation method unless otherwise specified. The selected method for the spot ablation technique and the isotopes measured in these analyses are detailed in Table 7 and Table 8, respectively. A set of generic operating conditions for the ICP-MS are detailed further in Appendix A-2.1.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Spot Ablation</th>
<th>Traverse Ablation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isotope Dwell Time (milliseconds)</td>
<td>30</td>
<td>30 (100 for ²⁸Si)</td>
</tr>
<tr>
<td>Sampling Time Per Cycle (seconds)</td>
<td>1.78</td>
<td>1.12</td>
</tr>
<tr>
<td>Total Acquisition Time (seconds)</td>
<td>63.65</td>
<td>89.46</td>
</tr>
</tbody>
</table>

The isotopes selected in this thesis (Table 8) were those that have relatively high natural abundances. The $^{57}$Fe isotope was the exception as it has the second lowest natural abundance of the iron isotopes at 2.12%. This lower abundance isotope was intentionally
chosen as the ablation and ionisation of arsenopyrite will introduce large volumes of Fe into the detector and if the counts of the isotope are too high it may overload the detector resulting in Fe being above the detection limits. As iron is used as an internal standard it is extremely important to avoid this outcome. Isotopes were also carefully selected to avoid potential isobaric interferences from isotopes of other elements or common dimers (two elements bonded together with an overall positive charge) which may be stable in the mass spectrometer. For example, arsenic and sulfur may form a dimer with a likely combined mass of 107 ($^{75}$As + $^{32}$S) and it is for this reason that $^{109}$Ag is selected instead of $^{107}$Ag, despite this isotope being less naturally abundant. As an additional example, $^{111}$Cd was selected over the more common isotopes $^{112}$Cd and $^{114}$Cd due to the isobaric interference from the $^{56}$Fe-$^{56}$Fe dimer and interferences from the $^{114}$Sn isotope. It should be noted that the isotope $^{88}$Sr was chosen early in the thesis without fully realizing that this isotope is likely to experience significant isobaric interferences from the $^{56}$Fe + $^{32}$S dimer. This may account for why the isotope did not appear to be effective as a discriminatory variable and was subsequently not used in the analyses of arsenopyrite samples (see section 3.1.1).

**Table 8. The isotopes determined every 1.78 seconds using the spot ablation method.**

<table>
<thead>
<tr>
<th>28Si</th>
<th>31V</th>
<th>52Cr</th>
<th>53Cr</th>
<th>55Mn</th>
<th>57Fe</th>
<th>59Co</th>
<th>60Ni</th>
<th>64Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>63Cu</td>
<td>66Zn</td>
<td>77Se</td>
<td>82Se</td>
<td>85Rb</td>
<td>88Sr</td>
<td>90Zr</td>
<td>90Zr</td>
<td>95Mo</td>
</tr>
<tr>
<td>98Mo</td>
<td>101Ru</td>
<td>102Ru</td>
<td>103Rh</td>
<td>104Pd</td>
<td>108Pd</td>
<td>109Ag</td>
<td>111Cd</td>
<td>115In</td>
</tr>
<tr>
<td>120Sn</td>
<td>123Sb</td>
<td>125Te</td>
<td>126Te</td>
<td>133Ba</td>
<td>135Ba</td>
<td>182W</td>
<td>197Au</td>
<td></td>
</tr>
<tr>
<td>199Hg</td>
<td>200Hg</td>
<td>202Hg</td>
<td>204Hg</td>
<td>205Tl</td>
<td>206Pb</td>
<td>207Pb</td>
<td>208Pb</td>
<td>209Bi</td>
</tr>
<tr>
<td>232Th</td>
<td>238U</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.4.1.2 Laser Ablation

As previously discussed, the spot ablation method for the analysis of arsenopyrite was the preferred sample introduction method. The laser operating conditions used during the spot method are detailed in Table 9.
Table 9. *The operating conditions for the laser ablation instrument.*

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Spot Ablation</th>
<th>Traverse Ablation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser Frequency (Hz)</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Laser Power (mJ)</td>
<td>0.33-0.38</td>
<td>0.33-0.38</td>
</tr>
<tr>
<td>Ablation Diameter (µm)</td>
<td>55</td>
<td>55</td>
</tr>
<tr>
<td>Laser Warm-Up (seconds)</td>
<td>5.0</td>
<td>5</td>
</tr>
<tr>
<td>Laser Ablation Duration (seconds)</td>
<td>30</td>
<td>60</td>
</tr>
<tr>
<td>Laser Traversing Speed (µms⁻¹)</td>
<td>0</td>
<td>22</td>
</tr>
</tbody>
</table>

2.4.2 Traverse Ablation LA-ICP-MS

2.4.2.1 ICP-MS

The traverse laser ablation method was intended to be used only in a qualitative manner to observe inhomogeneity of the elemental assemblages in arsenopyrite. The selected method for the spot ablation technique and the isotopes measured in these analyses are detailed in Table 7 and Table 10, respectively. Generic operating conditions of the ICP-MS are detailed further in Appendix A-2.1.

Table 10. *The isotopes determined every 1.1182 seconds during the traverse method.*

<table>
<thead>
<tr>
<th>²⁸Si</th>
<th>⁵¹V</th>
<th>⁵²Cr</th>
<th>⁵³Cr</th>
<th>⁵⁵Mn</th>
<th>⁵⁷Fe</th>
<th>⁵⁹Co</th>
<th>⁶⁰Ni</th>
<th>⁶⁴Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>⁶⁵Cu</td>
<td>⁶⁶Zn</td>
<td>⁷⁷Se</td>
<td>⁸²Se</td>
<td>⁹⁰Mo</td>
<td>⁹⁰Mo</td>
<td>¹⁰⁹Pd</td>
<td>¹⁰⁹Ag</td>
<td>¹¹¹Cd</td>
</tr>
<tr>
<td>¹²⁰Sn</td>
<td>¹²¹Sb</td>
<td>¹²³Sb</td>
<td>¹²⁵Te</td>
<td>¹²⁶Te</td>
<td>¹⁸²W</td>
<td>¹⁹⁷Au</td>
<td>²⁰²Hg</td>
<td>²⁰⁵Tl</td>
</tr>
<tr>
<td>²⁰⁶Pb</td>
<td>²⁰⁷Pb</td>
<td>²⁰⁸Pb</td>
<td>²⁰⁹Bi</td>
<td>²³²Th</td>
<td>²³⁸U</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.4.2.2 Laser Ablation

The traverse method used similar laser operating conditions as the spot method. The major difference is that the laser traversed across the sample at a speed of 22 µm per second. The operating conditions of the laser ablation system are detailed in Table 9.

2.4.3 Arsenopyrite Solution Analysis

The sampling issues associated with the collection, dissolution, and subsequent analyses of natural mineral species have been discussed previously in section 1.6.1.1. When arsenopyrite material was sampled it was not possible to separate associated ore mineral
or gangue inclusions before digestion. Consequently, their trace element contribution would be included with that from the actual arsenopyrite and “contaminate” the arsenopyrite elemental signature. It must be realised that in light of the potential for mineral inclusions in arsenopyrite together with inherent arsenopyrite mineral inhomogeneity, the samples analysed using dissolution may not provide data that is truly representative of the trace element concentrations in the actual arsenopyrite itself but simply a “bulk” analysis of the crystal (which contains inclusions). Even after every precaution has been taken, the solution data cannot be considered as equivalent to that obtained using laser ablation. Nonetheless, solution analysis will generate trace element concentrations that may be compared to the laser ablation iron-normalized elemental data and may be able to be used as the basis for a laser ablation-based calibration curve that could give an approximate concentration for the analytes determined using this technique.

2.4.3.1 ICP-MS

Arsenopyrite samples previously analysed using the LA-ICP-MS spot ablation method were digested in a concentrated nitric/perchloric acid solution. The resulting solution was analysed using an Agilent 7500cs instrument operated in solution mode. The arsenopyrite material was dissolved into solution to compare laser CPS data to the actual concentration of the trace element in arsenopyrite. The isotopes determined during the solution analyses are detailed in Table 11.

The ICP-MS was tuned and calibrated between each run (some of the operating conditions were marginally different between runs) in order to establish the optimal operating conditions for analysis at that specific time. The average operating conditions are detailed in Appendix A-2.1.
Table 11. The isotopes determined using solution based ICP-MS.

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>6</td>
</tr>
<tr>
<td>Be</td>
<td>9</td>
</tr>
<tr>
<td>Al</td>
<td>27</td>
</tr>
<tr>
<td>Ca</td>
<td>43</td>
</tr>
<tr>
<td>Sc</td>
<td>48</td>
</tr>
<tr>
<td>Ti</td>
<td>51</td>
</tr>
<tr>
<td>V</td>
<td>52</td>
</tr>
<tr>
<td>Cr</td>
<td>53</td>
</tr>
<tr>
<td>Mn</td>
<td>55</td>
</tr>
<tr>
<td>Co</td>
<td>59</td>
</tr>
<tr>
<td>Ni</td>
<td>62</td>
</tr>
<tr>
<td>Cu</td>
<td>63</td>
</tr>
<tr>
<td>Zn</td>
<td>68</td>
</tr>
<tr>
<td>Ga</td>
<td>69</td>
</tr>
<tr>
<td>Se</td>
<td>71</td>
</tr>
<tr>
<td>Te</td>
<td>73</td>
</tr>
<tr>
<td>Ag</td>
<td>107</td>
</tr>
<tr>
<td>Te</td>
<td>130</td>
</tr>
<tr>
<td>Cs</td>
<td>133</td>
</tr>
<tr>
<td>Ba</td>
<td>138</td>
</tr>
<tr>
<td>La</td>
<td>139</td>
</tr>
<tr>
<td>Ce</td>
<td>140</td>
</tr>
<tr>
<td>Pr</td>
<td>141</td>
</tr>
<tr>
<td>Nd</td>
<td>143</td>
</tr>
<tr>
<td>Sm</td>
<td>151</td>
</tr>
<tr>
<td>Eu</td>
<td>152</td>
</tr>
<tr>
<td>Gd</td>
<td>157</td>
</tr>
<tr>
<td>Tb</td>
<td>158</td>
</tr>
<tr>
<td>Dy</td>
<td>161</td>
</tr>
<tr>
<td>Ho</td>
<td>165</td>
</tr>
<tr>
<td>Er</td>
<td>166</td>
</tr>
<tr>
<td>Tm</td>
<td>169</td>
</tr>
<tr>
<td>Yb</td>
<td>172</td>
</tr>
<tr>
<td>Lu</td>
<td>175</td>
</tr>
<tr>
<td>Hf</td>
<td>180</td>
</tr>
<tr>
<td>Ta</td>
<td>181</td>
</tr>
<tr>
<td>W</td>
<td>182</td>
</tr>
<tr>
<td>Re</td>
<td>184</td>
</tr>
<tr>
<td>Os</td>
<td>185</td>
</tr>
<tr>
<td>Ir</td>
<td>191</td>
</tr>
<tr>
<td>Pt</td>
<td>195</td>
</tr>
<tr>
<td>Au</td>
<td>197</td>
</tr>
<tr>
<td>Hg</td>
<td>206</td>
</tr>
<tr>
<td>Bi</td>
<td>209</td>
</tr>
<tr>
<td>Th</td>
<td>232</td>
</tr>
<tr>
<td>U</td>
<td>238</td>
</tr>
</tbody>
</table>

2.4.4 Electron Probe Analysis

2.4.4.1 SEM

Electron probe instruments operate by directing a focused beam of electrons onto the surface of a sample where reflected electrons and X-rays may be observed using specific detectors. A tungsten filament cathode emits electrons which are focussed by a series of condenser lenses to generate a coherent and focussed electron beam. The electron beam is moved across the surface of the sample with a raster pattern by automatic adjustment of the deflection coils. The reflection and scattering of electrons from the surface of the sample are used to visually represent the topography and composition of the sample. High energy electrons from the beam eject electrons contained within the surface atoms. These lower energy ejected electrons (secondary electrons) are scattered in random directions as a result of the interaction of the beam with the surface of the sample. These electrons may be observed with a secondary electron detector which is located at an acute angle to the surface of the sample. The beam of electrons which are electrostatically reflected from the surface of the sample (backscattered electrons) are observed with a detector parallel to the beam path. The relative intensity of the secondary electrons is indicative of the topography of the sample surface.
X-rays are produced from the interaction of the beam electrons with the electrons of the atoms on the surface of the sample. The energy of the specific X-ray is a function of the energy levels within the atoms which produced the X-ray. The SEM used in this thesis detected X-rays using an Energy Dispersive X-ray (EDX) spectrometer and by observing the density distribution of the X-rays produced from the surface of the sample it is possible to define energy peaks which indicate the presence of an element within the sample. A SEM-EDX instrument is primarily designed to produce high resolution electron images with the trade-off being a lower precision and a higher detection limit of X-rays produced by trace elements within the sample.

2.4.4.2 EPMA

The EPMA is a scanning electron microscope with five dedicated Wavelength Dispersive Spectrometers (WDS) built into the instrument. The EPMA utilizes a focused beam of electrons to interact with the sample to provide an image, similarly to other scanning electron microscopes. The WDS detectors filter and collect the X-ray spectra produced from the beam electrons colliding with the surface of the sample. Each of the five WDS detectors can be tuned to specific wavelengths which can correspond to a wide variety of elements, allowing for the collection of X-rays of five different wavelengths simultaneously. The WDX detectors have a high precision and a lower detection limit for X-rays produced by trace elements in the sample than most EDX detectors.

2.5 Data Processing

The time-resolved data generated by the LA-ICP-MS analyses of arsenopyrite samples (Appendix E-1.1) requires various processing procedures before the data could be interpreted. This data was first processed with software specifically designed to convert time-resolved analyses into a mean signal for each element in each sample during the
period of ablation (Appendix E-1.2). The processed data was then inspected to ensure that mineral inclusions were not inadvertently ablated and added to the final dataset (Appendix E-1.3). Individual element data for each of the samples were then normalized to an internal standard (Fe). A median of the normalized data for a sample location or for a whole deposit could then be used in further data analysis protocols, such as; comparison of elemental ratios, Linear Discriminant Analysis (LDA), Principal Component Analysis (PCA), and Comparability Index (CI) analysis.

2.5.1 Data Processing Software

The raw time-resolved data produced using LA-ICP-MS was processed using a commercial software package named Glitter™ (Macquarie Research Limited©, 1999). This software removes the background counts of each individual isotope. From the background-subtracted data this software determines the mean CPS response of each isotope over a specified interval of data collection. When identifying the position of ablation during data processing with the software, an operator must recognise where “spikes” occur (usually as the result of ablating inclusions) and avoid signal integration at these points. Otherwise unrepresentative data will be produced.

2.5.2 Manual Sample Validation

The data processed using the Glitter™ software was compiled into an Excel spreadsheet (Appendix E-1.2) for subsequent manipulation and interpretation. Data from the samples which were identified as containing unwanted inclusions were identified and were not used in the final interpretational datasets. Data that were processed using Glitter™ and were deemed to be free of elemental contamination from inclusions were compiled into an additional spreadsheet which was used for data analysis and interpretation purposes (Appendix E-1.3). The data within this spreadsheet were re-scrutinized in order to be
absolutely certain that the data set contained no data resulting from any inclusions in arsenopyrite. Samples that displayed evidence for the ablation of silicates or other sulfides were removed from this final dataset (Appendix E-1.3) and have been highlighted in Appendix E-1.2.

Data for repeat analyses of the NIST 610 glass standard were compared in order to account for instrument drift and to ensure that no mass bias was occurring. Minor corrections to the data were undertaken if mass bias or drift were deemed to be significant within an analytical run. Instrument drift which affected each of the analytes to a similar extent was not corrected as the iron-normalized CPS values retain a similar relationship to the other CPS analytes. Mass bias was corrected after the data had been processed using Glitter by comparing the iron-normalized CPS values and applying a time-dependant weighting factor to analytes which displayed significant mass bias.

The data generated from the laser traverse analysis of arsenopyrite were not processed using Glitter or any other method, but were instead simply compiled into several spreadsheets in Appendix E-1.6. Laser traverse data were ultimately not used for any interpretational purposes but were simply used to investigate the mineral homogeneity of arsenopyrite.

**2.5.3 Internal Standardization**

The CPS data for the individual isotopes in the Final Interpretational dataset (Appendix E-1.3) were divided by the reciprocal fractional relative natural abundance of each respective isotope to obtain a calculated total CPS, representing 100% for the element. The CPS data for elements with multiple isotopes were converted into an average elemental CPS. The CPS data of each of the elements investigated in this study were
divided by the elemental CPS of Fe (also calculated to 100%) in order to generate an iron-normalized elemental ratio for each analyte. In this manner, Fe is used as an internal standard to generate trace element CPS ratios that are independent of matrix effects. In this thesis whenever an elemental concentration or relative abundance is mentioned in the text, it refers specifically to this iron-normalized ratio.

2.6 Data Interpretation and Analyses

2.6.1 Median Values

Each of the internally standardized trace element assemblages from the final dataset was sorted and compiled into corresponding deposit groups (Appendix E-1.3). A median was generated for each of the iron-normalized elemental ratios for each sample (highlighted in red). This is defined as a “sample median” value. Data for each of the samples was compiled into groups based on the deposit the samples belong to, in addition to the median CPS data for each element for all of the samples analysed from that deposit (highlighted in green). This corresponds to a “deposit median” value.

2.6.2 Linear Discriminant Analysis

Linear Discriminant Analysis (LDA) is a statistical method used to model the extent to which an observation belongs to a particular suite of user-defined groups. The data are described by a series of orthogonal vectors which are used to graphically represent the data in a two dimensional system. Discriminant analysis provides a statistically valid method to test the variation present within a specific set of data. The discriminant analyses were undertaken using the XLSTAT™ (Addinsoft Pty. Ltd.) statistical software using a defined number of analyzed elements to generate individual plots. The elements used for each of the LDA’s are described in the relevant sections and in Appendix E-1.4. On the basis of the amplitude of the elemental vectors, it is possible to determine what specific
chemical composition a group of samples has that distinguish it from the other groups. This analysis may also be used to assess the groupings of unknown samples (Martin, 2012, May and Watling, 2009).

2.6.3 Principal Component Analysis

Principal Component Analysis (PCA) is a statistical means of assessing the variability of the inter-relationships within a data set. This analysis focuses on reducing dimensionality in multivariate data and plotting linear combinations of the variables to describe patterns within the data set. A PCA is a quantitatively rigorous method for achieving an indication of co-association of individual groups of samples. The method generates a new set of variables which are called principal components, where each principal component is a linear combination of the original variables. All the principal components are orthogonal to each other so there is no redundant information. The principal components as a whole form an orthogonal basis for the spacing of the data. The analyses were undertaken using the XLSTAT™ (Addinsoft Pty. Ltd.) statistical software using all of the analyzed elements to generate individual plots. Unlike LDA analyses, the co-association of samples is not designated; and the process simply generates sample co-associations which are independent of user-defined groupings. In this thesis PCA’s are used to assess the differences in arsenopyrite trace element assemblages between various groups of arsenopyrite samples or deposits. Often, within this thesis, PCA is used to validate an LDA analysis by determining which of the user-defined groups will cluster together based solely on arsenopyrite trace element chemistry. Principal component analyses have been used in literature to identify multivariate associations between samples, and to identify sample grouping associations (Martin, 2012, May and Watling, 2009).
2.6.4 Comparability Index

The Comparability Index (CI) analyses are non-parametric tests which are based around a sorting sub-routine that identifies the logarithmic values of the iron-normalized CPS data and compares these with equivalent element values in the remaining database samples. These differences are then summed and sorted to obtain an approximation of the comparability of the spectra of elements within the data set. The series is sorted on the basis of a comparability index value which is the difference from a 100% fit of the questioned sample with itself. The 100% fit ensures that the maximum possible comparability point is fixed in the interpretational protocol. The worst fit of the questioned sample to one of the other samples in the database is calculated to 0% comparability rating. The CI analyses were performed using a macro script in Microsoft Excel™ and the plots were generated after the analysis had completed. Once comparability ranking has been achieved, it is then necessary to visually compare the spectral fingerprint of the high comparability samples. In this manner it may be possible to determine if the fit is genuine and not an artifact based only on statistics. In addition to simply referring to the numbers (percentage comparability), it is also advisable to plot the percentage comparability relative to the specific sample giving that comparability and its positional number in the database. In this way significant changes in the slope of the plot (“break in slope”) can be observed frequently. These changes in slope usually indicate the start of new populations and are a means of sorting data. It is the samples with the highest percentage comparability prior to a break in slope which indicate which samples may be classified as belonging to the same group. By using CI analyses, samples from the data set may be tested to determine which of the other samples they are similar to (comparable with). Comparability tests have been used previously in literature to identify unknown samples, or to determine sample co-associations, especially with respect to the forensic “fingerprinting” of samples (Watling et al., 1997, Green and Watling, 2007).
3.0 RESULTS & DISCUSSION

This chapter details the analysis and interpretation of arsenopyrite trace element data for the purpose of being an indicator mineral for gold deposit exploration in Australia. The results and discussion relating to the secondary objective of this thesis; the isotopic analysis of mercury compounds for the purpose of gold deposit exploration, is detailed in section 4.3.

3.1 Method Development

There has been a significant increase in the use of LA-ICP-MS for determining the trace element concentrations of various solid matrices over the last two decades (Watling et al., 1995, Mason, 2001, Jackson, 2006, May and Watling, 2009). In addition, this analytical technique is increasingly being used to measure the distribution of trace elements in selected mineral species for the purposes of identifying specific geological phenomena (Gaspar et al., 2008, Jochum, 2007, Becker, 2005). The use of ultraviolet wavelength laser ablation coupled to ICP-MS is well established (Guillong et al., 2003) and many authors use a 213nm Nd:YAG laser ablation system coupled to a quadrupole mass spectrometer due to its higher accuracy and precision than longer wavelength lasers (Motelica-Heino, 2001, Pickhardt, et al., 2005) and relatively cheaper cost compared to more specialised (higher accuracy and precision) devices. Therefore it is unnecessary to explain the method development of this instrumental in detail. However, because LA-ICP-MS analysis of minerals is still in its early stages, associated methods of data interpretations are continually being developed and refined.

3.1.1 Instrumentation

The basis of this analytical technique and the manner in which it works have been discussed previously in sections 1.7.1, and 2.2, respectively. The manner in which the
samples are prepared and collected has been discussed in section 2.1 and the sample preparation technique did not require any additional development as sample collection and preparation is similar for most rock/mineral samples being investigated using LA-ICP-MS (Watling et al., 1995). The majority of instrument method development was associated with determination of the relevant analyte isotopes to be used and the analytical parameters associated with collection of accurate data for each individual isotope.

Following analysis of some trial samples it was apparent that certain analytes were only ever present in ultra trace concentrations and/or were consistently below the detection limit for LA-ICP-MS analysis. These analytes were removed from the initial analytical elemental suite as their lack of consistent presence above the detection limit would have rendered them inappropriate. Nonetheless, an extensive initial suite of analytes was chosen for the development of the method (Figure 25). Almost all of the chalcophilic and siderophilic elements were initially selected for determination. During data analysis it became apparent that some elements were still either too dilute in arsenopyrite or had no association with either mineralizing events or associated geology. Therefore, these elements were of minimal use in this project and were removed from the final methodology. Many lithophillic elements displayed no association with arsenopyrite and were only detected as a result of ablating sub-μm silicate inclusions and were removed from the final methodology (with the exception of Si which was used to detect the unintentional ablation of silicate inclusion). After method development, this study focussed on variations in the elemental assemblages of, and inter-relationships between, Co, Ni, Cu, Zn, Se, Mo, Ru, Rh, Pd, Ag, Sn, Sb, Te, Au, Hg, Tl, Pb, and Bi as the basis of data interpretation (Figure 25).
Figure 25. The elements determined during the method development (blue plus green) together with the elements that were included into the final method for data analysis (green only). The mass of each elemental isotope which was used for the analysis is indicated in the top portion of the square.

3.1.2 Data Analysis

As detailed earlier, LA-ICP-MS data are semi-quantitative. This is the result of matrix effects which render any data generated using LA-ICP-MS as not being able to be compared to an analytical standard. Within a single laboratory, day to day instrumentation setup and tuning will also differ resulting in non-intercomparability of generated data.

This problem is exacerbated if an LA-ICP-MS method is going to be used internationally and data compared between instruments. The problem is overcome to some extent by the use of the NIST 610 and 612 Certified Reference Material glass standards for data normalization and to ensure comparability of data on a day to day basis. Although the NIST standards have different matrix properties to arsenopyrite, they can be used to ensure optimization of instrumental set-up parameters and relative count per second.
(CPS) data for analytes can be compared on a day to day basis to ensure long term comparability of data generated from the investigation of arsenopyrite using similar LA-ICP-MS instruments. Every effort has been made with the development of the analytical protocols described in this thesis to ensure that the final methodologies can be transportable internationally and that data produced using any instrument anywhere in the world are inter-comparable. The raw data from the ICP-MS (time resolved analysis) are presented in counts per second for the various isotope masses. Data were then processed using the Glitter™ program as described in section 2.5.1. This program, or programs like it, are in common use and do not require any further discussion. The data produced, however, still requires further modification in order to provide semi-quantitative data that are comparable between multiple analyses.

LA-ICP-MS is recognised as a semi-quantitative analytical technique because it is not possible to accurately control laser coupling efficiencies to a sample substrate. Coupling efficiencies are determined by the nature of the sample matrix and, in natural minerals such as arsenopyrite, the microstructure and chemical composition may change throughout the crystal (requiring the implementation of a specific laser ablation protocol (section 2.3.2.1). As a result of these variations, the amount and composition of material ablated varies significantly from shot to shot. However, the relative ratios of the analytical signals for individual isotopes are not affected by the amount of sample ablated, and are only influenced by the relative abundance of the isotopes in the specific mineral phase (Halter, 2004, Motelica-Heino, 2001). Differences between the analyte compositions of the arsenopyrite studied are therefore identified throughout this thesis using variations in the elemental ratios of individual analytes and not their quantitative chemical compositions. Iron is used as an internal standard as it was determined that the concentration of this element in arsenopyrite varied by a relatively insignificant amount.
between samples (section 3.2.2). Consequently, it was determined that iron could be used as an internal standard to “normalize” the CPS data for all analytes in the arsenopyrite and ensure that these data could be used when comparing all study data. The normalized data were then used to obtain approximate concentrations of elements in the matrix without the necessity of having to use a matrix-matched standard, a requirement that is practically impossible to achieve.

Between thirty to forty analyses were performed on the same arsenopyrite sample at different ablation locations in order to remove or reduce the impact of non-representative areas in the sample and obtain a so-called “bulk” analysis of the sample in question. In the initial method development, the largest possible number (30-40) of laser ablation sites were selected, provided that there was no physical overlap between the sites (including the debris halo). After analysis of the data from several dozen of these samples it was later determined that less than 30% of the ablation sites were unrepresentative of the sample as a whole (ablation of inclusions, exsolution, or mineral heterogeneity). Therefore, it was decided to reduce the number of ablation sites to 10 as this would still provide reproducible and interpretable data (averaging over 7 representative laser ablation sites per sample).

Median values are used, rather than mean values, when approximating a representative elemental assemblage for either a number of ablation site data on a single sample, or for multiple samples within a single deposit.

3.2 Sample Representivity

In any analysis it is imperative that, for accurate and meaningful data interpretation, the samples being analysed are representative of the location that they are sourced from and
the type of material they represent. The arsenopyrite samples used in this study are relatively homogeneous, and representative of the deposits they have been collected from (each sample collected at its location was examined under a hand lens and in polished section by the sample suppliers (experienced economic geologists) to ensure that they are pure end-member arsenopyrites and not one of the related species variants of arsenopyrite). In addition, the data produced from the investigation of these samples must be transferable between multiple groups internationally, otherwise the arsenopyrite trace element assemblages are purely academic and have no practical applications. However, a certified reference arsenopyrite standard, suitable for LA-ICP-MS analyses, does not exist and therefore to generate the best possible data which may be comparable worldwide, an internal standard (section 3.2.2) should be used to normalize the data obtained using the LA-ICP-MS instrument. This trace element data is independent of small differences in matrix, crystal orientation, and variations in instrument tuning parameters; allowing for inter-laboratory comparability of laser condition variations on a daily basis.

3.2.1 Arsenopyrite Homogeneity

It is necessary to assess if the arsenopyrite samples are approximately homogeneous in order to determine if the analysis of an unknown arsenopyrite sample may be influenced by chemical zoning and the presence of inclusions within the crystal. Should arsenopyrite approximate a homogeneous sample then it could be assumed that, irrespective of the laser ablation site (within reason), the data collected from the arsenopyrite is representative of the sample being investigated. Sample homogeneity was tested using a combination of EMPA and LA-ICP-MS protocols.
3.2.1.1 Electron Probe Analysis

Studies were conducted using an Electron Probe Micro-Analyzer (EPMA) in order to determine if any other microscopic minerals were within the arsenopyrite crystal. In addition, the EPMA was used to investigate the spatial variation in concentration of some of the major and minor elements in arsenopyrite.

Electron probe data indicated that of the three major elements of arsenopyrite (Fe, As, S), iron is the most homogeneously distributed throughout all crystals of arsenopyrite investigated in this study (Figure 26 to 29). While the distribution of S and As appears relatively homogenous in most crystals, there is an indication of the inhomogeneous distribution of these elements in some crystals (Figure 26). Consequently, their use as internal standards is limited. In the literature an antipathetic relationship between As and S has also been noted (Sharp, 1985), further confirming the inappropriateness of these elements as internal standards.

Most of the minor and trace elements displayed minimal variation in the concentration within the arsenopyrite crystal (Co in Figure 26). However, some scans have displayed evidence for the variation in trace element chemistry in arsenopyrite (Figure 27). This EPMA scan displays areas of inhomogeneous Co and Ni concentration which are independent of Fe or As concentrations. However, it should be noted that the case displayed in Figure 27 is an exception and that after data processing any ablation sites that exhibit anomalous trace element concentrations (typically high CPS counts of common silicate or sulfide mineral forming elements) are removed from the final dataset and do not feature in any subsequent data interpretational procedures.
Figure 26. Elemental distribution of As, S, Fe, and Co for the sample GC3 generated using an EPMA. The “heat map” scale of the relative concentration of each element is defined as an increase in elemental concentration by the following distribution black → blue → green → yellow → red → pink. Note that at least three generations of arsenopyrite may be detected by observation of the S and As concentrations.

Micrometre-sized mineral inclusions are prevalent in a large number of arsenopyrite samples, and the presence of these mineral inclusions may be observed as the darker areas within the lighter coloured arsenopyrite bulk matrix (Figure 28). It should be noted that the eight circular dark areas are pre-existing (1064 nm) laser ablation craters. Additionally, some sub-millimetre inclusions may also be observed in Figure 26 and Figure 27. Usually these mineral inclusions comprise less than 5% of the total volume of the arsenopyrite crystal. This trend may also be observed in additional SEM and EPMA scans of arsenopyrite minerals (Appendix E-3.2). Therefore, while it can be concluded that the arsenopyrite minerals contain a number of undesirable (from the point of view of complete homogeneity) mineral inclusions, overall the arsenopyrite composition is
relatively homogeneous and free of inclusions, and therefore ideal for LA-ICP-MS analyses.

Figure 27. The element heat maps of sample FIM5 generated by using the EMPA. Note that the eight regularly distributed black spots represent areas of previous laser ablation using a 1064 nm laser.
Figure 28. A back-scattered electron image of the arsenopyrite FIM 5. The arsenopyrite is the light gray large euhedral crystal filled with a few mineral inclusions such as ilmenite and mica (darker subhedral crystals). The sample has been previously ablated with a 1064 nm laser (the 8 regularly spaced dark circles).

The homogeneity of arsenopyrite was further investigated by a third party, FEI™ using QEMSCAN®, a high resolution electron probe system coupled with four EDX detectors (Figure 29). The data collected from analyses using this instrument further demonstrate that the arsenopyrite samples investigated in this thesis are relatively homogenous. The image on the bottom left of Figure 29 displays two distinct areas of Ti-rich arsenopyrite which are less than 200 μm in length. In these areas a Ti-rich mineral may be present at, or close to the surface. This analysis confirms that, with the exception of a small percentage of minor mineral inclusions at veins or mineral borders, the arsenopyrite samples are relatively homogeneous and should be ideal for LA-ICP-MS analyses.
The electron probe scans from the EPMA and QEMSCAN™ have a detection limit of approximately 100 ppm at best for elements in a solid matrix (Kuisma-Kursula, 2000). For the majority of the scans the concentrations of the most abundant trace elements (Co, Ni and Sb) display no variation (see Appendix E-3.2 for additional EPMA scans). From the electron probe analyses it can be concluded that the concentration of these trace elements does not significantly exceed 100 ppm nor does it vary in an observable manner using electron probe scans. Consequently, in order to identify any elemental
inhomogeneity at the <100 ppm level, it is necessary to employ a more sensitive technique, such as LA-ICP-MS scanning to identify its presence.

3.2.1.2 Laser Ablation Traverses

A total of 133 individual LA-ICP-MS traverses were performed across 17 different arsenopyrite samples for the purpose of observing mineral homogeneity. The detection limit for LA-ICP-MS is in the region of the parts per billion for most elements, depending on specific operating conditions and instrument tuning (Durrant and Ward, 2005, Jochum et al., 2007). This allows mineral homogeneity to be observed at a much lower level than with the electron probe scans. For these traverses the ICP-MS is programmed to acquire all of the desired analytes in a period of 1.12 seconds. The scan rate of the laser is set to 22 μm per second for a period of 60 seconds during which time approximately 50 full isotopic scans can be acquired. These parameters give a spatial resolution of approximately 25 μm. This spatial resolution allows for a more detailed identification of multiple arsenopyrite generations, crystal zoning, and mineralogical inhomogeneity, than can be achieved using the spot ablation method.

The 17 different arsenopyrite samples were to investigate the impact of mineral inclusions and veining in arsenopyrite on the trace element chemistry. The trace element data initially appears to show somewhat variable concentrations during the laser traverse (Figure 30). This would suggest that the arsenopyrite crystal has an inhomogeneous trace element distribution. However, it may be observed from this figure (and other scans in Appendix E-1.6) that the counts per second of the trace elements present in the arsenopyrite crystal generally follow the response for the $^{57}$Fe isotope. As demonstrated from the electron probe scans in section 3.2.1.1 (Figure 26 to 29) the Fe concentration displays no significant variation within the arsenopyrite crystal. Therefore, the variation
in responses for the elements (together with Fe) may be the result of variations in the laser-sample coupling efficiencies, which may be influenced by changes in crystal orientation and or hardness, leading to variable amounts of the ablated material being introduced into the ICP-MS rather than variations in the actual concentrations of elements within the crystal.

![HQ9 Traverse](image)

**Figure 30.** Laser traverses across the arsenopyrite mineral sample HQ9 displaying the CPS data of the more concentrated trace elements in arsenopyrite.

It is possible to observe where inclusions of lithophile elements occur by a relatively elevated $^{28}\text{Si}$ CPS, as observed in Figure 31 where approximately 50 seconds into the analytical run there is a significant spike in the counts per second data for Si. At this exact point, counts per second data for Fe, Co, Ni, and Sb drop significantly. This implies that at the 50 second point on the traverse the laser is ablating a silica rich inclusion which has physically displaced other sulfide minerals (predominantly arsenopyrite) resulting in the relevant increases and decreases in the analyte assemblage at that point. It should be noted that the signal for Si (and the antipathetic decrease in the other elements) increases slowly, reaches a peak, and then decays slowly. This phenomena arises as a result of the ejecta produced from the laser not being immediately removed from the laser ablation cell. The
cell has a “mixing time” where it will interact with the newly introduced carrier gas before leaving the cell. Therefore, not all of the ejecta will be removed immediately and essentially the presence of Si rich debris is slowly diluted over time with the introduction of newly ejected sulfide debris (Mason, 2001). The presence of some sulfide minerals are less easy to detect and require careful interpretation of the relative abundance of the chalcophilic elements, many of which are less abundant in pyrite and pyrrhotite compared to arsenopyrite.

![IK4 Traverse](image)

**Figure 31.** Laser traverses displaying the counts per second of the more highly concentrated trace elements across two arsenopyrite crystals in sample HQ9. A silicate inclusion has been ablated at approximately 50 seconds into the scan.

3.2.1.3 Manipulation of Laser Ablation Data

One of the requirements of being able to relate analytical data to specific mineralizing events is that all data are comparable and therefore they can form part of a general reference database representing results obtained from the ablation of a similar uniform matrix. Commonly, during an ablation protocol, observation of the total ion count indicates that there are variations in the total amount of analytes reaching the detector and
this is indicative of a change of matrix in the area being ablated. Changes in the arsenopyrite matrix may represent inclusions or complete changes in the local mineralogy of the arsenopyrite crystal and the data generated during their ablation must be removed prior to incorporation into the arsenopyrite reference database. During the data processing of the spot ablation data, any significant elemental inhomogeneities associated with inclusions and major matrix component changes can be removed by excising data associated with the specific time interval during which their ablation occurred. If the inhomogeneities are extensive then under these circumstances the entire sample data can be removed and not entered into the database.

All analytical data were compared to results obtained from a series of four cross over samples. These samples were ablated at regular intervals throughout this study to provide reference values which facilitated data normalization and intercomparability of all data produced. Cross-over samples were analysed in duplicate at the beginning, middle, and end of each analytical run throughout this thesis. Further to their use as described, the analysis of these samples provided an extremely large data set for individual ablation sites on these crystals and resulted in the production of detailed information that could be used to describe the natural variation of trace elements within these arsenopyrite samples. An example of CPS data for three of the most abundant trace elements present in one of the cross-over samples (GA47 261) is detailed in Figure 32. Data containing obvious evidence for the ablation of inclusions were removed prior to plotting. It may be observed from this figure that the raw data follow an approximate normal distribution with a slight bias towards the lower end of the CPS scale. This negative bias may be indicative of the incorporation of data from a small number of micrometre sized sulphide inclusions producing somewhat elevated values which were not detected and removed during data processing. The clarity of the CPS frequency distribution diagrams may be improved with
a greater number of divisions, or by logarithmically normalising the values. Nevertheless, the data demonstrated in Figure 32 confirms that it is necessary to use both an internal standard (section 3.2.2), to normalize data prior to data interpretation (as ablation of inclusions will then be more easily recognised) and the requirement to use median and not average data for interpretational purposes to minimize the chance of incorrect conclusions being drawn.

Figure 32. Density distributions of the raw counts per second of Co, Ni, and Sb in arsenopyrite from the cross over sample GA47 261 (179 analyses).
3.2.2 Iron as an Internal Normalization Standard

One of the recognised issues associated with LA-ICP-MS analysis is that the data produced during multi-element analysis, while relative, is not quantitative. In addition, variations in laser coupling efficiency (fluence) will lead to a variation in the amount of material ablated and consequently variations in the relative CPS response for equivalent amounts of an analyte in different samples. As discussed previously in section 1.6.1.1 and 3.1.2, it is impractical to develop matrix matched standards as it is not possible to synthesise arsenopyrite crystals that have a homogeneous distribution of a large suite of elements. Despite the issues associated with direct comparison between a standard and a sample, the data generated using the LA-ICP-MS will still be comparable and reproducible between analytical runs and between different instruments if the analyte data is normalized to an internal standard.

As stated previously (section 3.2.1), the concentration of Fe is essentially uniform in all arsenopyrite analysed in this study. By dividing the CPS data for each analyte with equivalent data for that of iron, it is possible to obtain normalized data for each analyte that is equivalent for each sample analysed. Variations in the coupling efficiency of the laser will impact the CPS of all the elements to essentially the same extent (Motelica-Heino, et, al., 2001); however the iron-normalized ratio for analytes will remain essentially constant despite the variations in coupling efficiency. The effect of the normalization of data may be observed in Figure 33, where 179 individual laser ablation analyses of the same arsenopyrite crystal were taken over a period of 3 years. The frequency distribution histograms for iron and cobalt (Figure 33 A and B) are similar (54.1 and 53.9 %RSD) and, when cobalt data are ratioed to equivalent data for iron (Figure 33C) a tighter distribution diagram is produced (21.3 %RSD).
Figure 33. Frequency distribution histogram and cumulative frequency diagram for the Fe, Co, and Co/Fe counts per second data from the cross over sample GA47261 (179 analyses).
While the iron-normalized ratio of an element is not directly equivalent to the concentration of that element, providing the iron concentration is equivalent in all arsenopyrite crystals analysed, the iron-normalized data for that element is directly inter-comparable between samples making accurate relative inter-comparison of sample data possible for all samples in the data base. Further proof of the appropriateness of iron as an internal standard can be seen with reference to data in Figure 26 and Figure 27 where the relative concentration of Fe does not change to an observable extent within an arsenopyrite crystal. Additionally, following analysis of approximately twenty different arsenopyrite crystals from a variety of deposits it was possible to confirm that the variation in iron content was within ±1% of the expected stoichiometric value (Appendix E-1.7) and consequently further confirm the appropriateness of the element as an internal standard.

3.2.3 LA-ICP-MS Reproducibility

3.2.3.1 Laser-Sample Interaction

Data produced for this thesis are compared to previous analysis of the samples which were undertaken using an infra-red laser operating at 1064 nm. Initial laser ablation of arsenopyrite samples was undertaken in 1995 by Watling and Stewart using a 1064 nm infra-red Nd:YAG laser ablation system (Stewart and Watling, 2009). This initial work was not published, primarily because the ablation incident caused significant fractionation between the elemental composition of the ablated material and original samples and as such the material being introduced into the ICP-MS was not representative of the sample. Using 1064 nm lasing conditions, the surface of the sample is heated by direct coupling of the laser beam with the sample surface resulting in explosive melting of the sample surface and the production of a significant percentage of the ejecta with

The mechanism of ablation, using a 213 nm laser, results from the production of a microplasma at the focal point of the laser light. This micro-plasma causes volatilization of the material immediately adjacent to the light focal point, with very little transmission of heat into adjacent areas of the sample (Eggins, 1998). Consequently, analyte fractionation or melting and the production of scattered melt debris on the surface of the sample is insignificant (Motelica-Heino, 2001). This has been confirmed using scanning electron microscopy (Zeiss SEM) in the areas adjacent to the laser craters. There is obvious evidence of melting only in the bottom of the crater while in the area immediately adjacent to the crater, possible melting phenomena are observed to a distance of only approximately 1μm from the wall (Figure 34). This area is extremely small and the volume of sample involved would mean that thermal effects are relatively insignificant when compared to the volume of ejecta that is produced and introduced into the ICP-MS.

A typical crater in arsenopyrite produced using the 213 nm laser (Figure 34) has a different size and morphology to that which is produced using a 1064 nm laser (Figure 35). Comparison of these figures highlights the fact that there is significantly less peripheral melting of the sample surface when performing ablation using a 213 nm laser when compared to using the 1064 nm laser. The effect of this thermal transfer (melting) is that significant fractionation of thermolabile elements and inter-metallic compounds occurs and consequently, any fractionation that may be caused by ablation using a 213 nm laser will be insignificant when compared to that obtained using a 1064 nm laser ablation system.
Figure 34. A) The SEM secondary electron image of a laser ablation crater created by the use of a 213 nm laser ablating the arsenopyrite sample, GC3. B) The SEM secondary electron image of a laser ablation crater created by the 213 nm laser ablation of sample 597B3 at an angle of approximately 60° from horizontal.
In order to demonstrate the difference between the two laser systems, counts per second data were compared from the same samples (Figure 36). Iron was not measured in the 1064 nm analyses and thus the raw (non iron-normalized) CPS data are compared. The elements Co, Ni, Sb, Te, Au and Bi exhibit an essentially positive inter-relationship (Figure 36 and Appendix E-1.3), while some elements, notably Cu, Zn, Sn, Hg and Pb, show a distinct lack of any relationship between data (Figure 36 and Appendix E-1.3). The CPS data for these elements display a more constrained range of values when using the 213 nm laser than when using the 1064 nm system, indicating the potential of significantly more fractionation under 1064 nm lasing conditions. This situation is especially highlighted in Figure 36 D where the mercury CPS data have over one hundred times greater range for 1064 nm data than for 213 nm data.
Figure 36. Comparison of the elemental counts per second for Co, Ni, Cu, and Hg (non Iron-normalized) of 440 individual samples analysed using 1064 and 213 nm LA-ICP-MS systems.

3.2.3.2 ICP-MS Consistency

LA-ICP-MS determination of the trace elements in arsenopyrite was conducted over a three year period. Consequently, it was necessary to ensure from the start that the laser and ICP-MS operating conditions were maintained and that the sample response was consistent for all analyte elements measured over this period. Therefore, a NIST 610 glass standard and four arsenopyrite crossover samples were analysed at selected intervals throughout each analytical run to ensure that data could be normalized and that results obtained at the beginning of each run could be compared with data produced at the end.
and that all data were inter-comparable for the duration of the research. The CPS data for Co and Ni generated from the multiple analyses of the NIST610 standard are detailed in Figure 37. It may be observed from this figure that the Co and Ni CPS from the NIST 610 glass standard follow a normal distribution with a percentage standard deviation of 52.4% and 47.6% CPS, respectively. The relative standard deviation generated from the multiple analyses of the NIST 610 standard over this three year period can largely be attributed to variations in the laser-sample coupling efficiency, instrumental setup and tuning conditions, including degradation of detectors and cones, and does not represent the precision of analyses within an analytical run which is usually better than ±2%. This day to day variation in CPS data over the extended period of this study confirms the necessity of using an internal standard (section 3.2.2) in association with the Certified Reference Material to ensure comparability of data for the entire analytical period and also to ensure comparability of data if the protocols are to be used either nationally or internationally.

**Figure 37.** Frequency distribution plots of the counts per second data for Co and Ni from the NIST 610 standard analysed for the duration of the entire thesis (775 analyses).
The drift for each of the analytical runs was calculated using the CPS of specific elements contained in the NIST 610 glass standard. Infrequently, small corrections were made to the data if any significant drift was observed throughout the analytical run to ensure that the CPS response for the samples was consistent and to reduce any potential mass bias that may have occurred throughout the run. This was performed by applying weightings to some of the iron-normalized CPS values of elements which were experiencing any significant mass bias. The CPS response for selected elements ablated from the NIST610 standard over a typical analytical run is displayed in Figure 38. Usually the drift and mass bias was minimal (as observed in Figure 38) and did not warrant any corrections.

**Figure 38.** A. The raw CPS data for various elements observed during the analyses of a NIST 610 standard during a typical analytical run (approximately 8 hours). B. The iron-normalized CPS values of the same elements observed in A.
3.2.4 Solution ICP-MS

The dissolution of arsenopyrite and the subsequent solution ICP-MS measurement of the dissolved material is a rapid, but relatively inaccurate and imprecise method for measuring the concentrations of trace elements in the arsenopyrite crystal lattice. This is because there is no way that inclusions of exsolved exotic mineral species can be excluded from the dissolution process. Consequently, because these phases are incorporated into the data of solution based analyses, the data do not represent what is actually in the arsenopyrite crystal. Under these circumstances the relative concentration of analytes incorporated into the arsenopyrite crystal lattice during crystallization cannot always be determined accurately, especially when they are present at low concentrations. However, the laser ablation data can be retrospectively interrogated and data that are specifically associated with ablation of included minerals species removed before interpretation. Consequently, LA-ICP-MS is used to measure the relative abundance of trace elements in arsenopyrite throughout this study. In the absence of sampling issues associated with the collection of material for solution ICP-MS, it would be expected that the concentration of a specific trace element in arsenopyrite to display a linear or semi-linear relationship with its corresponding iron-normalized CPS response. This comparison is displayed in Table 12. Elements that are typically associated with arsenopyrite lattice substitution and are therefore expected to be present at relatively high concentration levels, are commonly observed to have high iron-normalized CPS responses (Co, Ni, Se, Sb, Te, and Bi) and exhibit high correlation coefficients when data for the solution and laser ablation are compared. During arsenopyrite formation these elements have a strong thermodynamic affinity to form a solid solution with arsenopyrite and they will generally be present at minor or trace element levels in arsenopyrite (King, 2002). Therefore, these elements are less strongly affected by the sampling of inclusions in arsenopyrite and display linear relationships between laser and solution responses. High correlation coefficients are not
observed for trace elements which display a low iron-normalized CPS value (Ru, Ph, Pd, and Tl) (Table 12).

### Table 12. The relationships between the iron-normalized 213 nm LA-ICP-MS CPS and the analyte concentration as determined by solution ICP-MS. The gradient (c) is the concentration (ppb) of the trace element as a function of iron-normalized laser CPS (x).

<table>
<thead>
<tr>
<th>Element</th>
<th>Gradient</th>
<th>Correlation</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>c=3*10^8x</td>
<td>0.9046</td>
<td>Strong linear relation</td>
</tr>
<tr>
<td>Ni</td>
<td>c=2*10^8x</td>
<td>0.9948</td>
<td>Very strong linear relation</td>
</tr>
<tr>
<td>Cu</td>
<td>c = 5*10^10x</td>
<td>0.1423</td>
<td>Sulfide inclusion contaminated</td>
</tr>
<tr>
<td>Zn</td>
<td>No relation</td>
<td>N/A</td>
<td>Sulfide inclusion contaminated</td>
</tr>
<tr>
<td>Se</td>
<td>c=1*10^9x</td>
<td>0.8226</td>
<td>Linear</td>
</tr>
<tr>
<td>Zr</td>
<td>No relation</td>
<td>N/A</td>
<td>Silicate inclusion contaminated</td>
</tr>
<tr>
<td>Mo</td>
<td>No relation</td>
<td>N/A</td>
<td>No relationship</td>
</tr>
<tr>
<td>Ru</td>
<td>No relation</td>
<td>N/A</td>
<td>Low concentrations</td>
</tr>
<tr>
<td>Rh</td>
<td>No relation</td>
<td>N/A</td>
<td>Low concentrations</td>
</tr>
<tr>
<td>Pd</td>
<td>No relation</td>
<td>N/A</td>
<td>Low concentrations</td>
</tr>
<tr>
<td>Ag</td>
<td>No relation</td>
<td>N/A</td>
<td>Inclusions</td>
</tr>
<tr>
<td>Sn</td>
<td>No relation</td>
<td>N/A</td>
<td>Low concentrations</td>
</tr>
<tr>
<td>Sb</td>
<td>c = 7*10^8x</td>
<td>0.9969</td>
<td>Very strongly linear</td>
</tr>
<tr>
<td>Te</td>
<td>c = 9*10^8x</td>
<td>0.8932</td>
<td>Strong linear relation</td>
</tr>
<tr>
<td>Au</td>
<td>No relation</td>
<td>N/A</td>
<td>Nugget effect, sulfide inclusion</td>
</tr>
<tr>
<td>Hg</td>
<td>No relation</td>
<td>N/A</td>
<td>Mercury digestion volatilization</td>
</tr>
<tr>
<td>Tl</td>
<td>No relation</td>
<td>N/A</td>
<td>Concentrations too low</td>
</tr>
<tr>
<td>Pb</td>
<td>No relation</td>
<td>N/A</td>
<td>Sulfide inclusion contaminated</td>
</tr>
<tr>
<td>Bi</td>
<td>c=2*10^8x</td>
<td>0.7944</td>
<td>Linear</td>
</tr>
</tbody>
</table>

The two most common mineral groups which may be present as inclusions within arsenopyrite are silicates and sulfides. Silicate minerals are not susceptible to oxidation and will only be partially digested prior to solution ICP-MS analysis using the nitric/perchloric acid digestion procedure adopted in this study. The unreacted silicate material contributes to the mass of the sample but does not contribute a significant concentration of elements to the chemistry of the solution, resulting in a decrease in the calculated concentrations of all analytes. Sulfide minerals are commonly included in arsenopyrite and their dissolution and incorporation into the solution has a significant influence on the overall chemistry of the final solution. Some sulfides may contain minor or trace elements in greater concentration than arsenopyrite which will lead to high concentrations of these elements in solution.
Occasionally it is possible to identify the dissolution of mineral phases other than arsenopyrite by the concentration of specific major analytes being significantly higher than expected. However, often mineral phases will remain undetected as they may contribute to only a small percentage of the sample mass but can still influence the chemistry of the solution. Therefore, sampling of arsenopyrite solid material for trace element analysis is more representative and appropriate using the laser ablation method than the solution method.

Despite the sampling issues associated with the digestion and analysis of arsenopyrite, there is a strong positive correlation between the solution and the laser data for some of the higher concentration elements (Figure 39) and it is on the basis of this strong relationship that a cross-calibration curve for these elements between laser ablation CPS data and solution concentrations may be developed. In this manner it may be possible to calculate the concentration of a specific analyte using the iron-normalized CPS of the analyte in question. The calculation of analyte concentrations has not been performed in this thesis due to the small number of samples investigated in this section and due to a number of sampling issues which have not been adequately accounted for. However, it is possible, that with a considerably more detailed investigation into the relationships between the two sampling methods, a useable cross-calibration curve may be generated for each element.
3.3 Incorporation of Elements into the Arsenopyrite Mineral Lattice

It has been demonstrated in section 3.2 that arsenopyrite can incorporate trace elements into its crystal lattice and that these elements can be detected using modern LA-ICP-MS techniques. It is these elements that are substituted directly into the arsenopyrite lattice, incorporated in defects in the lattice, or nanometre-sized inclusions in the lattice, that are studied in this thesis. Micrometre and larger sized inclusions are considered to be a discreet mineral phase which has been enclosed within the main body of the arsenopyrite.
crystal during crystallisation. Consequently, when their presence is determined in an individual LA-ICP-MS scan, the entire scan is rejected. In the following section an attempt will be made to determine the most likely model for incorporation of selected trace elements into the arsenopyrite lattice.

The Ionic Model (IM) and Molecular Orbital Model (MOM) can be considered two end members in understanding lattice stability and the degree to which specific elements may substitute into the arsenopyrite lattice (section 1.5). The IM applies to minerals that are purely ionic and held together by the electrostatic attraction of oppositely charge ions, while the MOM essentially describes minerals held together solely by covalent bonds. Arsenopyrite is believed to be predominantly held together by covalent bonds and therefore the MOM may provide the greatest insight into understanding the mechanism, and extent, to which elements are incorporated into its lattice.

3.3.1 Inter-Element Relationships

The broad relationships between elements which may substitute into the arsenopyrite lattice may provide some insight as to which elements may be competing for lattice sites. This is relevant in determining which substituent elements compete for lattice sites (antipathetic relationships) and which elements are associated with the fluid chemistry and/or are influenced strongly by physical properties (sympathetic relationships). Several elements have sufficiently sympathetic relationships with each other to indicate that elemental incorporation is facilitated simply by the relative concentrations of those elements in the original ore forming solution. The observable iron-normalized CPS relationships between the elements is detailed in Table 13. While a number of elements display antipathetic inter-relationships, no elements of a similar Goldschmidt category (Goldschmidt, 1937) display strong antipathetic relationships. The Goldschmidt
classification groups naturally elements into one of four groups according to their affinity for geological host phases (atmophile, lithophile, siderophile and chalcophile). The lack of antipathetic relationships between elements of the same Goldschmidt category would suggest that there is not a significant competition for any of the lattice sites and that the antipathetic relationships are most likely the result of the differences in physiochemical conditions within the arsenopyrite forming solutions.

Table 13. The relationships between two iron-normalized trace element CPS in arsenopyrite. Elements that did not demonstrate a clear relationship were omitted, elements in a relationship that were not clear are designated as being “weakly” related to each other.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Relationship</th>
<th>Elements</th>
<th>Relationship</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>Ni</td>
<td>Strongly Sympathetic</td>
<td>Cu</td>
</tr>
<tr>
<td>Co</td>
<td>Se</td>
<td>Weakly Sympathetic</td>
<td>Zn</td>
</tr>
<tr>
<td>Co</td>
<td>Sb</td>
<td>Antipathetic</td>
<td>Se</td>
</tr>
<tr>
<td>Co</td>
<td>Te</td>
<td>Strongly Sympathetic</td>
<td>Se</td>
</tr>
<tr>
<td>Co</td>
<td>Au</td>
<td>Weakly Sympathetic</td>
<td>Mo</td>
</tr>
<tr>
<td>Co</td>
<td>Pb</td>
<td>Weakly Antipathetic</td>
<td>Rh</td>
</tr>
<tr>
<td>Co</td>
<td>Bi</td>
<td>Sympathetic</td>
<td>Rh</td>
</tr>
<tr>
<td>Ni</td>
<td>Se</td>
<td>Weakly Sympathetic</td>
<td>Pd</td>
</tr>
<tr>
<td>Ni</td>
<td>Sb</td>
<td>Antipathetic</td>
<td>Pd</td>
</tr>
<tr>
<td>Ni</td>
<td>Te</td>
<td>Weakly Sympathetic</td>
<td>Ag</td>
</tr>
<tr>
<td>Ni</td>
<td>Bi</td>
<td>Sympathetic</td>
<td>Ag</td>
</tr>
<tr>
<td>Cu</td>
<td>Zn</td>
<td>Strongly Sympathetic</td>
<td>Sb</td>
</tr>
<tr>
<td>Cu</td>
<td>Ru</td>
<td>Weakly Sympathetic</td>
<td>Te</td>
</tr>
<tr>
<td>Cu</td>
<td>Rh</td>
<td>Sympathetic</td>
<td>Te</td>
</tr>
<tr>
<td>Cu</td>
<td>Ag</td>
<td>Weakly Sympathetic</td>
<td>Au</td>
</tr>
<tr>
<td>Cu</td>
<td>Tl</td>
<td>Weakly Sympathetic</td>
<td>Tl</td>
</tr>
</tbody>
</table>

The lack of inter-relationships for some elements may be explained in terms of elemental substitution into a non-equilibrated crystal lattice during ore formation, either because the relevant element is present in the ore forming solutions at high concentrations or is favoured by the lattice under the formational conditions of the mineral. Under these circumstances it is possible that the relevant trends between elements that are substituted into the lattice may give an indication of either ore forming conditions or the nature of
the ore forming solutions which in turn may indicate the gold mineralization potential of the orebody. It is those relationships and similar ones which will be used as the basis of interpretational protocols and will be discussed in greater detail later in this thesis. In some cases there is going to be no observable inter-relationship and data for these elements should be treated with caution when trying to identify their potential indicator status.

3.3.2 Arsenopyrite Trace Element Substitution

As previously discussed in section 3.1, the elements that are being investigated for this project are those that are strongly associated with gold mineralization and are likely to be present in arsenopyrite at concentrations which can be detected using modern LA-ICP-MS instrumentation. The chemical properties of the substituent element will dictate the lattice site and the properties of the chemical bonds that the substituent makes with the neighbouring elements. The site of some substituent elements may be readily explained with the ionic model, others with the molecular orbital model, and others may be explained by a combination of the two. The presence of some trace elements that are detected in arsenopyrite cannot be explained with either model or a combination of the two models. The elements that fall into the latter class generally will not form favourable chemical bonds in the lattice and as such are typically present in ultra-trace quantities. Therefore, it may be extrapolated that these elements do not readily isomorphously replace any of the lattice elements, but may be present in crystal defects in regions of lattice inhomogeneity or may be present as nanometre sized mineral or fluid inclusions.

3.3.2.1 Fe Site

As discussed in section 3.2.2, the concentration of Fe does not vary significantly (>2%) from the stoichiometric value in any of the arsenopyrite crystals. This finding is also
reinforced by the low calculated concentrations of the trace elements as determined by the ICP-MS investigation of dissolved arsenopyrite solutions (section 3.2.4 and Appendix E-1.7). The lack of significant transition metal substitution at the Fe site may be a result of the high energy needed to introduce electrons into the \(a_{ll}\) and \(\sigma^*\) orbitals (Figure 17). Elements that have a greater number of valence electrons than Fe (most of the other transition elements) will required significantly more energy to fill the non-bonding orbitals than elements with the same number of valence electrons. The relatively low substitution for Fe may be observed from the low average combined iron-normalized CPS data for elements which are likely to replace Fe as well as the discrepancy (Figure 40). The apparent low relative abundance of substituent for the Fe site may also be the product of the significant difference between the CPS for Fe and the substituent (Figure 41). Overall, the substitution into the Fe site is minimal and any influence on the crystal structure of arsenopyrite, contributing to any crystal distortion, is likely to be minimal.

![Figure 40](image-url)  
*Figure 40. A frequency distribution of the combined iron-normalized CPS responses for Co, Ni, Cu, and Zn in the sample median arsenopyrite data for 626 samples.*
While it has been demonstrated that minimal substitution occurs at the Fe site, Co is observed in appreciable quantities in arsenopyrite and it is likely that Co will substitute for Fe. Cobalt substitution for iron may be partly due to the element being able to exist in the +2 oxidation state which has a similar ionic radius (0.0745 nm) to Fe\(^{2+}\) (0.078 nm) (for a full detailed list of ionic radii see Shannon, 1976). Additionally, Co may substitute for Fe due to electrons present in the valence shell of Co\(^{2+}\) completely filling the a\(_{\Pi}\) anti-bonding orbital (Figure 17). However, cobalt at this site requires a greater amount of energy to form covalent bonds than iron present at the same site. Consequently, cobalt substitution for iron takes place relatively infrequently (where it is represented by the minerals glaucodot or danaite). Additionally, cobalt may exist in the +3 oxidation state which, despite having a smaller ionic radius than Fe\(^{2+}\) in that state, Co\(^{3+}\) substitution will result in a valence shell of 6 electrons which would fill all of the orbitals in the same manner as Fe\(^{2+}\) thus, giving the crystal the same stability, in terms of the covalent bond energies, as having Fe in the metal site.
It is difficult to ascertain, based solely on LA-ICP-MS data, if Co directly substitutes for
Fe, but it may be possible with more sophisticated analytical techniques and instruments
such as synchrotron EXAFS. However, access to this equipment was not available during
the period of research. In theory, if there were abundant Co in solution during the growth
of arsenopyrite there should be competition between Co and Fe for substitution at the Fe
sites. However, it may be observed that the LA-ICP-MS data for arsenopyrite crystals
displays a strongly linear sympathetic relationship between the raw CPS of Co and Fe
(Figure 41). Despite the issues of laser coupling, it may be inferred that the cobalt is
present as a substitution for iron, as the slopes of the three crossover samples (Figure 41),
which have been analysed several hundred times during the course of the production of
this thesis, each have a distinct slope, demonstrating variations in the relative Fe/Co ratio
in the three crystals.

The substitution of Ni into the Fe site in the arsenopyrite crystal lattice may be expected
with reference to the IM as the Ni$^{2+}$ ion (0.069 nm) has a smaller ionic radius than Fe$^{2+}$
(0.078 nm) (in nature the nickel substitution is represented by the minerals
rammelsbergite and wolfachite). In addition, the molecular orbital model may explain the
substitution of Ni into the Fe site. The additional two valence electrons of Ni may fill the
$\alpha_{II}$ anti bonding orbital and may begin to fill the $\sigma^*$ orbital, both of which are at similar
energy levels. The MOM would suggest that additional energy would be required for Ni
to replace Fe which would also suggest that Fe and Ni should be in competition for this
site. The competition between Ni and Fe cannot be directly observed and it is therefore
uncertain if Ni does replace Fe in the arsenopyrite lattice although this may be difficult
to determine because of the extremely large differences in their concentration and the
precision of the LA-ICP-MS technique at the high concentrations in which iron is found.
However, similar to the relationship observed in Figure 41, the Ni and Fe CPS correlation
is strong and the slope is different for various samples. Nickel is unlikely to substitute for As or S as it is too electropositive and does not contain enough valence electrons to form a Ni-Fe covalent bond.

The ionic radius of Ni$^{2+}$ is considerably smaller than the 0.0745 nm radius of the Co$^{2+}$ and the 0.078 nm radius of Fe$^{2+}$, consequently it would be expected that Co$^{2+}$ would more likely substitute for Fe under most circumstances. However, when arsenopyrite is investigated using solution based ICP-MS, it is apparent that, for the majority of samples, Ni is at a higher concentration than Co (Figure 42). Additionally, nickel and cobalt also display a strong sympathetic concentration relationship with each other (Table 13), suggesting that while there may be competition for the Fe site between these two elements, this competition is overshadowed by more significant factors during arsenopyrite genesis.

![Concentrations of Co and Ni in Arsenopyrite](image)

**Figure 42.** The concentrations (in ppm) of Co and Ni from 21 arsenopyrite samples collected and analysed using the solution ICP-MS method described in section 2.3.5.
Copper is most likely to be present within arsenopyrite at the Fe site due to Cu\(^{2+}\) (0.073 nm) having a similar ionic radius as Fe\(^{2+}\) (0.078 nm) which fulfils the criteria required for significant substitution under the ionic model. Copper in the +2 oxidation state tends to favour a square planar arrangement with four bonds short bond lengths and two bonds of a longer length (Kivelson and Neiman, 1961). With the exception of the metallic bond, there is a similar spacing arrangement of covalent bonds between Fe, As, and S in the arsenopyrite lattice (Fuess et al., 1986). This lattice spacing may assist in reducing the energy required for Cu substitution at the Fe site. If the metallic bond were not present, Cu\(^{2+}\) would be an extremely favourable substituting ion. However, the alternating metallic bonding prevalent in arsenopyrite has a negative impact on the energy required for Cu substitution. Separation of the metal sites will reduce the amount of metallic bonding. This separation will increase the energy requirements for Fe to covalently bond with As and S, due to the single electron in the a\(_{II}\) anti bonding orbital no longer being paired with another electron from a neighbouring Fe site. The reduction in metallic bonding and the separation of metal centres would suggest that Cu is more likely to be more significantly concentrated in arsenopyrite crystals which are either strained or significantly deformed during crystal growth. Without detailed microscopic and X-ray diffraction investigation of the spacing of lattice units (which is beyond the scope of this thesis) it is difficult to ascertain the degree to which crystals are strained or contain defects, however, it can be stated that arsenopyrite may be significantly strained and may fracture as a result of the strain (Ford and Ferguson, 1985). From observation of the processing of raw CPS data using Glitter™ it is apparent that Cu (and Zn to a lesser extent) commonly have a stable “baseline” CPS which may contain spikes or patches of unevenness (Figure 43). This may suggest that in the absence of crystal strain Cu may substitute for Fe (giving a low but constant baseline signal), but in areas of crystal strain or distortion Cu may be more significantly substituted for Fe in the crystal lattice giving rise to much higher CPS data.
for that analyte. In areas of high strain the arsenopyrite crystal may fracture and these voids may then be filled in with Cu-rich minerals (Figure 29 and Appendix E-1.6). It must be considered that some of the more significant spikes may be attributed to exsolution of copper rich minerals giving rise to microscopic areas of significantly increased copper concentration. Typically these spikes are removed from the final data set before processing. Similarly to cobalt and nickel, there is a positive sympathetic relationship between CPS data for copper and iron. This indicates that other factors are having a significant impact on the substitution of these elements into arsenopyrite, or that perhaps microcrystalline inclusions of chalcopyrite occur in areas of strain or weakness within the arsenopyrite crystal.

![Figure 43. The CPS data of $^{65}$Cu every 1.778 seconds during the laser ablation analytical run of arsenopyrite samples from the Fimiston, Hemlo, and Bayleys gold deposits and the “Arsenopyr” cross-over sample. The initial 15 seconds is the period before the laser ablation commences.](image)

3.3.2.2 As or S Site

Selenium and tellurium both have a similar ionic and electron configuration to sulfur. In addition, both of these elements have a similar Lewis harness to sulfur (Parr and Pearson, 1983). Therefore, Se and Te are likely to form bonds with iron of a similar stability to
sulfur and their incorporation into the arsenopyrite lattice is predominantly as a replacement of sulfur, with the potential for minor substitution at the As site (due to common isomorphous substitution of S and As in arsenopyrite). Both Se and Te have a similar number of oxidation states and ionic radii to S. According to the ionic model it would be expected that these two elements would readily substitute for S in the arsenopyrite lattice. Additionally, these elements share the same number of valence electrons with S and would contribute the same number electrons to covalent bonds, fulfilling the requirements for significant substitution under the molecular orbital model. The substitution of Se and Te at the S site would imply that these elements are forming a covalent bond with elements at the Fe site. The elements decrease in Lewis hardness in the following order S>Se>Te. The elements likely to be present at the Fe site increase in hardness in the following order Fe$^{2+}$<Ni$^{2+}$<Cu$^{2+}$<Zn$^{2+}$. Therefore, with reference to the HSAB theory, it would be expected that the Fe-Se or Fe-Te bond would have a greater stability than an Fe-S bond. It would be expected that elements that replace Fe are likely to form stronger bonds with sulfur than with Se or Te which would imply that Se and Te should have an antipathetic relationship with elements likely to substitute at the Fe site. It was discovered that Se and Te share an extremely weak antipathetic relationship with the hardest Lewis acid (Zn) which may be present at the Fe site. Due to the weakness of the relationship it is not possible to confirm if Se and Te are specifically located in the As or S site in the arsenopyrite lattice.

It is expected that Sb and Bi can both potentially substitute into the As site as both these elements have a +3, and +5 oxidation state in common with arsenic (Shannon, 1976). However, the ionic radii of Sb$^{3+}$ (0.090 nm) and Bi$^{3+}$ (0.110 nm) are both significantly larger than the radius for As$^{3+}$ (0.072 nm), which would imply that they would not readily replace As with respect to the ionic model. The molecular orbital model may also be used
to assess the replacement of As with either Sb or Bi as all three of these elements share the same number of electrons within the valence shell. These three elements will all contribute the same number of electrons necessary to form a covalent bond with iron. Arsenic was not determined during the LA-ICP-MS analysis of arsenopyrite, as high concentrations of this mono-isotopic analyte would overload the ion multiplier and result in a zero signal when the device automatically shuts down during analysis. Therefore, the relationship between the potential substituents to arsenic cannot be directly quantified.

3.3.2.3 Sites of Incorporation for Other Elements

It has been previously demonstrated in section 3.3.1 that gold will be present in observable quantities in a large number of arsenopyrite crystals. Gold is commonly found in trace quantities in sulfide minerals and is rarely a major element in mineral phases other than elemental gold and electrum in mineralizing systems (Gammons and Williams-Jones, 1995, Cook et al., 2013). It is expected that gold is most likely present in arsenopyrite as small isolated inclusions, as the energy required for it to be a lattice substituent for Fe, As, or S is a significant limiting factor. Evidence for the presence of gold as a discrete mineral phase within the arsenopyrite crystal may be observed from the density distribution of gold CPS data for numerous LA-ICP-MS analyses (Figure 44). The CPS density distribution in Figure 44 indicates that the relative concentration of gold for over 90% of the data is at a consistently low level. This observation is consistent with a significant number of arsenopyrite samples chemically analysed in this project. However, several of the arsenopyrite samples investigated in this manner have a gold CPS greatly in excess of the median value. This would suggest the likelihood of frequent ablation of included or exsolved gold within arsenopyrite. In addition, evidence for the ablation of gold inclusions may be observed as small spikes or irregularities in the gold CPS trace during data processing with the Glitter™ software. These small gold
concentration irregularities appear to be a consistent feature of many arsenopyrite samples, especially those associated with gold deposits, and it is likely that these irregularities result from ablation of nanometre sized inclusions. While it would be inappropriate to consider included or exsolved mineral phases within the arsenopyrite crystal as being part of the actual arsenopyrite lattice itself, the presence of a significant number of these small inclusions are an observable feature of most arsenopyrite crystals. Therefore, the irregular ablation of Au in arsenopyrite is considered to be part of the trace element assemblage of the sample. However, any significant spikes in the CPS data for gold observed during data processing are indicative of the ablation of micrometre or larger sized inclusions. These anomalous values will result in the data for this sample not being included in the final dataset.

**Figure 44.** *The density distribution of the iron-normalized Au CPS from the cross over sample GA47 261 (179 analyses).*
On the basis of the ionic or molecular orbital model, silver is unlikely to be a substituent for any of the major elements in the arsenopyrite lattice. Silver is only commonly present in the +1 oxidation state which would be an incorrect charge to undertake replacement of any of the major elements. In addition, the ionic radius of Ag\(^+\) (0.114 nm) is also inappropriate to facilitate substitution at any of the lattice sites (Shannon, 1976). On the basis of the molecular orbital model, silver has too few electrons to substitute for either As or S and too many electrons to substitute for Fe (the energy requirements would be restrictively high). Silver has similar chemical characteristics to gold and it is expected that, like gold, this element will also not readily replace lattice elements. Therefore, it would be expected that silver would display a tendency to form exsolved mineral aggregates in arsenopyrite similar to that observed with gold. Evidence for the presence of exsolved silver may be observed from the density distribution of Ag CPS data from the analysis of several hundred arsenopyrite samples (Figure 45). The distribution of Ag CPS data in Figure 45 is unsurprisingly similar to the distribution of Au CPS in arsenopyrite (Figure 44), further emphasising the likelihood of Ag being present as exsolved mineral aggregates in an arsenopyrite crystal.

It should be noted that for the majority of samples, the iron-normalized CPS of Ag and Au do not display a sympathetic relationship (Figure 46). This would suggest that if these elements are present as microscopic inclusion then they are rarely present in appreciable concentrations within in the same inclusion. This is unexpected as gold and silver commonly form electrum (gold and silver alloy) in a significant number of gold depositional environments (Gammons and Williams-Jones, 1995). However, the samples highlighted in Figure 46 display a strong linear sympathetic relationship between Ag and Au CPS. This relationship is only observed in the higher CPS data of both Au and Ag which would suggest both that electrum is only accurately determined in larger inclusions
and that at lower concentrations inclusions do not contribute sufficient analytes to the analytical signal for data to be significantly above the detection limit and therefore precise. As explained earlier, data displaying evidence for contamination from inclusion are removed and not included in the final dataset. However, some samples which contain appreciable concentrations of exsolved gold and silver minerals have relatively elevated CPS data for these elements and may inadvertently be included in the data base. In the case of these samples, when sample or deposit median chemical data are used for interpretation purposes, the influence of slightly elevated data are obviated and does not affect interpretational protocols (Figure 46, deposit median values).

Figure 45. A frequency distribution of the relative response of iron-normalized Ag CPS data collected from 615 arsenopyrite samples from gold and non-gold depositional systems. It should be noted that few samples have an Ag/Fe ratio greater than $4 \times 10^{-5}$. 

Silver Frequency Distribution
Figure 46. The iron-normalized Ag and Au CPS data for the analysis of over six thousand individual laser ablation sites from 626 arsenopyrite samples from gold and non-gold deposits, and the deposit median values for these deposits. Note the strong sympathetic relationship between Ag and Au (when both are in high concentration) circled in black.

Tin, mercury, thallium, and lead are generally present in concentrations significantly above detection limits for arsenopyrite analysis using LA-ICP-MS. The incorporation of these elements in arsenopyrite is not readily explained with the ionic model as none of these elements have the same common oxidation states as either As or S and although they share some similar common oxidation states with Fe, their individual cations are considerably larger than those for iron. This would suggest that while substitution may occur at the Fe site it would be limited. The substitution of these elements into any of the lattice sites cannot be explained with the molecular orbital model either. These elements do not share a similar valence electron shell to any of the lattice forming elements of arsenopyrite. It is possible therefore that these elements are entrained within the arsenopyrite crystal and may be present within nano-metre sized inclusions or present in defects within the arsenopyrite crystal. In either case these elements appear to have an equivalent (although significantly reduced) CPS response over time when compared to
Fe during a laser ablation analysis of an arsenopyrite crystal (Figure 47). Therefore, while it may be stated that these elements are present within the arsenopyrite matrix, without more detailed investigation their specific location within the lattice remains conjectural.

![Tin, Mercury, Thalium, and Lead in Arsenopyrite](image)

**Figure 47.** The counts per second of four isotopes belonging to Sn, Hg, Tl, and Pb measured every 1.778 seconds during an ablation of the sample HQ9. Note that the CPS of $^{120}$Sn and $^{205}$Tl have been multiplied by 5 and 20, respectively, while the CPS for $^{57}$Fe and $^{208}$Pb has been divided by 5000 and 20 in order to fit all of the ablation profiles of each isotope on the same graph.

While it may be considered that the use of trace elements present within arsenopyrite as indicators for style and grade of gold mineralization could potentially be made easier by using relative concentrations of associated PGM’s (Ru, Rh, and Pd), the extremely low concentration of these analytes within the crystal makes this approach problematic. Additionally, because of their low abundance, it is difficult to obtain any precise evidence for the determination of potential lattice locations for these elements in the arsenopyrite crystal. Usually these elements are close to the detection limit of the LA-ICP-MS instrumentation and the occurrence of these elements above their respective detection limit rarely displays a significant signal/noise ratio when processing the data with
Glitter™. When these elements are detected above background, their CPS profile follows the ablation profile of iron, suggesting that they may be present within the crystal structure of arsenopyrite (Figure 48). In addition, it would appear that the relative responses of these elements is also related to the ablation profile of Au (Figure 48) suggests that they are preferentially incorporated into Au inclusions. However, it is currently not possible to determine their specific lattice location without a more detailed analysis and preferably using arsenopyrite that is more enriched in these elements.

Figure 48. The counts per second of $^{102}$Ru, $^{103}$Rh, and $^{108}$Pd measured every 1.778 seconds during the ablation of sample MTM8. The orange line represents the CPS of $^{197}$Au divided by 10 to fit within the scale of the graph. The dashed line is the CPS data of $^{57}$Fe divided by $10^4$ to fit within the scale of the graph, and the shape of this line represents the relative mass of arsenopyrite ablated.

3.4 Relationships between Arsenopyrite Chemistry and Geology

The previous sections within the Results and Discussion Chapter have examined the incorporation of trace elements into arsenopyrite and the potential for these elements to
be influenced by the physiochemical conditions of the hydrothermal fluid during mineral formation. It has been detailed previously in section 1.5, that the pressure and temperature of the hydrothermal fluid impacts the chemistry of arsenopyrite. This effect is typically insignificant when compared to the effect that the chemistry of the hydrothermal fluid, at the depositional environment, has on the arsenopyrite chemistry. The overall fluid chemistry at the depositional environment is the product of the reaction between the host rocks present at the site of mineralization and the metal and ligand source. Consequently, the interpretation of arsenopyrite trace element chemistry at a specific site has the potential to provide a better understanding of the fluid chemistry of particular hydrothermal systems and the information derived from this interpretation has the potential to be used as an indicator of gold and base metal mineralization.

In the pursuit to discover new gold orebodies it is essential to identify the appropriate regional geological indicators which can signify the presence of an appropriate economic orebody. The identification of trace element assemblages of arsenopyrite, being a reflection of conditions of the hydrothermal fluid, may be one such indicator. Understanding the arsenopyrite assemblage indicators early in the exploration process may allow a geologist to determine if an area has the potential to contain an economic orebody. By further interpretation of the arsenopyrite chemistry, it is possible that the style of mineralization and the potential endowment of the system may also be estimated. In addition, the determination of the geological timeframe and the chemical makeup of the hydrothermal fluids, from which a deposit may have been formed, are of major significance in understanding depositional mechanisms for ore emplacement. In this way it may be possible for an exploration geologist to identify regional geochemical anomalies that signify if an area has been subject to mineralization processes in the geological past and thereby more quickly identifying potential “hot spots” in a regional setting.
3.4.1 Resource Deposit Type

Arsenopyrite is associated with both gold and base metal deposits and in a few rare circumstances it may also be formed by the remobilization of sulfides from hydrothermal fluids during a metamorphic episode. Therefore, some arsenopyrites formed under the influence of metamorphism processes are not associated with the economic concentration of gold or base metals. Consequently, it is important to identify the genetic origin of an arsenopyrite so that an unknown sample may be quickly identified as being related to gold mineralization or not. This sub-section compares arsenopyrite samples from gold deposits and those from unrelated systems in order to identify any chemical differences between the two groups. In addition, this section will also investigate the differences between arsenopyrites from different types of base metal and magmatic hydrothermal deposits in order to determine if any systematic relationships between arsenopyrite trace element chemistry and an ore emplacement event may be observed. It is expected that arsenopyrite from a system that concentrates gold will have a different trace element signature from an arsenopyrite sample from a base metal or unrelated system. This suggestion is based on the probability that the significant differences in physicochemical conditions between gold deposits and other systems will be reflected in arsenopyrite trace element chemistry. If this generic relationship is observed and can be quantified then there is the potential to use arsenopyrite trace element chemistry as an indicator of various forms of mineralization.

Following detailed LA-ICP-MS analysis and data interpretation, the broad differences in median arsenopyrite trace element assemblages between gold and non-gold systems were developed and displayed in Figure 49. Overall, these two systems display a number of significant differences in arsenopyrite chemical assemblages, most notably; Co, Ni, Se, Ag, Te, Au, and Bi concentrations. An elevated concentration of Au in arsenopyrite
associated with gold depositional systems is expected, as these systems are already elevated in gold and this element is more likely to incorporate in arsenopyrite at higher concentrations if it is already at relatively high concentrations in the solution.

Figure 49. The median iron-normalized trace element data for arsenopyrite samples collected from gold and non-gold deposits.

However, if the data for these deposits is interrogated in more detail by plotting the iron-normalized CPS data for each individual deposit (Figure 50), no significant differences can be determined. Consequently, it is inappropriate to differentiate the systems based solely on the iron-normalized trace element CPS data. However, more sophisticated and detailed analyses will be performed in latter sections to assist in defining and differentiating these groups.
Figure 50. Deposit median Ni, Se, and Au iron normalized CPS values some of the geological systems analysed in this thesis (62 deposits and 2 non-mineralized). The first three groups (Archean, Proterozoic and Phanerozoic Au) represent arsenopyrite from gold deposits. The last three groups (Base Metals, Magmatic Hydrothermal and Non-Mineralized) represent arsenopyrite from non-gold systems.

Linear Discriminant Analysis (LDA) was performed on the dataset (Figure 51) and the data generated from this LDA describes that the two systems are significantly
differentiated from each other and that 87.13% of the samples are correctly grouped and 90% of the validation samples are also correctly grouped. Of the data analysis techniques, it is apparent that an LDA of the two groups provides the greatest ability to discriminate between them in terms of trace element chemistry of arsenopyrite. Therefore, an unknown sample may be chemically analysed and compared to the groupings generated from the LDA (Figure 51) to give a high degree of probability of assigning the unknown sample to the correct group. Several random samples from both gold deposits and non-gold deposits were investigated in this manner and the majority were identified as belonging to their correct group.

**Figure 51.** An LDA of the deposit median trace element chemistry of arsenopyrite from gold deposits and the sample median trace element chemistry of arsenopyrite from non-gold systems (79 deposits).

A Principal Component Analysis (PCA) was also performed on the same dataset as the LDA (Figure 51) to assess the validity of the groupings and elements used to perform these groupings (Figure 52). It should be noted that the PCA detailed in Figure 52 uses the 1st and 5th functions as this provides the best discrimination between the two groups, despite the fact that functions 2, 3, and 4 have higher total variance (17.03%, 12.84%, and...
8.84%, respectively). In this manner the differences between groups may be observed without any user influence or bias. It may be observed from Figure 52 that the samples from the two groups tend to differentiate from each other based on similar trace element assemblages generated from the LDA (Figure 51). Therefore, the results obtained using LDA have been confirmed and may be considered to be without apparent bias.

**Figure 52.** A PCA of the deposit median trace element assemblages of arsenopyrite from gold deposits and sample median trace element assemblages of arsenopyrite from non-gold systems (79 deposits).
From the comparison of the LDA and PCA analyses, arsenopyrite samples from gold deposits are demonstrated to contain elevated concentrations of Co, Ni, Mo, Se, Te, and Au relative to arsenopyrite from non-gold systems (Figure 51). This observation confirms that the trend is similar to the trends that have been previously detailed in Figure 49 and Figure 50. Arsenopyrite from non-gold systems can be differentiated from those which are associated with gold systems by the elevated CPS data for of Cu, Zn, Pd, Ag, Sn, Sb, and Pb.

The depositional environments of the gold deposits investigated in this thesis are from many areas throughout Australia, in addition to a deposit from both the USA and Canada. The samples from the non-gold suite consist of a number of samples from New South Wales and Tasmania, Australia and several samples from scattered non-gold systems throughout the world. Despite the large variation of depositional environments within the non-gold group (and to a lesser extent, within the gold group) it may be observed from Figure 51 and Figure 52 that the samples from these deposits exhibit a strong grouping. Therefore, it would appear that, at the scale of gold and non-gold systems, the local depositional environment may have less impact on the arsenopyrite trace element chemistry than the physiochemical conditions of the primary hydrothermal fluid source which has formed the arsenopyrite.

Overall, the fluids that form the gold and non-gold systems are significantly different from each other in terms of physical and chemical conditions. The broad differences in fluid physicochemical conditions between these systems may be observed in Table 14. It has been previously stated that the temperature and pressure of a hydrothermal system has only a minor effect on the chemistry of mineral formation and as such, the physical effects of the local fluid mixing environment on arsenopyrite trace element chemistry are
considered negligible when compared to the influence exerted by the primary hydrothermal fluid chemistry.


<table>
<thead>
<tr>
<th>Fluid Conditions</th>
<th>Gold</th>
<th>Non Gold</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>200-400</td>
<td>500-900</td>
</tr>
<tr>
<td>Pressure (MPa)</td>
<td>50-700</td>
<td>10-70</td>
</tr>
<tr>
<td>pH</td>
<td>5.2-6.2</td>
<td>variable</td>
</tr>
<tr>
<td>NaCl (%)</td>
<td>2-10</td>
<td>10-70</td>
</tr>
<tr>
<td>Sulfur (mol L⁻¹)</td>
<td>10⁻³ - 5x10⁻²</td>
<td>variable</td>
</tr>
</tbody>
</table>

The higher pressure and lower temperature of gold bearing fluids, compared to non-gold, commonly results in the CO₂ concentrations in gold bearing fluids being significantly higher than those in non-gold systems (Lowenstern, 2001). While it is not believed that CO₂ is directly involved in the transportation of gold in orogenic systems, due to weak Au-CO₂ bonding, the presence of CO₂ in hydrothermal fluids is indirectly involved in the transport of gold, most commonly acting with the HCO₃⁻ anion as a buffer (Phillips, 2004). The greater buffer capacity of the gold-bearing fluids assists in maintaining a close to neutral pH. It is at this pH that the bisulfide ion is the dominant sulfide species. The bisulfide ion is the most important ligand in gold complexation and is involved in the complexation of other soft Lewis Acids. This would help to explain the relatively higher concentrations of Se, Te, and Au in arsenopyrite from gold depositional systems.

In a simplified manner, many of the differences in fluid chemistry can be explained by the Hard-Soft Acid-Base (HSAB) theory (Pearson, 1968). The ligands that form gold deposits (bisulfide dominated) are primarily of a “softer” Lewis basicity than those that form base metal or magmatic hydrothermal deposits (chloride dominated). The softer Lewis basicity of the gold-forming fluids is defined by high sulfur concentrations and a reduced redox state of the fluid. This is primarily due to Au⁺ being an extremely soft
cation which will readily create a covalent bond with bisulfide ligands (Ahrland et al., 1958). Therefore, it is required that a soft Lewis base is able to transport this cation. As stated previously, the abundance of soft sulfide ligands is likely to transport other soft Lewis acids and this is observed by the relative abundance of Se and Te in arsenopyrite from gold deposits (Figure 51 and Figure 52). However, it may also be observed from Figure 51 and Figure 52 that other soft Lewis acids (Sb and Pb) appear to be more concentrated in samples from non-gold systems. It is difficult to fully assess the affinity of Lewis acids to ligands as it is the oxidation state of the Lewis acid which drastically dictates the “harndess” of the Lewis acid (Ahrland et al., 1958). Without having a detailed knowledge of the redox potential of the fluids it is difficult to assess the exact oxidation state of the cations during transportation and deposition.

The ore forming cations for non-gold systems require a harder Lewis acid to form a chemical bond during metal-ligand complexation. This is reflected in the high concentration of salinity in non-gold systems as Cl⁻ ligands are critical in the transport of base metals (Phillips, 2004). However, this does not directly translate into a greater concentration of harder Lewis acids, at the expense of soft Lewis acids, in arsenopyrite from non-gold systems. This would suggest that there is not a direct relationship between the concentration of a species in a hydrothermal solution and those in arsenopyrite. Instead, there are other significant factors which impact the chemistry of arsenopyrite. It may also be observed from Figure 49 to Figure 51 that the samples from non-gold systems typically display lower concentrations of most of the trace elements (with the only significant exceptions being Ag) when compared to gold deposits. This is contrary to the predominance of a wider variety and concentration of metals in the non-gold systems.
It should be noted that the average difference in Au concentration between these groups is within an order of magnitude and a significant number of non-gold samples have higher Au concentrations than some arsenopyrite samples representing gold deposits. It would be expected that arsenopyrite from gold deposits would have significantly higher Au concentrations than arsenopyrite from systems that do not concentrate economic quantities of gold. The reasoning behind the less than representative Au concentrations may stem from the discrete mineral phases of elemental gold that have been observed in some of the gold deposit samples analysed in this thesis. Gold in solution will require less energy to nucleate onto an existing elemental gold mineral phase than alternatively forming part of an arsenopyrite crystal matrix. Consequently, the relative abundance of an ore element in arsenopyrite may not necessarily be a true reflection of the chemistry of the ore forming fluid.

A number of samples are “incorrectly” identified by the LDA process (Figure 51) and could therefore be considered as being associated with the incorrect group. The gold deposit samples incorrectly identified as non-gold samples include; Big Bell, Boorara, Harnett, Hemlo, Plutonic, Spargoville, Transvaal, Youanmi, Enterprise, Goodall, and Woolwonga. The non-gold samples incorrectly identified as a gold deposit sample include; Broken Hill, and Yaoganxian. It should be noted a few hundred thousand ounces of Au have been mined from the Broken Hill deposit (Gustafson et al., 1950), which may explain why arsenopyrite from this deposit is chemically similar to those from orogenic gold deposits. The data for Broken Hill and Yaoganxian are based on the analysis of single crystals of arsenopyrite from each deposit and therefore the interpretation of data can neither be said to have a high degree of statistical significance nor represent arsenopyrite from data these deposits. Consequently, until further samples can be found
for analysis, data for these deposits cannot be considered further as they cannot be verified.

The reasoning for the “incorrect” sample identification of gold deposits considered non-gold, generated from the LDA, is that the statistical method used to identify the groups considers these samples as having similar arsenopyrite trace element chemistry as the incorrect group when separated with the individual trace element variables used. While this may be the case for a specific group of trace elements it may not be the case when considering the bulk element geochemistry of the sample. Consequently, a series of Comparability Index (CI) plots (Appendix E-1.5) were used to establish if the bulk element chemistry of the samples was any more accurate at identifying which groups the incorrectly identified samples belonged to. The results of the CI analyses are presented in Table 15 and from observation of these statistics; it is clear that these samples do not necessarily have an arsenopyrite trace element chemistry consistent with the group that they have been incorrectly identified as belonging to. For example, when a sample from the Big Bell deposit is subjected to comparability index calculations, the first 257 of 626 samples in the data base that associate with the Big Bell signature are from gold deposits. Under these circumstances it could easily be considered that Big Bell is truly a gold deposit as it obviously is. Data for associations of some other deposits that have indicated that they are non gold are given in Table 15. In all cases the best CI fits to the search sample are all represented by gold deposits. It should be mentioned that it is important to employ multiple statistical techniques when analysing and interpreting the data as each test (especially parametric tests like LDA) has their own downsides. As the CI analysis is non-parametric, it is able to provide a more accurate interpretation without any biases from the user.
Table 15. A series of CI analyses performed on samples from gold deposits “incorrectly” grouped in the LDA, where the number of the top ranking correct identifications are listed (out of a total of 626 samples).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Deposit</th>
<th>Number</th>
<th>Sample</th>
<th>Deposit</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>BB11</td>
<td>Big Bell</td>
<td>258</td>
<td>TV1</td>
<td>Transvaal</td>
<td>265</td>
</tr>
<tr>
<td>B7 173.8</td>
<td>Boorara</td>
<td>60</td>
<td>YM1</td>
<td>Youanmi</td>
<td>30</td>
</tr>
<tr>
<td>HEML 11</td>
<td>Hemlo</td>
<td>157</td>
<td>ENT1</td>
<td>Enterprise</td>
<td>111</td>
</tr>
<tr>
<td>JS8</td>
<td>Plutonic</td>
<td>46</td>
<td>GODL10</td>
<td>Goodall</td>
<td>145</td>
</tr>
<tr>
<td>SpW2</td>
<td>Spargoville</td>
<td>117</td>
<td>WW2</td>
<td>Woolwonga</td>
<td>35</td>
</tr>
</tbody>
</table>

The limited overlap and consequent misclassification of samples using LDA analysis (Figure 51) is largely caused by the requirement that only two user defined populations (gold and non-gold) are allowed to be recognised. Both of these populations contain samples representing a wide variety of ore depositional environments, types, and grades and consequently in themselves represent a number of individual types of mineralization that may not fit into a single sub-class. The non-gold deposit group covers arsenopyrite from magmatic hydrothermal deposits, base metal deposits, and unmineralized systems. Therefore, the “a priori” LDA analysis detailed in Figure 51 does not account for other defined groups and as such its effectiveness is reduced (especially when compared to PCA and CI analyses). In order to better differentiate the groups, it may be necessary to subdivide the non-gold group into three distinct sub-groups (section 3.4.2). A similar situation exists for the gold deposits and their sub-classification is discussed in section 3.4.3. Because of the simplistic “a priori” approach to identification of gold or non-gold deposits it is therefore probable that some samples will be misclassified into the wrong group and further sub-division of data may be necessary to avoid unnecessary confusion.

3.4.2 Non-Gold Resource Type

Arsenopyrite may also be formed in hydrothermal systems that are unrelated to gold mineralization where it is typically related to poly-metallic base metal or magmatic hydrothermal deposits. In this thesis the majority of these samples are collected from
magmatic hydrothermal deposits within the New England region in New South Wales, Australia. The number of arsenopyrite samples investigated in this thesis from non-gold deposits (58) is significantly lower than the number from gold deposits (568) and due to the fewer number of samples, statistical analyses had to be performed using data for each individual measurement of a sample rather than median data for that sample.

The non-gold deposits investigated in this thesis are easily differentiated from deposits that are gold bearing, based on the observations in section 3.4.1. These deposit types may be further differentiated from each other using trace element assemblages of arsenopyrite and their association with the primary ore metals (Figure 53), which are indicative of the bulk hydrothermal fluid chemistry. The Pb-Zn deposits may easily be differentiated from the Cu, Sn-W, and Ag deposits (79.4% correctly identified) by the higher CPS of Ni, Sb, and Au in arsenopyrite. Similarly, samples from Cu deposits may be distinguished from the other arsenopyrite samples because of their elevated concentrations of Te.

Arsenopyrite from the Pb-Zn deposits display higher concentrations of Co and Ni and lower concentrations of Zn and Pb than their non-gold deposit counterparts (Figure 53). The ore forming solutions related to Pb-Zn deposits have high concentrations of Pb and Zn in solution (which are obviously required in order to form such a large ore system). This would imply that the lower abundance of Pb and Zn in arsenopyrite demonstrates that the arsenopyrite chemistry is not a true and direct reflection of the ore forming fluid. The reasoning for the lower than anticipated Zn and Pb concentrations in the arsenopyrite may be explained by the large quantities of the chief ore minerals; sphalerite (ZnS) and galena (PbS) that are formed in a distinct zonation pattern within and around the source intrusive (Simmons et al., 2005). During mineral formation elements will preferentially nucleate onto an existing seed crystal that facilitates its incorporation with the minimum
energy required. This means that zinc will preferentially nucleate onto pre-existing sphalerite seed crystals, lead onto galena and arsenic onto arsenopyrite. Consequently, while some lead and zinc will incorporate into arsenopyrite present in the mineralizing system during formation, the majority of these elements will be incorporated into their respective ore forming mineral and thereby reduce the amount of these elements available for incorporation into arsenopyrite. This is dissimilar to the higher concentrations of Au which are observed in arsenopyrite associated with gold deposits (Figure 43 and Figure 45), potentially because native gold is always present in gold deposits and usually this native gold is contained in economic quantities in sulfide minerals (Huston et al., 1995).

**Figure 53.** An LDA of the trace element data of arsenopyrite from non-gold samples showing disposition of deposit types. The data used for the LDA is taken from individual laser ablation sites (408 individual laser ablation sites).
Arsenopyrite associated with copper deposits may be better differentiated from the arsenopyrite associated with Ag and Sn-W deposits using an iterative LDA procedure following removal of the Pb-Zn arsenopyrite samples (Figure 54). In this analysis the arsenopyrite samples from the copper deposits can be seen to have a higher concentration of Ni and Co relative to arsenopyrite from Ag and Sn-W deposits.

**Figure 54.** An LDA of the trace element data for arsenopyrite from non-gold mineral deposits. Samples associated with the low temperature Pb-Zn deposit has been removed. The data circled in black represents samples from the Callington deposit (390 individual laser ablation sites).

The Ag and Sn-W deposits have previously displayed a similar arsenopyrite chemical assemblage despite the differences in geological setting and fluid chemistry. A third
iterative LDA was performed on the remaining samples from the Ag and Sn-W deposits where 80.3% of the samples are then correctly grouped (Figure 55). The arsenopyrite samples from the Ag deposits have higher concentrations of Co, Ag, Au, and Pb when compared to samples from Sn-W deposits. Conversely, arsenopyrite from Sn-W deposits is relatively enriched in Se, Te, and Bi.

![Figure 55](image)

**Figure 55.** An LDA of the trace element data for arsenopyrite from Ag and Sn-W deposits (356 laser sites).

### 3.4.3 Gold Deposits

The samples from the gold deposits investigated in this thesis can be sub-divided into three groups based on the established age of formation of the deposit: Archean, Proterozoic, and Phanerozoic. Each of these time periods encapsulates a significant global gold formation event. The approximate ages of formation for these deposit groups are; ~2.6, ~1.8-1.55, and 0.5 Ga, respectively (Groves, 1993, Stewart, 2013, Willman, 2007).

The majority of the gold deposits investigated in this project are from Australia and come from three different orogenic environments; the Yilgarn Block (Archean), the Pine Creek...
Geosyncline (Proterozoic), and the Lachlan Fold Belt (Phanerozoic). In addition, arsenopyrite samples from the Hemlo (Canada) and Homestake (USA) deposits, which were formed during the Archean and Proterozoic respectively, will be compared to their Australian temporal counterparts.

Iron-normalized trace element data for the relevant arsenopyrite samples formed during the Archean, Proterozoic, and Phanerozoic periods are compared (Figure 56). The differences between arsenopyrite data from these three periods are less significant when compared to equivalent data for gold and non-gold associated arsenopyrites (section 3.4.1); as they represent differences in the depositional environment and hydrothermal fluid chemistry associated with gold related arsenopyrite genesis. Interactions between the depositional environment and the hydrothermal fluid chemistry of the ore solutions will cause significant variation of the localised chemistry within the mineralized zone. This will result in deposit specific changes in the arsenopyrite trace element chemistry. On the basis of the initial differences in the trace element chemistry of arsenopyrite between these groups (Figure 56), there is an indication that the arsenopyrite from Proterozoic gold deposits can be distinguished from the other two groups because of their elevated Co, Ni, and Bi concentrations (also these deposits have a Mo/Ag ratio of <1). Arsenopyrites from Phanerozoic gold deposits have a Co/Ni ratio of <1 (median value of 0.57) and although some Archean gold deposits also have a similar Co/Ni ratio to this, the ratios for samples from Archean gold deposits are usually much closer to 1. This distinction is however somewhat tenuous and further research (detailed later in this section) has been undertaken to help establish improved protocols that isolate Archean deposits from both their Proterozoic and Phanerozoic equivalents. Phanerozoic arsenopyrite samples have a median Se/Te ratio of >10, while arsenopyrite from both Proterozoic and Archean gold deposits have Se/Te ratios of <10, further differentiating
the Phanerozoic group of arsenopyrite from those of the other two. Other than marginally lower Bi concentrations, arsenopyrite samples from the Archean deposits do not demonstrate any particularly distinctive features.

The generic differences in the median chemistry of arsenopyrite between the gold deposit groups may be further elucidated using LDA procedures (Figure 57). This initial differentiation of the deposit groups was performed using the median values for each of the samples. The LDA graph generated by using the sample median data contained 568 individual arsenopyrite samples resulting in a graph that is too variable to be able to easily differentiate samples from the Archean and Proterozoic groups. While all of the samples from the Victorian Phanerozoic orogen are all correctly identified as belonging to the correct group, 7% and 1.6% of the Archean and Proterozoic samples respectively, were incorrectly identified as belonging to the Phanerozoic group. After several random samples were investigated using a predictive LDA investigation it is clear that the majority are correctly identified. Nevertheless, the LDA presented in Figure 57 displays a number of samples which are positioned incorrectly and have subsequently been
identified as belonging to an incorrect group (30.3% of the total number of samples). This incorrect group identification is most likely attributed to the differences between the deposits grouped together (for example, the Archean group consists of 35 individual deposits covering an area over tens of thousands of square kilometres). In addition, the chemical differences between arsenopyrite samples may arise from the variable local fluid physiochemistry within a deposit (discussed in greater detail in section 3.5). Overall, the differentiation of the Phanerozoic samples from the other two groups may be achieved using the LDA displayed in Figure 57. However, more detailed analyses are required in order to better define and differentiate samples from the Archean and Proterozoic groups.

**Figure 57.** An LDA of the sample median trace element assemblages of arsenopyrite formed during the Archean, Proterozoic, and Phanerozoic (568 samples).
An additional LDA was performed, using the sample median values, in order to more clearly identify the differences between arsenopyrite from the Phanerozoic deposits and arsenopyrite formed in gold deposits during different time periods (Figure 58). Observation of the LDA demonstrates that, with the exception of Se and Mo, the trace element concentrations in the Phanerozoic arsenopyrite samples are consistently lower than those from the non-Phanerozoic samples. There is a significant degree of overlap between the Phanerozoic and non-Phanerozoic group displayed in Figure 58. This is primarily due to over 92% of the samples used for this LDA being from non-Phanerozoic gold deposits (Archean and Proterozoic). The LDA aims to correctly identify the greatest number of samples (92% correctly identified in Figure 58) by defining the parameters which best identify the groups. This will typically lead to the group with the greatest number of samples having a broad set of chemical identifiers leading to, in this case, the Phanerozoic group being subsumed into the non-Phanerozoic group. This issue may be obviated and will be addressed later in this section.

**Figure 58.** An LDA using sample median trace element data for arsenopyrite from the Phanerozoic gold deposits compared to a group of arsenopyrite data from Archean and Proterozoic gold deposits (568 samples).
The sample median trace element assemblages of arsenopyrite from the Archean and Proterozoic deposits may be differentiated from each other by performing an additional LDA analysis by only using samples from these two groups (Figure 59). Although not specifically shown in Figure 59, the correct identification of samples belonging to these two groups in this analysis are 72.5% (363 samples), with a correct identification of the validation samples being 68.2% (15 samples). This LDA demonstrates, once again, that the Archean and Proterozoic arsenopyrite sample median data are only correctly identified approximately 70% of the time using sample median values. This would imply that the two groups have arsenopyrite with a similar chemical assemblage (especially with reference to arsenopyrite samples from the Phanerozoic group).

If a single unknown arsenopyrite sample from an Australian orogenic gold deposit were to be chemically analysed using an LA-ICP-MS system, there is approximately a 70% probability of identifying which Australian orogen the sample was taken from, by using...
the LDA protocols previous described in this section. This may be achieved by first determining if the sample is from the Victorian Phanerozoic orogen by assessing the sample chemistry against samples from the Phanerozoic deposits (Figure 57 and Figure 58). On the basis of this comparison, if the samples are not considered to have originated from a Victorian Phanerozoic deposit, then a comparison of the chemical assemblage of the unknown sample to the groups (similar to the differentiation in Figure 59) may establish whether the sample came from an Archean or Proterozoic deposit.

The establishment of the depositional time period may be improved by using the deposit median, rather than the sample median data. This assists in removing outlier arsenopyrite data which may compromise groupings and differentiation when using LDA protocols. It is for this reason that deposit median values are used in subsequent LDA’s used in this section. By using deposit median data for each of the gold deposits, the number of data points is reduced to 59. Deposit median data, when plotted using LDA, indicate that 90.6% of the samples are correctly identified and that 100% of the validation samples are also correctly identified (Figure 60). It may be observed from Figure 60 that the Phanerozoic and Proterozoic samples form their own discrete groups with the Archean samples being between these groups with relatively insignificant overlap between the groups. The five deposits specifically indicated in Figure 60 are those which have been identified as belonging to the incorrect group, however when performing a predictive LDA investigation the samples from 3 Mile Hill and Goodall were identified as belonging to their correct groups. Further analyses of all the samples which were incorrectly identified in Figure 60 has been performed and is reported later in this section.
Figure 60. An LDA of the deposit median trace element chemistry of arsenopyrite from the three gold deposit groups (59 deposits).

A PCA was performed on the same data set (Figure 61) to assess the accuracy of the groupings generated from the LDA displayed in Figure 60. As stated previously in section 3.4.1, a PCA is used to differentiate samples based on arsenopyrite trace element chemistry in the absence of user defined groups and potential user bias. Therefore, it may be observed from the data displayed in Figure 61 that the Proterozoic deposits form a distinctive group based on elevated concentrations of Co, Ni, Mo, Se, In, Pb, and Bi in...
arsenopyrite. This is similar to the elemental assemblage used to define the Proterozoic group in the previous LDA (Figure 60). The Phanerozoic group is encapsulated within the Archean group and is primarily clustered around the 0,0 point in the graph generated by the PCA (Figure 61). This would suggest that generically the Phanerozoic samples have lower levels of trace elements in arsenopyrite when compared to the Proterozoic and Archean samples (Figure 57 and Figure 58). The Archean group is not as well defined in the PCA when compared to either of the LDA’s. However, elevated concentrations of Sb, Au, and Hg in arsenopyrite can be used to differentiate the Archean from the Proterozoic groups (Figure 61). This elemental assemblage is also used previously in the LDA displayed in Figure 60 to define the Archean group. It should be noted that in Figure 60 and Figure 61 the Archean group has overlap with both the Proterozoic and Phanerozoic groups. A potential explanation for this observation may be that the Proterozoic/Phanerozoic hydrothermal fluid has travelled through and reacted with some Archean greenstones/granites and/or Cambrian aged shoshonitic basalts prior to final deposition, thereby influencing the fluid chemistry to somewhat resemble a hydrothermal fluid associated with Archean gold mineralization. Overall, the LDA groupings may be considered valid as the samples located within the groups in Figure 57 and Figure 60 have similar arsenopyrite chemistries.
Figure 61. A PCA of the deposit median trace element assemblages of arsenopyrite from 59 gold deposits. The blue, maroon, and green circles represent the agglomerations of samples from the Archean, Proterozoic, and Phanerozoic samples, respectively. Note that the Hemlo, Cosmo-Howley, and Homestake gold deposits have been specifically named and will be discussed later.

Samples from two of the deposits which were incorrectly identified in Figure 60 were collected from the Three Mile Hill and Greenfields deposits. Both of these deposits are Archean gold deposits in the Coolgardie region (~4 km north of the town of Coolgardie, Western Australia) in the Yilgarn Craton and within a kilometre of each other.
Consequently, they are part of the same system and share similar geological features (Appendix E-2.1). It is therefore no surprise that these two deposits are both closely related in terms of trace element chemistry in arsenopyrite. The Coolgardie region comprises of a complexly deformed belt of mafic and ultramafics rocks with minor black shale overlain by felsic volcanoclastic and metasediments. The two gold deposits share a great number of generic geological similarities with the other Archean deposits detailed in the LDA (Figure 60). It is therefore possible that in attempting to separate the Archean from the Proterozoic groups, these deposits may have been inadvertently misclassified as being part of the Phanerozoic group. To determine if this is the case an LDA of the chemistry of arsenopyrite from deposits formed during the Phanerozoic and Archean were compared to each other (Figure 62), and in this LDA both the Three Mile Hill and Greenfields are correctly identified as belonging to the Archean group.

**Figure 62.** An LDA between deposit median trace element data from arsenopyrite collected from Archean and Phanerozoic gold deposits (40 deposits).

The deposit median trace element assemblages of arsenopyrite from the Alligator, Goodall, and Woolwonga Proterozoic deposits were incorrectly identified as being part of the Archean group in the LDA presented in Figure 60. The Goodall deposit is
technically incorrectly identified by the LDA process as belonging to the Archean group, however, visual inspection of Figure 60 will demonstrate that while the Goodall sample is proximal to samples from the Archean group, it is equally proximal to samples from the Proterozoic group. From observation of the LDA the Alligator and Woolwonga deposits (highlighted in Figure 60) are proximal to a number of Archean deposits from the Randalls region. The Alligator deposit is adjacent to the Randalls-Santa deposit and the Woolwonga deposit is adjacent to the Randalls-Anomaly deposit. The Randalls deposits are dissimilar to the other Archean deposits by being hosted in BIF and therefore, it would be expected that deposits with similar host rocks (Archean and Proterozoic Si-S facies BIF) would have similarities in trace element chemistries of arsenopyrite assuming that the hydrothermal fluid has circulated locally in the BIF. An LDA was generated using the deposit median data with the user-defined groupings based upon the age of formation and the host rocks (Figure 63). It may be observed from this figure that, when accounting for deposit host rocks, the Proterozoic BIF deposits are again dissimilar to the Archean deposits; with the Alligator and Goodall sample are correctly grouped. This results in an LDA with 95.45% correct identifications (2 samples incorrectly identified) and 100% correct validation samples. The Mt Monger Milo deposit has been incorrectly identified as belonging to the Archean BIF group. Additionally, Woolwonga has again been misidentified; this time as belonging to the Archean BIF group. Visual inspection of the two misclassified samples will demonstrate that the classification scheme used by the LDA is statistical in approach; and this does not necessarily account for the overall grouping of samples. Therefore, it can be stated that the Mt Monger-Milo and Woolwonga samples were placed and categorized into their correct group.
Figure 63. An LDA of deposit median trace element data from arsenopyrite samples hosted in Archean greenstone, Archean BIF, and Proterozoic BIF deposits (44 deposits).

It may be observed from Figure 63 that the deposits hosted in banded iron formations display similar arsenopyrite trace element assemblages which are slightly different from the samples hosted in greenstones. An LDA has been generated to better understand the differences in trace element chemistry of arsenopyrite between the Archean and Proterozoic samples, independent of the type of host rock (Figure 64). It may be observed from this figure that 100% of the samples (including the validation samples) have been
identified as belonging to the correct group. After this additional scrutiny of data, the arsenopyrite from the Woolwonga deposit has been correctly identified as being associated with a Proterozoic deposit. This suggests that the incorrect identifications in Figure 60 and Figure 63 may be the result of the LDA attempting to separate three distinct groups; and that the Woolwonga deposit, which shares a similar chemical assemblage to both BIF groups, has been misidentified in the process. It may also be observed from Figure 64 that the Archean and Proterozoic deposits share a dissimilar arsenopyrite chemistry that is independent of host rocks. This suggests that the sources of the hydrothermal fluids are significantly physicochemically different from each other.

Over twenty CI analyses were performed on random samples in the dataset to investigate the validity of sample groupings generated from the LDAs detailed previously in this subsection (Appendix E-1.5). For the majority of samples at least ten of the database samples were identified as belonging to the correct age group; and over half of these top ten
samples were from the same gold deposit. The random testing of samples with CI analyses further confirms that the sample groups generated in the LDA are not arbitrary or generated out of user bias; but instead represent significant multivariate differences between the groups.

3.4.3.1 Archean Gold Deposits

The deposits within the Yilgarn Craton formed synchronously between 2.64-2.63 Ga ago (Groves, 1993). The depositional environment of the Yilgarn craton in Western Australia is typically made up of metamorphosed greenstone belts showing characteristics of sub-greenschist to amphibolite facies metamorphism. The greenstones of the Yilgarn are typically folded, faulted, and flanked by later voluminous Archean granite batholiths and volcanics (whitestones), which have significantly distorted the array of greenstone belts in the Yilgarn (Figure 65). The granites outcropping in the Yilgarn are not believed to be associated with the fluid source for the nearby deposits, as they have formed later in the genetic history of the craton (Groves, 1993). Gold mineralization in the Yilgarn occurs syn- to post- peak metamorphism. The fluids generated by metamorphic dewatering and magmatic sweating are widely believed to be the likely components for the fluid source (Mikucki, 1998). The circulation of the hydrothermal fluids is most likely the result of convection currents brought about by granitic batholithic intrusions (Groves, 1993). The positioning, lithological, and structural setting of the Archean deposits in the Yilgarn is detailed in Figure 65.
Figure 65. The locations of the Archean deposits formed within the Yilgarn craton, Western Australia. The pink areas represent the Archean granites and the light green represents the greenstone assemblages of the Yilgarn (DMP, 2013).

The Yilgarn craton is divided into four board provinces based on the genetic history of the craton and the lithology of the provinces themselves (Figure 66). In a similar fashion, the samples from the Yilgarn Craton have been divided into their respective provinces based on the location of the deposits (Figure 67). Within the Yilgarn craton the ore-forming processes and host rocks of these deposits are quite similar (with the exception of the BIF-hosted Randalls deposits). As detailed in the previous sub-section (3.4.3), the trace element chemistry of the Archean arsenopyrites exhibits a somewhat uniform assemblage which is easily distinguishable from other gold deposits formed in Australia. Consequently, the differences in arsenopyrite chemistry between the Archean samples are minimal.
Figure 66. A geological map of the Yilgarn Craton displaying the provincial subdivisions and the locations of some orogenic gold deposits, intrusion related Au-Mo-W deposits, and porphyry systems (Duuring, 2007).
Figure 67. The position of the Provinces within the Yilgarn Craton, Western Australia (DMP, 2013).

An LDA was performed on the deposit median trace element data of arsenopyrite to demonstrate the differences in arsenopyrite chemistry between these provinces (Figure 68). The differences in chemistry between the samples from the three Archean provinces (the Eastern Goldfields and the Southern Cross Provinces have been combined) are:

- The Northern Province (Cue-Murchison) is defined by relatively elevated Sn and Pb and by a relative deficiency of Mo, Ag, Te, and Bi in arsenopyrite.
- The Southern Province (SW Gneiss) is defined by a relative abundance of Ni, In, Au, and Hg together with a deficiency of Se in arsenopyrite.
- The Eastern Province contains data for the greatest number of samples, and this group is defined by the relatively elevated concentrations of Mo, Ag, Te, and Bi in arsenopyrite.
Figure 68. An LDA of the deposit median trace element assemblages of arsenopyrite from deposits within the three provinces in the Yilgarn craton (35 deposits).

Samples from the Southern Province are represented by samples from two deposits which have been investigated in this study (Griffin’s Find and Calyerup). Both of these deposits have similar geology to each other, with mineralization being contained within metamorphosed (to granulite facies) Archean sediments/volcanics. Mineralization is in close association with granitoid gneisses of monzonitic composition. These two deposits are hosted in a significantly different gold-stage depositional environment from deposits within the other Archean provinces. However, it would be inappropriate to fully define a
group with only two samples. Therefore, the arsenopyrite assemblage of this Province should only be used as a guide or for comparative purposes.

Deposits from the Eastern and Northern Provinces share some broad similarities with each other in terms of host rocks and depositional environment. While both of these Provinces contain gold deposits as part of a large first-order shear structure, they are each related to different latter shear structures and therefore it is unlikely that both of these regions share a similar fluid source. The gold deposits in the Northern Province are possibly associated with an I-type granitoid formed in the north-western portion of this province (Wang, 1993). While the gold deposits from the Eastern Province investigated in this study do not have a direct relationship to any of the outcropping granitoids (Groves, 1993). It is evident that the fluid sources and relationship between granitic intrusions and gold mineralization are different between these two provinces. Therefore, it is unsurprising that the hydrothermal fluid chemistry is different between these systems, resulting in differencing trace element chemistry in arsenopyrite.

3.4.3.1.1 Eastern Goldfields Camps

This study has investigated the trace element chemistry of arsenopyrite from 27 deposits within the Eastern Goldfields Province. These deposits may be sub-divided into groups on the basis of their camp within the Eastern Goldfields. Deposit camps are a group of deposits belonging to the same geological structure and are in relatively close proximity to each other. In the study the deposits of the Eastern Province are sub-divided into seven camps; Leonora, Kalgoorlie, Coolgardie, Southern Cross, Kambalda, Randalls, and Norseman (Figure 69). These seven camps will be compared to each other, on the basis of trace element chemistry of arsenopyrite, to determine if any relationships may be observed.
The deposit median values for the deposits from the Eastern province were subjected to a series of iterative discriminant analyses (Figure 70 and Figure 71). This series of iterative discriminant analyses were used to remove specific groups (distinct data clusters) from the dataset so that each group may be differentiated from the others. The group selected for removal at each step was that which displayed the greatest differentiation from the others, on the basis of trace element chemistry of the associated arsenopyrite samples. It should be noted that validation samples have not been included in any of the discriminant analysis as there are only a limited number of samples representing each camp and the removal of even a single sample would significantly influence the results.
Figure 70. An LDA of the deposit median trace element assemblages of arsenopyrite from the Eastern Goldfield camps (27 deposits).

It is apparent that a number of the deposit camps may be identified and differentiated from the others (Figure 70), with deposits from the Norseman, Kalgoorlie, and Southern Cross camps readily differentiated from the other camps. While the Randalls, Coolgardie, Kambalda, and Leonora camps are partially differentiated from each other, but it is evident that there are significant differences between these samples.
A previous study (Oversby, 1975) has demonstrated that the deposits within the Norseman camp have a radiogenic isotopic signature that is different from the other deposits in the Eastern Goldfields. This is most likely due to the Norseman region having a thinner greenstone section than the rest flanked by granitoid-gneiss bodies. Sulfur isotope data suggests that the ore fluid shows a strong relationship with the nearby granitoids, which would suggest that the ore-forming fluid has a stronger magmatic component as compared to the many other deposits in the Yilgarn (Oversby, 1975). Fluids released from intrusive bodies tend to have elevated concentrations of Cu, Mo, and Sn proximal to the intrusion, and at greater distances from the intrusion Zn, Ag, Au, Hg, and Pb tend to become more prevalent (Hedenquist, 1994). Therefore, the elevated concentrations of Sn in the Norseman arsenopyrite samples may be a reflection of the elevated Sn concentration within the ore forming fluid during gold deposition. It should be noted that the Norseman group consists of only two deposits and the arsenopyrite assemblages may not be representative of the group as a whole.

The LDA analysis (Figure 70) demonstrates that the samples from the Kalgoorlie camp are differentiated from the others by relatively elevated concentrations of Cu, Zn, Sb, Au, and Hg in arsenopyrite. The Kalgoorlie camp contains the largest number of deposits investigated in this thesis (6) and is representative of one of the largest gold producing camps in the world. The Kalgoorlie group of deposits has the highest median gold endowment out of any of the camps investigated in this section (>1 Moz). Therefore, it is possible that the favourable fluid focussing and deposition mechanisms may be responsible for this increased endowment, and have an effect on the arsenopyrite trace element chemistry. It is no surprise that the Au concentration in arsenopyrite is elevated as there is likely to be higher concentrations of Au within solution which may be
sequestered into the arsenopyrite matrix. The effect of endowment on arsenopyrite chemistry will be discussed in more detail in section 3.4.4.

The Southern Cross camp is defined by elevated Co, and Ni concentrations in the arsenopyrite samples collected from these deposits (Figure 70). The Southern Cross group consists of two deposits; the Transvaal and Yilgarn Star deposits. These two deposits are located on the central portion of the Yilgarn craton and are contained within the Southern Cross fold belt. This fold belt has similar lithostratigraphy to the Murchison region (Northern Province). The Eastern portion of the craton (Kalgoorlie region) was accreted onto the Murchison-Southern cross orogen prior to the formation of the Yilgarn craton (Myers, 1995). Therefore, it is unsurprising that the arsenopyrite from the Southern Cross deposits are easily differentiated from arsenopyrite collected from deposits within the Eastern Goldfields.

The Kalgoorlie, Norseman, and Southern Cross camps were readily differentiated from the rest of the dataset detailed in Figure 70, while the remaining four camps may be identified by iterative LDA protocols. To undertake this, the Kalgoorlie, Norseman, and Southern Cross groups were removed from the dataset and another LDA was performed on the remaining four groups (Figure 71). On the basis of this new analysis, the four groups are easily distinguishable from each other and in this manner it is possible to successfully separate each of the Eastern Goldfields arsenopyrite groups using two iterative discriminant analyses.
Figure 71. An LDA of the deposit median trace element assemblages of arsenopyrite from the Eastern Goldfield camps. Deposit median data for the Norseman, Kalgoorlie, and Southern Cross camps have been removed from this analysis (17 individual deposits).

The Randalls group of deposits were differentiated from the remaining four camps due to their elevated Mo and Te concentrations in arsenopyrite (Figure 71). The differences in Randalls group arsenopyrite chemistry to the other Archean deposits has been discussed previously in section 3.4.3, and demonstrated in Figure 63. The Randalls group of deposits is different from their other Archean counterparts in that they are hosted in BIF.
It would be expected that the differences in host rock environment would be immediately apparent in arsenopyrite trace element chemistry. However, this is not the case as may be observed from the similarity of the Randalls samples to the others in Figure 70. This may imply that the host rock environment, while having an effect, is not the most significant influence on the trace element chemistry of arsenopyrite. It should also be noted that the Randalls Camp host rocks are amphibolite facies metamorphic and gold is deposited post peak metamorphism, and since such rocks have already been heavily dehydrated it would be expected that there would be a lesser influence of the host rocks on the introduced hydrothermal fluid in these scenarios.

The geology of the Kambalda and Coolgardie group of deposits are similar to each another, and it is not a surprise that these groups have similar median arsenopyrite chemistry (Figure 70). These camps are within 200 km of each other and are contained within two adjacent greenstone belts. Nevertheless, arsenopyrite samples from deposits within these two groups may be differentiated based on the relative concentrations of trace elements in arsenopyrite using an iterative set of LDA’s (Figure 71).

The arsenopyrite from the Leonora deposits are differentiated from the remaining four camps because of their relatively elevated Zn, Ag, Sb, Pb, and Bi (Figure 71). It may be observed from the locations of the various deposits (Figure 69), that the Leonora camp is the northernmost and it borders on the Cue-Murchison region (Northern Province). The border between these two camps is defined in Figure 66 and it may be observed that the deposits from the Leonora camp are not part of the same belt. However, they may have a similar fluid source. If this were the case then it may be expected that the deposits from the Leonora group would display similar arsenopyrite assemblages to the Northern Province. It may be observed from Figure 68 that the Northern Province is differentiated
from the other deposits in the Eastern Goldfields because of their elevated Cu, Zn, Sn, Sb, and Pb. Overall the two northernmost camps may be defined by elevated levels of Zn, Sb and Pb, which may suggest that the northernmost deposits in the Yilgarn craton may share a similar fluid source.

3.4.3.1.2 Norseman-Wiluna Belt

The Norseman-Wiluna Belt is a semi-continuous greenstone belt trending NNW-SSE between Wiluna in the north and Norseman in the south. This belt contains a large number of well endowed gold deposits along its 800 km length and 150 km width (Figure 72). The belt is considered a single primary fluid-focussing structure with secondary and tertiary structures branching off. It is within these secondary and tertiary structures that gold deposits are commonly formed (Barley, 1989). The orogenic gold deposits of the Yilgarn may be considered to be part of the crustal continuum, that is, deposits formed by similar hydrothermal fluids but at different crustal depths (Mikucki, 1998, Groves, 1993). The deposits within the Norseman-Wiluna belt directly represent areas of mineralization formed at different crustal depths during the late Archean. The differences in fluid chemistry for the deposits along the belt will be investigated with particular reference to the crustal continuum theory.

The deposits along this belt are formed synchronously, but the variable deposit chemistry and host rock metamorphic grade suggest that these deposits have formed under different pressure and temperature conditions (Figure 73). Alteration post-mineralization is limited and cannot account for the different grades of metamorphic host rock (Groves, 1993). Deposits from the northern portion of the belt are hosted in greenstones metamorphosed to the lower greenschist facies, with the metamorphic grade increasing towards the south of the belt. The belt is considered to be a series of extensive continuous shear zones, at a
depth of at least 5 km, which had experienced metamorphism (which will be of different grades depending on the depth) and then subsequent gold mineralization some 2.64 Ga ago. In addition, the inferred major 1st order crustal structure commonly hosts pre- and post-gold mineralization felsic dyke swarms, commonly mimicking the primary fluid pathways. Subsequent to shearing, the belt has dipped N-NW. In the following 2.64 Ga after deposit formation, weathering and isostatic equilibration has brought the entire structural composite nearer the surface. Today the outcrops from the northern portion are inferred to represent shallower regions of the shear zone (<5 km depth), while those at the southern portion represent regions form the ancient deeper portion of the zone (~20 km depth) (Groves, 1993).

The sulfides from the Norseman region have a lead isotope signature indicating crustal derivation which is more pronounced than that of the other deposits throughout the Norseman-Wiluna Belt (Ho, 1992). As such, the fluid source for the Norseman area is also more likely to be derived from crustal material than the other deposits throughout the belt (Figure 74). This is interpreted to be due, at least partly, to the stronger granitic influence of the source fluid from the nearby granitoids. Other deposits throughout the belt display sulfides with a more primitive lead signature, implying that they were formed from a fluid which, in turn, has derived its lead from a more primitive source. The primitive lead isotope signatures of sulfides from deposits within the Archean greenstone belts in the Yilgarn craton are probably the result of lead deposited from sulfur and chloride rich hydrothermal fluids which have sequestered radiogenic lead from the ancient Yilgarn mafic and ultramafic greenstones.
Figure 72. A simplified geologic map of the Norseman-Wiluna Belt. The interpreted marginal basin and volcanic arc associations represent the metamorphosed greenstones as derived from two sources (Barley, 1989).
Figure 73. Schematic hypothetical reconstruction of a continuous hydrothermal system over a crustal range of 25km showing potential fluid and radiogenic isotope sources (Groves, 1993).

Figure 74. The Pb isotopic compositions of galena taken from deposits in the Norseman-Wiluna belt (Ho, 1992).
As previously discussed in section 3.4.3.1.1 and detailed in Figure 73, the Norseman deposits are known to display a stronger magmatic influence than the other deposits along the belt. It should be noted that, despite this magmatic component, the Norseman deposits formed synchronously with other deposits along the belt. This would suggest that perhaps a single regional-scale fluid migration event was initiated by the emplacement of granitic bodies and associated with the crustal-scale metamorphism in the greenstone belts. This single fluid event flowed through the Norseman-Wiluna belt (as it was an area of regional low pressure) and formed many deposits through secondary features.

All the deposits throughout the belt may have been formed under the influence of a single regionally derived fluid migration event but gold would have been emplaced at different depths. This hypothesis is supported by the crustal continuum theory for the source of Archean gold bearing fluids (Groves, 1993). Relationships pertaining to the influence of a hitherto undesignated igneous fluid may be used as an indicator of the depth of formation of the gold deposit. Consequently, the chemistry of arsenopyrite may reflect the changing nature of the fluid as it migrates upwards towards the surface and may be used as an indicator to determine the depth of gold deposit formation.

For the purpose of this thesis the deposits in the belt are placed into three groups representing shallow (Leonora), intermediate (Kalgoorlie region), and deep (Norseman) depths of mineralization. An LDA is performed on the dataset and the differences in trace element chemistry of arsenopyrite from the various depths of mineralization may be observed (Figure 75). The progression of elements from higher pressure and temperature to lower can be visualized as a clockwise progression around the 0:0 point which begins at Norseman in the extreme right of the figure. Trace element variations in arsenopyrite formed under progressively lower pressure/temperature regimes (Norseman →
Kalgoorlie → Leonora) are reflected by a change from Co, Mo, Sn, Bi → Se, Te, Hg → Ni, Cu, Sb.

Figure 75. An LDA of the deposit median trace element assemblages of arsenopyrite from 16 gold deposits located along the Norseman-Wiluna greenstone belt. The Kalgoorlie Region includes samples from the Coolgardie, Kambalda, and Kalgoorlie camps.

Mercury has a strong association with gold deposits and is usually more pronounced in shallow epithermal deposits (Varekamp and Buseck, 1984). This is because mercury minerals and native mercury are only stable at low temperatures. It is less
thermodynamically favourable for mercury to form a solid sulfide species as the temperature of ore genesis increases (Varekamp and Buseck, 1984). During mineralization mercury remains in solution and is precipitated distal to the area associated with the main mineralizing event. Therefore, variations in the relative concentrations of the incompatible high temperature elements (Mo, and Sn) relative to Hg can be used to indicate the temperature and pressure of formation. By using this ratio from the arsenopyrite trace element chemistry it may be possible to discriminate between the Norseman, Kalgoorlie, and Leonora groups within the Norseman-Wiluna belt (Figure 76). The general trend is for an increase in Mo and Sn concentrations and a decrease in Hg concentrations in the arsenopyrite as the temperature and pressure of the deposit increases.

**Figure 76.** The deposit median \((\text{Mo} \times \text{Sn})/\text{Hg}\) trace element ratios for arsenopyrite from gold deposits within the Norseman-Wiluna belt. The \((\text{Mo} \times \text{Sn})/\text{Hg}\) ratios are multiplied by \(10^9\) for ease of display.
3.4.3.1.3 Hemlo Comparison

Although this thesis concentrates primarily on Australian deposits, three arsenopyrite samples were obtained from the Canadian deposit, Hemlo. During the Archean the Yilgarn Craton and the Superior Craton (Northern America) were both within the supercontinent known as Kenorland (Lubnina and Slabunov, 2011). The analysis of these samples afforded the opportunity of comparison between deposits formed on this Archean supercontinent. Deposits at Hemlo and within the Western Yilgarn Craton share similar host rocks (metamorphosed greenstones) and were formed approximately synchronously (Cameron and Hattori, 1985, Groves, 1993).

When performing a PCA on the deposit median arsenopyrite assemblages of gold deposits, it can be observed that the Hemlo deposit lies within the Archean grouping (Figure 61). A CI analysis performed on a sample from the Hemlo deposit is detailed in Table 16 and confirms that the arsenopyrite from the Hemlo deposit shares a significant number of similarities to its Australian counterparts. To further demonstrate the similarity between deposits from Hemlo and the Yilgarn, arsenopyrite samples from the Hemlo deposit were analysed using CI protocols to determine their closest counterpart amongst the arsenopyrite samples from Australian gold deposits (Table 16). Unsurprisingly, the Hemlo samples exhibited a high degree of comparability with the Archean greenstone deposits of the Yilgarn craton. Although only three samples were available from the Hemlo deposit, the similarity of their trace element assemblages to that of equivalent samples from the Yilgarn may indicate a generic association of deposits from the two areas and confirm that the principles governing the interpretation of arsenopyrite data from the Yilgarn can be used for the same purpose in Canadian samples.
Table 16. A table of the percentage comparability between the samples HEML11 and HEML12 to the dataset of gold deposits.

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<td>PH 2/8</td>
<td>Yilgarn</td>
<td>95.5</td>
</tr>
<tr>
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<td>94.5</td>
<td>HARN3</td>
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<td>FIM3</td>
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<tr>
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<td>93.8</td>
<td>MM1</td>
<td>Yilgarn</td>
<td>94.6</td>
</tr>
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</table>

It may be observed from Table 16 that the two samples from the Hemlo deposit have high chemistry similarities to arsenopyrite samples from the Fimiston and Big Bell gold deposits (labelled FIM, and BB/BIGB, respectively). The Fimiston samples were collected from the Fimiston orebody which is part of the >50 Moz Golden Mile deposit. As a working hypothesis it might be interpreted that the similarity between the Hemlo and Fimiston samples may be related to the considerable gold endowment of both of these super-giant deposits. The unique geological features required to create a super-giant gold deposit may have had an effect on the fluid chemistry which, in turn, is reflected in the arsenopyrite trace element chemistry. The phenomenon of endowment being reflected in the chemistry of arsenopyrite samples will be discussed in detail in section 3.4.4 (with a direct comparison between the Hemlo and Big Bell deposits).
3.4.3.1.4 Host rocks

A hydrothermal fluid undergoes significant physicochemical changes as it is being channelled into the depositional site especially in relation to its interaction with host rocks. The chemistry of the fluid changes in response to chemical reactions with the host rocks at the depositional site, the effects of which do not necessarily reflect the chemistry of the original fluid (Ridley and Diamond, 2000).

As discussed previously, the arsenopyrite samples from Archean BIF-hosted gold deposits share a number of similarities to arsenopyrite from Proterozoic BIF-hosted deposits. These similarities may be attributed to similar depositional environments despite the differences in fluid sources and original fluid chemistry. The majority of the Archean Western Australia deposits are predominantly hosted in mafic to ultramafic greenstones (Witt, 1998). The deposits from the Randalls camp (east of Kambalda) are hosted in a BIF within a feldspathic sandstone and laminated siltstone rock assemblage. The comparison of arsenopyrite from greenstone and BIF deposits demonstrates that deposits of generically different host rock composition will result in arsenopyrites with different chemistries (Figure 77).

**Figure 77.** An LDA of the deposit median trace element assemblages of arsenopyrite from deposits hosted in Archean greenstones and Archean BIF.
It should be noted that the Archean greenstone deposits consist of a number of deposits located in many camps within the Yilgarn craton. It has been previously demonstrated that arsenopyrite from the SW Gneiss terrane and the Cue-Murchison regions were generated from significantly different fluid sources than the Eastern goldfields deposits. Therefore, it is possible that the data detailed in the LDA displayed in Figure 77 may be heavily influenced by arsenopyrite samples from gold deposits with a dissimilar fluid source to the Randalls BIF deposits. Therefore, it is necessary to compare deposits of a similar fluid source but with the main difference being between the host rocks; one being BIF hosted (Randalls) and the other greenstone hosted (Kambalda) (Figure 78). The disposition of data detailed in this LDA clearly demonstrates that the Kambalda and Randalls group of deposits may be readily differentiated from each other on the basis of the trace element chemistry of their associated arsenopyrites. It would appear that, in the absence of other potential variables, BIF’s endow arsenopyrite with greater concentrations of Mo and Bi when compared to greenstone hosted arsenopyrite. Conversely, ultramafic greenstones appear to increase the concentration of Co, Ni, Cu, Zn, and Ag in the arsenopyrite that they host. Cobalt and nickel are both strongly associated with primitive melts and are present in significant concentrations (20-200 ppm) in ultramafic rocks (Condie, 1976). Therefore, it is unsurprising that the deposits formed from the leaching of materials from ultramafic greenstones (Kambalda deposits) are enriched in Co and Ni, and this enrichment is also reflected in elevated concentrations of these elements in arsenopyrite. Conversely, slates and shales make up a significant portion of the BIF in which the Randalls deposits are hosted. These rocks are usually relatively enriched in Mo and Bi (Eilu and Groves, 2001) and thus, if the hydrothermal fluid circulated in the sedimentary package, the leaching of such material is likely to be incorporated in the growing arsenopyrite crystal.
3.4.3.2 Proterozoic Gold Deposits

The Proterozoic era was a time during which the formation and preservation of a significant number of gold deposits occurred. The Pine Creek region was a significant area of mineralization formed during the Proterozoic and this region is now one of the largest goldfields in Australia. The Homestake deposit (which was one of the deposits to drive the gold rush in America during the 19th century) was also formed during the Proterozoic. All of the Proterozoic gold deposits analysed in this thesis are deposited in analogous banded iron formations (and associated rock assemblages) and have similar tectonic and structural settings to each other. During the Proterozoic period a supercontinent called Columbia (also known as Nuna) had formed, and in this supercontinent the Trans-Hudson orogen and the Pine Creek orogen were located adjacent to each other (Evans et al., 2011, Meert, 2002, Rogers and Santosh, 2009). Therefore, the analysis and comparison of arsenopyrite from the Pine Creek and Homestake Proterozoic deposits may provide data that demonstrate the similarities and differences between these two orogens.

Figure 78. An LDA of the trace element chemistry of arsenopyrite from deposits within the Kambalda and Randalls camps (11 deposits).
3.4.3.2.1 Pine Creek Region

The Pine Creek region is the northernmost goldfield of Australia and is located approximately 100 km south-east of Darwin in the Northern Territory. The region consists of a number of small gold deposits and the giant Cosmo-Howley deposit. The geological setting and deposit locations within the Pine Creek region is detailed in Figure 79. In this sub-section only samples from Cosmo-Howley, Enterprise, Fenton, Goodall, and Mount Porter will be investigated. This is due to the lower number of arsenopyrite samples from the other deposits in the Pine Creek region, which are too few to perform any statistical test on. The samples from the Cosmo Howley deposit represent in pit mine samples and core material in BIF down to approximately 500 m vertical depth within the eastern fold limb and along the 400-500 m strike length. The Mount Porter samples represent the sub-economic grade extensions to the deposit in deep diamond drill holes to the NNW. The Goodall samples are all from high grade stockpiles from a singular ore deposit. The Enterprise samples represent samples from the base of the operating open pit and a scatter of diamond drill cores throughout the deposit. The Fenton samples represent drill cores of magnetic anomalies along the 80 km length of the Fenton Shear Corridor.

Within the investigated Pine Creek group of samples individual deposits can be chemically differentiated from each other on the basis of small differences between the trace element chemistry of arsenopyrites using iterative LDA analyses (Figure 80 to Figure 83). While the arsenopyrite samples from the Pine Creek deposits display some slight differences to each other, it should be noted that the differences in trace element chemistry between these deposits is significantly smaller compared to the differences between the Pine Creek and Yilgarn deposits (Figure 59).
Figure 79. The generalized geology of the Pine Creek region and the surrounding areas (Needham et al., 1988).

As stated previously, the Cosmo-Howley deposit is the largest gold deposit (>1 Moz) in the Pine Creek region which has been investigated in this study. The chemistry of arsenopyrite from this deposit has been compared to that for arsenopyrite from other gold deposit groups in a PCA (Figure 61), and the data generated from this PCA confirms that the chemistry of arsenopyrite samples from this deposit is similar to that of other Proterozoic samples. When the Pine Creek and Cosmo Howley samples are compared directly using an LDA (Figure 80), the Cosmo Howley samples can be differentiated from the other Pine Creek samples on the basis of their higher Se, Mo, Te and Hg concentrations. The relatively higher levels of these elements may be related to the higher endowment of this deposit which may also represent more effective fluid focussing within this deposit. The phenomenon of forming larger gold deposits, and its influence on arsenopyrite chemistry, is discussed in greater detail in section 3.4.4.
Figure 80. An LDA of the sample median trace element assemblages of arsenopyrite samples collected from deposits within the Pine Creek region (142 samples).

After the removal of the samples from Cosmo-Howley deposit, an additional iterative LDA was performed on the dataset to further attempt to differentiate the Pine Creek deposits (Figure 81). The Goodall group of samples display a relatively distinct grouping without any overlap with samples from the other groups. Of the Goodall samples, 100% of the samples were correctly identified as belonging to the Goodall group. Therefore, the samples from Goodall deposit may be differentiated from the other Pine Creek deposits by relatively elevated concentration of Cu, Zn, and Ag.
Figure 81. A second LDA of the sample median trace element assemblages of arsenopyrite samples collected from deposits within the Pine Creek region. The Como-Howley samples have been removed from this analysis (117 samples).

After the removal of the Goodall samples from the dataset, a third iterative LDA was performed (Figure 82). In this LDA three distinct groups may be observed. The samples from the Enterprise deposit appear to have the greatest differentiation from the other two, with 83.4% of these samples being correctly grouped. The arsenopyrite from the Enterprise deposit is defined by the elevated concentrations of Cu, Zn, Au, and Pb. It is unsurprising that the samples from the Fenton and Mount Porter groups have the most similar median arsenopyrite trace element assemblages as determined by the LDA. This is most likely the result of both groups containing arsenopyrite samples collected from multiple locations within a deposit and not just from orebodies. The arsenopyrite samples
from outside of orebodies have slightly different arsenopyrite chemistry to samples within orebodies and this phenomenon will be discussed in greater detail in section 3.5.2.

Figure 82. A third LDA of the sample median trace element assemblages of arsenopyrite samples collected from deposits within the Pine Creek region. The Como-Howley and Goodall samples have been removed from this analysis (92 samples).

Despite the similarity of the samples within the Mount Porter and Fenton groups (which may be expected due to both groups containing samples from exploratory drill holes, rather than from orebodies) the final two groups from the Pine Creek region are able to be differentiated from each other in a final LDA (Figure 83). The two groups were differentiated from each other with 94.4% of the samples being correctly identified. The arsenopyrite samples from the Mount Porter deposit are defined by elevated concentrations of Se, Sb, Hg, and Pb. The arsenopyrite samples from the Fenton region...
have lower concentrations of all of the elements (with the exception of a slightly increase in Cu and Pd). Overall, it is possible to identify the chemical assemblage “signature” of each of the gold deposits within the Pine Creek region. Additionally, this implies that an arsenopyrite sample belonging to one of these deposits may be identified as belonging to the correct deposits using an iterative LDA process.

Figure 83. The final LDA of the sample median trace element assemblages of arsenopyrite collected from deposits within the Pine Creek region. The Como-Howley, Goodall, and Enterprise samples have been removed from this analysis (79 samples).

3.4.3.2.2 Homestake Comparison

The Homestake deposit is the only non-Pine Creek gold deposit in the Proterozoic suite of gold deposits described in this thesis. As discussed previously, approximately 1.8 Ga ago Australia and America were proximal and formed the bulk of the supercontinent Columbia (Meert, 2002, Rogers and Santosh, 2009). This time period saw significant gold-forming activity within the supercontinent and due to the spatial proximity of these orogens at this time, it is possible that these two gold forming events came under the influence of similar crustal-scale structural, tectonic, and geological processes. An LDA was performed on the sample median data from deposits of the Pine Creek region and from the Homestake deposit (79 samples) to assess the similarities between samples from
these two regions (Figure 84). Despite the appearance of significant overlap in the chemistries of the two groups, they are actually well defined from each other with 96.8% of the 269 samples plotted being identified as belonging in the correct group.

![Homestake and Pine Creek Sample Median LDA](image)

**Figure 84.** An LDA of the sample median trace element assemblages of arsenopyrite from the Homestake deposit and from deposits within the Pine Creek region (269 samples).

The trace element chemistry of arsenopyrite from the Cosmo-Howley deposit (29 samples) displays enough similarities to the chemistry of samples from Homestake and these two deposits could be considered analogous (Figure 61). Sample data from the Cosmo-Howley deposit were analysed and directly compared with data from samples from Homestake and the other Pine Creek deposits to determine if Cosmo-Howley samples had more in common with Pine Creek or Homestake samples (Figure 85). From data in this LDA it can be stated that the arsenopyrite samples from the Cosmo-Howley deposit share more in common with arsenopyrite from the Homestake deposit, than they do with the Pine Creek samples. The elevated concentrations of Se, Mo, Ag, Sn, Te, and Hg in arsenopyrite from Cosmo-Howley and Homestake differentiate these two deposits from the others in the Pine Creek region. Homestake and Cosmo-Howley are both large gold producers and have gold endowments in excess of 1 Moz, whereas the other Pine Creek samples are from deposits that contain considerably less gold. Therefore, it is
possible that the similarities of Cosmo-Howley and Homestake (with reference to their differences to Pine Creek) may be indicative of a unique process whereby larger gold deposits are formed. This similarity is further emphasised when performing a predictive LDA investigation on samples the samples detailed in Figure 85, as a minority of the Cosmo-Howley samples are incorrectly identified as belonging to Homestake and vice-versa. However, none of the samples from either of these deposits are identified as belonging to the Pine Creek group.

![Proterozoic Sample Median LDA](image)

**Figure 85.** An LDA of sample median trace element assemblages of arsenopyrite from the Cosmo-Howley, Homestake, and Pine Creek region gold deposits (269 samples).

A PCA was performed on the gold deposits of the Proterozoic era to further assess the similarity of the Cosmo-Howley and Homestake deposits and to better understand the
influences on the chemistry of these two deposits (Figure 86). In terms of arsenopyrite chemistry, the Cosmo-Howley and Homestake deposits share a number of similarities, as both the LDA and PCA analyses demonstrate the relatively increased concentrations of Se, Mo, Sn, and Hg in arsenopyrite samples from the Cosmo-Howley and Homestake deposits which differentiates these two deposits from the others in the Pine Creek region. It should be noted that in Figure 86 the two PCA functions (F1 and F2) used to differentiate the data account for over 48% of the total variance, further reinforcing the significant chemical differences between the samples from these two deposits and the samples from the other Pine Creek deposits.

![Figure 86. A PCA of the deposit median trace element assemblage of arsenopyrite from Proterozoic gold deposits.](image-url)
3.4.3.3 Phanerozoic Gold Deposits

The Phanerozoic gold deposits investigated in this thesis consist of a suite of turbidite hosted gold deposits from the central Victorian goldfields. The Victorian goldfields are hosted within the Lachlan Fold belt which runs through Victoria and NSW, Australia (Figure 87). The majority of mineralization occurred around 440 Ma ago with lesser regional mineralizing events occurring between 420 - 400 and 385 - 365 Ma ago (Willman, 2007).

![Figure 87. An image of the principal goldfields within the Lachlan fold belt in Victoria, Australia. (X) Mt Dryden greenstone zone, (Y) Heathcote greenstone zone, (Z) Mt Wellington greenstone zone (Tomlinson et al., 1988).](image-url)
Differentiation of the deposits and the identification of their trace element signatures were achieved using a series of iterative LDA’s (Figure 88 to Figure 91). An initial LDA of the arsenopyrite sample median data demonstrates that the samples from the Ballarat and Cohens deposits are significantly different from the others (Figure 88).

**Figure 88.** An LDA of the sample median trace element assemblages of arsenopyrite from deposits within the Victorian goldfields (40 samples).
The LDA presented in Figure 88 demonstrates that the Cohens suite of arsenopyrite samples, collected from the Cohens gold reef located within the Walhalla fold belt, Mt Wellington greenstone zone (Figure 87), are defined by relatively elevated Cu, Ag, and Sb concentrations. The increased concentration of Sb in arsenopyrite may be the result of deposits along the Walhalla fold belt having an overall stronger Sb association than other deposits in the region (Gao and Kwak, 1997). The strong differentiation of the Cohens samples from the other Victorian gold deposits may also be the result of the differences in the geological environment of Walhalla-Woods Pointfold belt compared to the other fold belts. The gold reefs within the Walhalla fold belt are deposited in marine sediments consisting of turbidites, slate, siltstone, and sandstone with associated calc-alkaline dyke swarms within metasedimentary units (Weir et al., 1988). The Cohens reef is the largest single reef in the Victorian goldfields (has been mined to a depth of over 1.3 km) and has produced 1.8 million ounces of gold. In addition, the vein paragenesis at Cohens is more complex (Si-CO$_2$ → CO$_2$ → Si-CO$_2$-S → Si-Au) than those of the other deposits investigated in this study (Stewart, 2013). Therefore, it is unsurprising that the unique chemical conditions associated with the formation of this deposit are reflected in the significantly different arsenopyrite chemistry.

The arsenopyrite samples from the Ballarat deposit are strongly differentiated from the other Victorian samples by relatively elevated concentration of Mo, Te, Pb, and Bi (Figure 88). The Ballarat deposit lies along the Heathcote greenstone zone as do the Wattle Gully and Bendigo suite of deposits. Therefore, it is surprising that the Ballarat samples are strongly differentiated from the others within the same greenstone zone; especially when arsenopyrite samples from the Stawell deposit (Mt Dryden greenstone zone) appear to share greater similarities with Bendigo and Wattle Gully samples than samples from the Ballarat deposit. The Ballarat deposit is hosted in the Lancefieldian
sedimentary rocks which contain a higher proportion of sandstone when compared to other deposits in the Heathcote zone (Schaubs and Zhao, 2002). The sandstones of this region are predominately devoid of any significant trace elements (Gao and Kwak, 1997), therefore, it would seem unlikely that the elevated concentrations of Mo, Te, Pb, and Bi were derived from the nearby lithological units. Instead, the most likely scenario for the higher concentration these trace elements in arsenopyrite is that the hydrothermal fluid responsible for the deposit has collected these elements during travel through distal country rocks and they have then been co-precipitated within the arsenopyrite now found in the deposit.

After the removal of the Ballarat and Cohens samples, another iterative LDA was performed on the dataset (Figure 89). It is immediately apparent from the second LDA that the samples from the Stawell and Microwave Tower Spurs are differentiated from the others. The arsenopyrite samples from the Microwave Tower Spurs deposit (located in the Bendigo goldfields) demonstrate a strong grouping related to their relatively elevated concentration of Mo (Figure 89). Arsenopyrite samples from this deposit have a similar trace element chemistry to samples from other Bendigo goldfield deposits (Hansel Mundy, New Prince of Wales, and South New Moon). Nevertheless, the data for the samples from this deposit appear to demonstrate a strong grouping which is easily differentiated from the data for the Bendigo deposits.
Figure 89. An LDA of the sample median trace element assemblages of arsenopyrite from the Phanerozoic deposits. The Ballarat and Cohens samples have been removed from this analysis (33 samples).

The samples from the deposits yet to be differentiated after two LDA protocols (Figure 88 and Figure 89) are those from the Bendigo Goldfields (with the exception of Microwave Tower Spurs) and the Wattle Gully deposit. The Wattle Gully deposit lies within the Castlemaine goldfield which is located to the south of the Bendigo goldfield (Figure 90). The Bendigo and Castlemaine goldfields are both located along the Heathcote greenstone zone which is separated by the Harcourt granodiorite batholith. Both goldfields have broadly similar geological features (Willman, 2007), therefore, it is
unsurprising that these two groups have arsenopyrite of similar trace element chemistry. These deposits may be further differentiated from each other using an additional iterative LDA (Figure 91). This figure demonstrates that the Wattle gully deposits may be differentiated from the Bendigo suite due to a relatively elevated concentration of Bi in arsenopyrite. The arsenopyrite from the Wattle Gully deposit is associated with a black slate-vein (laminated and crack-seal) contact (Gao and Kwak, 1997) and it is perhaps the reaction with the slate during arsenopyrite formation that has lead to a higher Bi content in arsenopyrite.

Figure 90. Geology of the central and eastern Lachlan fold belt, Victoria (Willman, 2007).
Figure 91. An LDA of the Phanerozoic sample median trace element assemblage of arsenopyrite samples from the South New Moon, New Prince of Wales, Pearl, Hansel Mundy, and Wattle gully deposits (22 samples).

3.4.4 Gold Endowment

The relative endowment of a deposit is a product of several geological factors, and their efficiency with respect to the transport and precipitation of gold (section 1.3.4). A combination of all of these factors will be required for giant and supergiant deposits to form (Hodkiewicz, 2003).
3.4.4.1 Comparison of Analogous Deposits

Throughout the research undertaken in this thesis it has become apparent that differences between the geological settings of deposits is a significant contributor to the differences in trace element chemistry of arsenopyrite associated with these deposits. In order to determine whether changes in the endowment of a deposit are also reflected by changes in the chemistry of arsenopyrite contained within those deposits, the chemistry of a number of arsenopyrite samples from deposits that reflect wide variation in endowment, but similar depositional environment and mineralogy, have been compared. In this manner, and in the absence of interference from other physicochemical variables, it may be possible to observe if a relationship exists between arsenopyrite chemistry and the endowment of a deposit.

3.4.4.1.1 Homestake and Cosmo-Howley

The Homestake and Cosmo-Howley deposits are two deposits which are almost identical to each other (Stewart, 2009, Caddey et al., 1991, Matthaei, 1995). The three significant differences between these deposits are their current location, individual gold endowment, and average minable gold grade. The Homestake deposit (42 Moz) is significantly better endowed than Cosmo-Howley deposit (1-4 Moz) and also contains a greater number of discrete orebodies. The analysis of the data for trace element distribution in arsenopyrite, with respect to Proterozoic deposits, has been detailed in section 3.4.3.2.2 (Figure 84 to Figure 86). From these analyses it is evident that the arsenopyrite from the Homestake deposit displays a number of chemical similarities with arsenopyrite from the Australian Proterozoic deposits. In addition, these analyses demonstrate the similarities between the samples from the Cosmo-Howley and Homestake deposits.
The trace element chemistry of arsenopyrite from the Homestake and Cosmo Howley deposits were compared to determine the degree of similarity between these deposits (Figure 92). As can be seen in this figure, the arsenopyrite samples from the Homestake deposit can be defined and differentiated from the Cosmo-Howley deposit (94.4% of the samples correctly identified and 100% of the validation samples also correctly identified). The samples are differentiated by the relatively elevated concentrations of Se, Sn, Ag, Sb, Te, Au, and Hg in arsenopyrite from Homestake.

![Homestake and Comso-Howley Sample Median LDA](image)

**Figure 92. An LDA of the sample median trace element assemblages of arsenopyrite from the Homestake and Cosmo-Howley deposits (104 samples).**

The trace elements in arsenopyrite which are used to define the Homestake deposit (Se, Sn, Sb, and Te) may simply be the product of different hydrothermal fluid sources which have sequestered elements from slightly varying country rock. However, as discussed in section 3.4.4.1.5, some of these elements (Sn, Se, and Hg) appear to be generically enriched in arsenopyrite from more highly endowed deposits. If this is correct then the relative concentrations of these elements in arsenopyrite could be a potential indicator of the gold endowment of that deposit.
3.4.4.1.2 Paddington and Boorara

The Paddington gold deposit is a stock work system with mineralization restricted to basalts and the granophyric phase of fractionated dolerite. The gold is contained within quartz-carbonate veins or within a narrow alteration halo around these veins. The Boorara deposit is also a stock work system with mineralization restricted to altered dolerite with gold being contained in quartz veins. These two deposits may be considered to be analogous in terms of litho-structure and mass alteration. The Paddington deposit has been mined since 1897 and over 1 Moz of gold have been removed from it. A further 0.6 Moz inferred reserve in the ground gives the deposit a total endowment of over 1.6 Moz. When Boorara was discovered it initially appeared to be a Paddington analogue (Stewart, 2009). On further investigation and exploration, it was determined that the gold grade of the Boorara deposit was not sufficiently high for the deposit to have an endowment greater than 200,000 oz. The Boorara deposit was mined and has yielded approximately 30,700 oz of gold and has a further estimated 90,000 oz of gold contained within the system (uneconomical grade). This gives the Boorara deposit an estimated endowment of 120,700 oz. The trace element chemistry of arsenopyrite samples from the geologically analogous Paddington and Boorara deposits were compared to determine if any systematic differences in arsenopyrite chemistry between the two sets of samples could be observed which may indicate greater gold endowment (Figure 93). It is evident from this analysis that these two deposits are easily differentiated from each other, with the more highly endowed Paddington deposit being differentiated from Boorara by having arsenopyrite with relatively elevated concentrations of Co, Se, Mo, Sn, and Bi. Arsenopyrite samples from the Paddington deposit were collected from the working pits over a period of 15 years while the samples from the Boorara deposit were collected from core logs during development drilling regime. Therefore, the Boorara samples may not
be wholly representative of the deposit orebody and this may somewhat further contribute to the chemical differences between these two groups of samples.

**Figure 93.** An LDA of the sample median trace element data for arsenopyrite samples from the Paddington and Boorara deposits (23 samples).

### 3.4.4.1.3 Hemlo and Big Bell

The Hemlo gold deposit is a world-class super-giant deposit located in Ontario, Canada. The deposit is located within a sequence of amphibolite facies metamorphosed clastic and volcanoclastic rocks of the Schreiber-Hemlo greenstone belt (Cameron and Hattori, 1985). The Big Bell gold deposit is located in the Murchison region of the Yilgarn craton in Western Australia. Mineralization is associated with a highly deformed amphibolite grade metamorphosed felsic sequence hosted within a narrow, steeply dipping sheared greenstone belt. Both of these deposits are highly endowed, with tabular ore lodes being approximately 12-40 m wide. The Hemlo deposit has a total endowment of approximately 40 Moz making it a supergiant deposit. The Big Bell deposit has an endowment of 3.5 Moz making it a giant gold deposit. These two deposits are geologically analogous and were formed approximately synchronously within the Kenorland supercontinent (see section 3.4.3.1.3). Therefore, the trace element chemistry of arsenopyrite may be
compared between these two deposits to determine if any systematic chemical differences may be associated with their gold endowments (Figure 94). It may be observed from this analysis that the elevated concentrations of Sn and Hg in arsenopyrite define the Hemlo deposit while all other elements investigated in this study (Figure 94) define the Big Bell deposit.

![Hemlo and Big Bell Sample Median LDA](image)

**Figure 94.** An LDA of the sample median trace element data from arsenopyrite samples collected from the Hemlo and Big Bell Deposits (10 samples).

### 3.4.4.1.4 Homestake and the Randalls Deposits

The Randalls group of deposits and the Homestake deposit are lithological analogues formed almost a billion years apart. However, it should be noted that for most of its history the Homestake deposit has been dated as Archean in age (Noble, 1950) leading to the global exploration for a new Homestake-like deposit within Archean cratons (Randalls, Canadian goldfields) (Stewart, 2013). The Randalls region features tightly folded BIF units hosted in mostly sediments and ultramafics which were formed contemporaneously with many of the other gold deposits in the Eastern Goldfields. The geology and setting of the Homestake deposit will be discussed in greater detail in section
3.5.2.1, but it should be noted that the Homestake deposit has mineralization constrained to tightly folded BIF anticlines. The Randalls region contains a number of discrete deposits that display spatially distinct features and on further investigation of the Randalls region it was believed that the Maxwells deposit would be the most analogous to the Homestake deposit. It was initially predicted that this deposit would have an ore reserve of over 1 Moz of gold, with the other deposits in the region being below 1 Moz each. However, following further exploration, it was suggested that the Maxwells deposit was significantly lower than 1 Moz. As of 2011 Integra mining Ltd have stated that the probable reserve of the deposit would equate to approximately 291,100 oz at a grade of 5.80 g/t to give the Maxwells deposit an estimated total gold endowment of 400,000 oz.

Arsenopyrite samples from the Randalls region (including the Maxwells deposit) and from Homestake were compared using an LDA to determine if samples from the Maxwells deposit displayed a chemical similarity to samples from the Homestake deposit (Figure 95). It is evident from this analysis that the samples from the Maxwells deposit may be differentiated from the other Randalls deposits. The Maxwells deposit appears to have lower concentrations of trace elements in arsenopyrite than the other two groups. Nevertheless, arsenopyrite samples from the Maxwells deposit appear to have some chemical similarity with both the Homestake and Randalls arsenopyrite samples.

Arsenopyrite from the Homestake deposit appears to have a higher concentration of all the elements included in the analysis (with the exception of Ni) than arsenopyrite from the Randalls samples (Figure 95). The Homestake deposit appears to be defined by the higher CPS data for Se, Sb and Hg, while samples from the Maxwells deposit are comparatively depleted (low CPS data) in the other elements investigated in this study.
Figure 95. An LDA performed on the sample median trace element assemblages of arsenopyrite samples collected from deposits in the Randalls region (including the Maxwells deposit) and from the Homestake deposit (108 samples).

As previously stated, of the Randalls group of deposits; it is the Maxwells deposit which has the greatest geological similarity to the Homestake deposit. An LDA was generated using the samples from the Maxwells (samples are derived from discovery drill samples and the initial open pit) and Homestake deposits in order to better identify the differences in chemistry (Figure 96). As observed in Figure 95 and Figure 96, the Maxwells deposit appears to have arsenopyrite which has lower CPS data for the trace elements measured.
in this thesis (with the exception of the slight enrichment of Mo and Te). The arsenopyrite from the Homestake deposit is defined by containing relatively elevated concentrations of Co, Se, and Sn.

**Figure 96.** An LDA of the sample median trace element data from arsenopyrite samples collected from the Homestake and Maxwells deposit (82 samples).

The relative depletion of trace elements in arsenopyrite samples from Archean deposits has been observed previously in Figure 59 (with the exception of Sb and Zn). Therefore, the depletion of trace elements in the Maxwells arsenopyrite samples may simply be the product of the primary Archean hydrothermal fluids being relatively depleted in most trace elements, which is reflected in the relatively lower concentrations of these trace elements in arsenopyrite formed during the Archean. Therefore, conclusions with respect to the comparison of these deposits may not actually be considered completely robust, as the progenitor fluids may be significantly chemically different between these deposits.
3.4.4.1.5 Summary of Analogous Deposits

It is evident from the sub-sections within section 3.4.4.1, that analogous deposits may be differentiated from each other on the basis of their arsenopyrite trace element chemistry (Table 17). Some of the LDA’s demonstrate an elevated CPS data for Co, Ni, Zn in arsenopyrite from the less well endowed deposits, but these elements are not common to all of the less well endowed deposits. The elevated concentration of Sn and, to a lesser extent Se and Hg, in arsenopyrite is common to all of the more highly endowed deposits and is potentially a reflection of the physiochemistry of the fluids which form these larger deposits. The specific reason for their elevated concentrations is, at the stage of writing, unknown.

Table 17. A summary of the arsenopyrite trace elements which define the differences between the analogous deposits. The data from the Homestake and Randalls comparison has not been included due to the deposits not being analogous.

<table>
<thead>
<tr>
<th>Deposits</th>
<th>Arsenopyrite Trace Elements</th>
<th>LDA</th>
<th>Overall</th>
</tr>
</thead>
<tbody>
<tr>
<td>More Endowed</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Homestake</td>
<td>Se, Ag, Sn, Te, Au, Hg</td>
<td></td>
<td>Sn ± Se, Hg</td>
</tr>
<tr>
<td>Paddington</td>
<td>Co, Se, Mo, Sn, Bi</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hemlo</td>
<td>Sn, Hg</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Less Endowed</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cosmo-Howley</td>
<td>Co, Ni, Zn, Bi</td>
<td></td>
<td>± Co, Ni, Zn,</td>
</tr>
<tr>
<td>Boorara</td>
<td>Cu, Zn, Ag, Hg, Pb</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Big Bell</td>
<td>Co, Ni, Se, Sb, Au</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.4.4.2 Archean Deposits

Twenty nine Archean deposits of known endowment from the Yilgarn craton together with the Hemlo deposit from Canada are investigated in this sub-section. The classification for the endowment of the gold deposits has been previously described in section 1.3.4 (Singer, 1995) and is detailed in Table 18.
Using the endowment classifications (Table 18), an LDA has been generated to separate the Archean gold deposits using the trace element chemistry in arsenopyrite (Figure 97). There are only two deposits representing the giant and supergiant groups, and as such, these groups may be under-represented in this analysis. Therefore, these two groups were combined into a group which represents the uppermost 10% of gold deposit endowment (giant deposits). It should be noted that some deposits in the Intermediate and Small Deposit groups are borderline for their classifications. Due to the approximate nature of the estimation of deposit endowment it should be recognised that some of the deposits from the Small Deposit group may eventually yield higher amounts of gold and therefore ultimately belong in the Intermediate group. After a predictive LDA investigation of the samples, the Iron King (a small deposit) was identified as being in the Intermediate Deposit group.

**Table 18.** The Au endowment (in koz) and classification size (Singer, 1995) of the Archean deposits investigated in this sub-section.

<table>
<thead>
<tr>
<th>Deposit</th>
<th>Au (koz)</th>
<th>Size</th>
<th>Deposit</th>
<th>Au (koz)</th>
<th>Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 Mile Hill</td>
<td>372</td>
<td>Intermediate</td>
<td>Hemlo</td>
<td>40000</td>
<td>Super Giant</td>
</tr>
<tr>
<td>Bardoc</td>
<td>131</td>
<td>Small</td>
<td>Iron King</td>
<td>5</td>
<td>Small</td>
</tr>
<tr>
<td>Bayleys</td>
<td>372</td>
<td>Intermediate</td>
<td>Kanowna Belle</td>
<td>4250</td>
<td>Giant</td>
</tr>
<tr>
<td>Big Bell</td>
<td>3420</td>
<td>Giant</td>
<td>Mount Martin</td>
<td>402</td>
<td>Intermediate</td>
</tr>
<tr>
<td>Boorara</td>
<td>121</td>
<td>Small</td>
<td>Ora Banda</td>
<td>997</td>
<td>Intermediate</td>
</tr>
<tr>
<td>Callyrup Creek</td>
<td>4</td>
<td>Small</td>
<td>Paddington</td>
<td>1625</td>
<td>Intermediate</td>
</tr>
<tr>
<td>Cave Rocks</td>
<td>186</td>
<td>Small</td>
<td>Plutonic</td>
<td>3009</td>
<td>Intermediate</td>
</tr>
<tr>
<td>Fimiston</td>
<td>54394</td>
<td>Super Giant</td>
<td>Randalls- Cock Eye</td>
<td>111</td>
<td>Small</td>
</tr>
<tr>
<td>Golden Crown</td>
<td>1900</td>
<td>Intermediate</td>
<td>Randalls- Maxwell</td>
<td>400</td>
<td>Intermediate</td>
</tr>
<tr>
<td>Great Fingall</td>
<td>1043</td>
<td>Intermediate</td>
<td>Randalls- Santa</td>
<td>220</td>
<td>Intermediate</td>
</tr>
<tr>
<td>Greenfields</td>
<td>165</td>
<td>Small</td>
<td>Spargoville</td>
<td>50</td>
<td>Small</td>
</tr>
<tr>
<td>Griffins Find</td>
<td>87</td>
<td>Small</td>
<td>Transvaal</td>
<td>752</td>
<td>Intermediate</td>
</tr>
<tr>
<td>Harbour Lights</td>
<td>657</td>
<td>Intermediate</td>
<td>Yilgarn Star</td>
<td>2600</td>
<td>Intermediate</td>
</tr>
<tr>
<td>Harlequin</td>
<td>700</td>
<td>Intermediate</td>
<td>Youanmi</td>
<td>1200</td>
<td>Intermediate</td>
</tr>
<tr>
<td>Harnett</td>
<td>1619</td>
<td>Intermediate</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 97. An LDA of the deposit median trace element assemblages of arsenopyrite from gold deposits formed during the Archean grouped on the basis of deposit endowment. The Giant and Super Giant classifications are grouped together (29 deposits).

On the basis of these initial observations, it may be possible to use the interpretation of the trace element assemblages in arsenopyrite, in conjunction with traditional estimation methods, to ascertain the probable gold reserves of a potential deposit using an iterative process. Because the major mining companies are often only interested in the larger (top 50% in terms of endowment) gold deposits it may be of interest to these companies to rapidly ascertain if the prospective deposit may be considered as potentially this size. Establishing the endowment of a deposit may be achieved using LDA analysis to identify the difference in the inter-element chemistry between arsenopyrite from small and larger
deposits (Figure 98). Using the chemical assemblage of arsenopyrite and this type of iterative LDA approach, it is possible in 96% of cases (and 100% of the validation samples) to differentiate between the potentially small and larger deposits, a situation that should have considerable economic importance to the larger mining companies especially before significant resources are expended on a more detailed investigation.

![Figure 98. An LDA of the deposit median trace element assemblages of arsenopyrite from small gold deposits and from the better endowed deposits (29 deposits).](image)

After it is determined that the arsenopyrite samples studied may be indicative of a deposit with an endowment of greater than 190 koz, it may be possible to ascertain if the deposit is an intermediate or giant deposit. While some intermediate sized deposits may be profitably mined by large mining companies, usually these companies are attempting to discover the next giant or supergiant deposits to significantly enhance their profits. An LDA was performed on the data set after the identification and removal of all deposits that were identified as being potentially small (Figure 99). From this LDA, it is immediately apparent that the two groups (giant and intermediate) may be strongly differentiated from each other. Consequently, from this initial study it seems extremely possible to differentiate small, intermediate and giant deposits from each other at a very
early stage of the exploration and development cycle of a mine and certainly before significant capital is expended.

Figure 99. An LDA of the deposit median trace element assemblages of arsenopyrite taken from intermediate and giant (including super-giant) deposits (20 deposits).

It should be noted that in Figure 97 and Figure 98 none of the samples were incorrectly identified as belonging to an endowment based group with a smaller endowment than the resulting mine has established that it should belong to. It is interesting that in some instances a sample (or validation sample) was “incorrectly” identified as belonging to a group with a larger endowment than currently identified. Using the data in Figure 97 the Boorara deposit was identified as having a Medium endowment. In addition, samples from the Great Fingall, Ora Banda, and Yilgarn Star deposits were identified has having a signature consistent with the Giant and supergiant deposits. These “misidentifications” may simply be as a result of the incomplete geological information which has been used to calculate deposit endowment. Often the data used to calculate the endowment is incomplete and does not include information on areas within the deposit which have a low gold grade (but are ultimately part of the total endowment of the system).
Additionally, many of the surface gold deposits have experienced significant Quaternary weathering which has led to the removal of an unquantifiable amount of gold from the system. It should be noted that deposits with refractory ore will have reported gold endowments which are lower than the contained gold in the system and are only indicative of the gold which can be economically mined, the Ora Banda deposit is one such example. The endowment of a gold deposit may also be lower than the total contained gold in the system by premature mine closure or abandonment of tenements. Overall, the calculated endowment of a deposit will be lower than the total amount of gold which has actually precipitated into the system. Therefore, it is recommended that these deposits are further investigated to ascertain if these systems have been under reported or under-investigated as there is potential for hidden undiscovered orebodies to be in the depositional system.

3.5 Variations of Mineral Trace Element Chemistry within a Deposit

With a significant decrease in the number of gold orebodies that have a surface expression, and are therefore relatively easy to identify with traditional geochemical exploration initiatives, it is becoming imperative for exploration companies to develop and use exploration techniques that can increase their potential to find buried and blind orebodies beyond the limits of their more obvious chemical and mineralogical expression (Kelley, 2006). Arsenopyrite may be observed many hundreds of metres from significant gold concentration and the slight differences between the chemistry of arsenopyrite samples from within the same deposit may be used to better understand the processes involved with the formation of the deposit. On the basis of this information, a geologist may be able to interpret these slight chemical variations and use this data to discover the location of orebodies or simply indicate the presence of a potential orebody in the area. It should be noted that the results and discussions detailed in section 3.5 are representative of the final iterative analyses of the trace element chemistry of arsenopyrite from gold
deposits. These investigations describe the chemical differences within a single system and are not necessarily able to be used backwards to determine features at the camp or province scale.

3.5.1 Lithology

It has been previously discussed in section 3.4.3.1.4, that the mineralogy of the deposit host rocks has an impact on the fluid chemistry which, in turn, is observed in the trace element chemistry of arsenopyrite. In a similar fashion, the ore forming fluid will change in physiochemical composition during gold mineralization and concurrent secondary mineral formation. This commonly leads to the formation of hydrothermal alteration haloes which have been detailed in section 1.2.2.1. It is important for exploration geologists to account for the proximal lithology on the arsenopyrite trace element chemistry in order to ascertain other information from the trace element chemical assemblage. The proximal lithology may mask the endowment of the system or may make exploration or drilling targets more difficult to generate.

3.5.1.1 Mount Porter

The samples from the Mount Porter deposit consist of arsenopyrite collected from diamond drill cores within an exploration regime close to the primary orebody. The locations of the arsenopyrite samples collected from the core material are detailed in Table 4. An LDA was performed on the sample median trace element data of arsenopyrite from the Mt Porter deposit and these data have been grouped on the basis of the associated proximal lithology (Figure 100). It can be observed from this analysis that the arsenopyrite samples may be differentiated from each other due to the slight influence of host rock composition on the arsenopyrite-forming hydrothermal fluid.
Figure 100. An LDA of the sample median trace element assemblages of arsenopyrite crystallized in various lithologies within the Mount Porter prospect (15 samples).

Data for the arsenopyrite samples from Mount Porter indicate that arsenopyrite hosted by dolerite has a different chemistry from arsenopyrite hosted by BIF (Figure 100). In this LDA the arsenopyrite samples hosted in BIF are defined by a relatively higher concentration of Ag, Au, Pb, and Bi, while the arsenopyrite associated with the dolerite has elevated levels of Co. An LDA was performed on arsenopyrite samples hosted in BIF and dolerite from Mount Porter (Figure 101) to compare the generic effects of BIF and greenstone (dolerite) on arsenopyrite chemistry. This analysis demonstrates that, within
the samples from the Mount Porter prospect, the arsenopyrite crystallized in BIF is characterized by elevated concentrations of Zn, Mo, Pd, Ag, Te, Au, Tl, Pb, and Bi. It has been previously observed in section 3.4.3.1.4 that arsenopyrite hosted in greenstone terranes has a trace element chemistry different to that in synchronously formed BIF hosted deposits (Figure 77). The arsenopyrite from Archean greenstone deposits was defined by relatively elevated concentrations of Co, Cu, Ag, Sb, and Pb. The arsenopyrite from the Archean BIF hosted deposits was defined by elevated Se, Mo, Te, and Bi concentrations. The differences in arsenopyrite composition may be the result of the influence of the primary hydrothermal fluid source and the material scavenged by the hydrothermal fluid during ascent through the crust. Nevertheless, the elements Te, Pb, and Bi are similarly enriched in arsenopyrite associated with the Archean and Mount Porter BIF’s (Figure 77 and Figure 101). Similarly, arsenopyrite samples from greenstones of the Archean and Mount Porter deposits share higher concentrations of Co, and Sb compared to arsenopyrite hosted in BIF.

Figure 101. An LDA of the sample median trace element assemblages of arsenopyrite crystallized in dolerite and BIF within Mount Porter (11 samples).
The elevated concentrations of Co and Sb in the arsenopyrite samples associated with greenstones must be considered as being primarily derived from the local host rock. Primitive rocks usually contain high concentrations of Co and Sb which may be part of the mineral assemblage or may be present as a minor element in some silicate minerals (Eilu and Groves, 2001). As stated in section 1.2.2.1, the hydrothermal fluid will react with the host rock resulting in the transformation of existing mineral phases and the creation of new ones in response to the changes in chemistry of the system. During this process elements will be leached from the existing host rock and will be remobilized and incorporated into new mineral phases. Due to the ease of isomorphous substitution of Co and Sb into the arsenopyrite lattice sites it is not surprising that these elements are remobilized and incorporated into arsenopyrite. The enrichment of both elements in observed at the camp scale (section 3.4.3.1.4) and is present within the localized chemical changes caused by alteration at the deposit scale.

It has been previously noted that the association of arsenopyrite with shale material commonly results in the elevated concentration of Bi in the arsenopyrite. As described previously, unaltered BIF typically contains elevated concentrations of Te, and Bi (Eilu and Groves, 2001), and therefore the elevated concentrations of Te and Bi in arsenopyrite associated with BIF may be the result of the leaching of these elements during alteration.

### 3.5.1.2 Boorara

Sixteen arsenopyrite samples from the Boorara deposit were collected from three exploratory drill cores. The sample locations and the various lithologies associated with the samples are detailed in section 2.1.2.1.3. An LDA was undertaken using the trace element chemistry of arsenopyrite from the Boorara deposit in order to differentiate the samples on the basis of the grain size of dolerite and the presence of chlorite (information
obtained from core logs, Appendix E-2.1) (Figure 102). In this analysis it is evident that the arsenopyrite samples associated with the chloritic dolerite are significantly different, in terms of chemistry, than the samples from the more fractionated leuco-dolerite rocks. It would appear that the arsenopyrite samples associated with this chloritic dolerite are primarily enriched in Co, Ni, Cu, Zn, Ag, and Pb.

![Boorara Lithology Sample Median LDA](image)

**Figure 102.** An LDA of the sample median trace element assemblages of arsenopyrite crystallized within various lithologies in the Boorara deposit (16 samples).

To investigate the effect of alteration of primary rocks on the chemistry of arsenopyrite, an additional LDA was performed on the dataset with the focus on the differences
between arsenopyrite associated with chloritic and leuco-dolerite (Figure 103). It is evident from both of these analyses that the arsenopyrite associated with the chloritic (altered) dolerite, has significantly higher concentrations of Co and Ni in the crystal lattice than arsenopyrite in unaltered dolerite. As detailed previously, Co and Ni are present as significant concentration trace elements in mafic rocks (Eilu and Groves, 2001). The elevated concentrations of these elements is most likely the result of pyroxenes in the dolerite being hydrothermally alerted to chlorite and from this reaction some of the trace elements in the pyroxene may be released into the hydrothermal solution and subsequently incorporated into the nearby arsenopyrite proto-crystals. It should also be noted that the chloritic alteration is most common in the basal areas of the dolerite intrusion and these positions have a much higher normative Co and Ni compared to the other dolerite in the deposit.

Figure 103. An LDA of the sample median trace element assemblages of arsenopyrite associated with dolerite and chloritic dolerite in the Boorara deposit (16 samples).

An LDA was performed on the dataset of arsenopyrite samples associated with the non-chlorite dominant dolerite to ascertain if the grain size of the host rock may have any
significant effect on the chemistry of arsenopyrite crystallized within the rock (Figure 104). From this analysis it is evident that the relative difference in the grain size of the host rock has some impact on the trace element chemistry of the associated arsenopyrite. However, the explanation for the specific suite of elements which define the arsenopyrite samples from these groups is currently unknown and may be an interesting avenue for latter investigation.

Figure 104. An LDA of the sample median trace element assemblages of arsenopyrite located in dolerites of varying grainsize in the Boorara deposit (13 samples).
3.5.2 Spatial Distribution within a Deposit

This section represents a preliminary investigation into the relationship between arsenopyrite chemistry and the spatial distribution of the specific arsenopyrite crystal within a deposit. The physicochemistry of ore forming fluids will vary throughout the deposit in response to mineral precipitation, fluid mixing and diffusion, and interactions with host rocks (section 3.5.1). In the case of epigenetic geological processes, as the ore fluid flows through the proto-deposit its chemistry will change. This change will impact on the deposit mineralogy and will determine which mineral phases are able to be precipitated, affecting what elements these phases sequester, and what trace elements remain in solution. Scientific studies have made some advances in identifying the characteristics of an ore fluid at the mineral-scale (Cook et al, 2013, Eadington, 1983, Vaughan, 1978, and others). Similarly, the distribution and relative relationships between the trace elements in arsenopyrite will be a reflection of the physicochemical characteristics of the fluid that has formed it. The significant changes in fluid chemistry may be observed by the formation of elemental haloes present around hydrothermal deposits. The mineralogy and chemistry of these haloes may be explained by the relative stabilities of the aqueous complexes of a variety of volatile and non-volatile elements (Eilu and Groves, 2001). In addition, the chemistry of the arsenopyrite will also change to reflect these conditions and these changes may be used to determine the location of arsenopyrite spatially with respect to the morphology of the deposit. By understanding the changes in the physicochemical conditions that can occur within the ore forming fluids and the relation of these changes to the spatial evolution of the orebody, it may be possible to identify and potentially predict the current position of the main fluid conduit within the deposit.
3.5.2.1 Homestake Deposit

The research that has been undertaken thus far in this thesis has identified certain attributes of the trace element chemistry of arsenopyrite that theoretically may be used to determine the original depositional environment and mechanism of emplacement of ore bodies and also to potentially determine the position of the main fluid source responsible or the introduction of ore forming fluids into the area. With this in mind research detailed in the following sections was designed to determine if the trace element assemblages of the 79 arsenopyrite samples collected from 5 ledges (orebodies) within the Homestake deposit could provide insight into these two aspects.

The Homestake gold deposit located at Lead in South Dakota, USA is one of the world’s largest gold mines. Background information and the locations of the 79 arsenopyrite samples collected from this deposit are detailed in section 2.1.2.1.1 and Appendix E-2.1. The lithology of the Homestake gold deposit region consists primarily of three geological formations deposited during the Proterozoic. In stratigraphic order (oldest to youngest) these three formations are; Poorman, Homestake, and Ellison. The Poorman Formation is approximately 600 metres thick composed of phyllite with minor ankerite. This is overlain by the Homestake Formation which is 60-100 metres thick composed of quartz-sideroplesite schist altered to a cummingtonite-grunerite-garnet schist in areas of higher metamorphic grade (BIF). The pyrrhotitic, cherty, shale/phylite lithofacies of the Poorman Formation is transitional to the Homestake BIF lithofacies. Stratigraphically above the Homestake Formation lays the Ellison Formation which is approximately 900 metres thick and consists of quartzite and interbedded quartz-mica phyllites. Arsenopyrite commonly reaches a volume of 5-30%, together with pyrrhotite, within the ore positions (>4.5 g/t Au) in the Homestake Formation (Morelli et al., 2005, Stewart, 2013).
3.5.2.1.1 Homestake Formation Model

Extensive research performed on this deposit has produced two different hypotheses concerning the emplacement of gold in the depositional environment.

1. The first theory states that the Homestake Formation was an iron-dominated sedimentary unit devoid of sulfur and gold. The gold-bearing fluid was derived from a deep metamorphic/igneous fluid and was introduced into the deformed Homestake Formation leading to mineralization (Caddey et al., 1991).

2. The second theory states that the Homestake Formation was created by the influence of a deep-sea exhalative source (possibly analogous to a “black smoker”), and contained the majority of ore materials within it. The Homestake Formation was then deformed and metamorphosed and the fluids associated with these processes led to the remobilization of gold and other elements into highly concentrated lodes (Rye, 1974a).

After the Homestake Formation was formed (by either theory) the region underwent metamorphism and extensive deformation. The first deformational event caused the Homestake Formation to be extensively folded, while the second deformational event produced cross-cutting folds that resulted in dilations at the intersections of fold axes. Up to thirteen discrete deformational events have been observed at the deposit, many of which contribute to the distortion and dilation of the Homestake Formation (Caddey et al., 1991). It is in these dilatational areas that the greatest concentration of gold has occurred (Noble, 1950). The morphology of the deformed Homestake Formation is detailed in Figure 18, Figure 105 and in Appendix A-1.1.1.

Both the Caddey and Rye theories propose that during the Proterozoic era (between 1.84-1.72 Ga ago) hydrothermal fluids led to the concentration of gold into what are now the ore zones. It is possible that this fluid was driven by the emplacement of the nearby Yates
basalt Formation. The critical difference between these hypotheses is that one states that this fluid was gold bearing (Caddey) and the other theory states that this fluid simply remobilized the existing gold within the Homestake Formation (Rye). The current Homestake formational theory proposes that the hydrothermal fluid is being introduced into a barren Homestake group (Caddey et al., 1991); this style of epigenetic mineralization is more common for the deposits formed during the Phanerozoic.

**Figure 105.** A) The locations of the samples taken from the Homestake deposit represented in plan-view. B) The locations of the same arsenopyrite samples as (A) represented in a W-E (cutting through the y-axis) cross section. Note that the radius of the dot is relative to the height above sea level (A) or distance into the y-axis (B). The line connecting the samples represents the Homestake Formation (dotted line is folded below the surface).

The relative trace element CPS data for arsenopyrite within the Homestake deposit were determined in order to test the validity of both formational theories (Figure 106). The relative CPS data for the elements were plotted as a function of the absolute distance (in three dimensions) from the samples collected from the bottom of Main Ledge (ML). This point is selected as it represents the most proximal sample to the anticipated fluid conduit for the two conflicting theories (Caddey et al., 1991, Rye, 1974b). However, in reality the fluid source and conduit may extend many thousands of metres below this position. The
rational for suspecting Main Ledge as one of the primary ore fluid pathways is that it produced over 20 Moz of Au, extends for over 4km depth, had significant gold stripped by erosion at the surface, and was also the focal point of significant Tertiary intrusive events (Caddey et al., 1991, Stewart, 2013). In Figure 106 there is some early evidence for a possible relationship between the element concentrations (at least for Sb) in arsenopyrite and distance of the sample from the bottom of Main Ledge. Additionally, if the sample data from the open cut pit were to be removed, the relationship between distance from the bottom of ML and Mo and Sb CPS (and to a lesser extent Ni ) would be significantly improved and would add further credibility to this observation (Figure 107). The slight relationship between arsenopyrite positioning and trace element chemistry with regards to Ni and Sb does not necessarily favour either of the formation theories, nor does it refute them, nonetheless the existence of that relationship is apparent and significant.

![Figure 106](image)

**Figure 106.** The location median iron-normalized CPS data of Ni, Mo, and Sb in arsenopyrite compared to the absolute distance (in three dimensions) from the location of sample 599E, at the bottom of Main Ledge (19 locations).

To directly test the second theory of deposition (syn-formational exhalative), the relative concentrations of trace elements in arsenopyrite are compared to the distance of the
arsenopyrite crystal analysed from the theoretical exhalative source of the deposit. Unlike in Figure 106, this distance is calculated relative to a structurally undeformed Homestake Formation and therefore represents the theoretical situation occurring at the time of the proposed exhalative deposition (Figure 107). If it is assumed that in close proximity to, or underneath Main Ledge, is a potential exhalative vent then it might be expected that specific minerals and their associated trace elements will, depending on their relative stability, form haloes around this exhalative vent. Higher temperature elements and minerals are more likely to precipitate proximal to the vent than their more thermo-labile counterparts. The precipitation of minerals at various distances from the main exhalative vent will therefore result in the development of elemental haloes around the vent. This trend may be broadly observed by reference to Figure 107, as the concentration of Ni and Mo decreases with increasing distance from Main Ledge. Antimony may potentially remain in solution at lower temperatures and this is demonstrated by its slight increase in concentration with respect to the distance of the samples from Main Ledge. This observation is in keeping with, and may support the exhalative model.

The chemistry of arsenopyrite with relation to the distance along the Homestake Formation from the bottom of Main Ledge does not necessarily confirm the exhalative model. This may be due to the highly folded post-deformation Homestake Formation acting as a significant fluid focussing structure in its own right. The hydrothermal fluid may originate from a point proximal to the bottom of Main Ledge and may move through the already folded formation, depositing elements during its movement. Therefore, the interpretation of Figure 107, as justifying the first (non-exhalative) model, could still be maintained as a possible mechanism of formation for the Homestake deposit. Additionally, it should be noted that there may also have been additional fluid conduits which will complicate interpretations.
Figure 107. The median iron-normalized CPS response of Ni, Mo, and Sb in arsenopyrite samples from the 13 locations within the Homestake Formation. It should be noted that the samples from Main Ledge have not been included in this diagram as they will not represent the lateral chemical zoning occurring within the deposit.

Consequently, the formation mechanism of the Homestake deposit remains conjectural and the interpretation of the data collected from the LA-ICP-MS analysis of arsenopyrite is not conclusive. Therefore, the formation model will not be investigated any further in this thesis. Nevertheless, in both of the formation mechanism theories, a large fluid event leads to the mobilization and subsequent deposition of gold, sulfides, and other minor mineral phases into the system. The hydrothermal deposition mechanism will be used as the default emplacement mechanism as it is the current model for the system (Caddey et al., 1991). The change in the chemistry of the fluid as it travels through the depositional zone is potentially significant in further developing relationships between the positioning of an arsenopyrite sample within a deposit and their specific trace element chemistry.

### 3.5.2.1.2 Trace Element Variation of Arsenopyrite

Each of the Homestake ledges is considered to be a (relatively) homogeneous and discrete orebody (Caddey et al., 1991, Stewart, 2009). An LDA was performed using the trace element chemistries of arsenopyrite from different localities within the deposit to assess
if each ledge is homogeneous and if the data for each ledge can be differentiated from the others (Figure 108). From this data it is clear that the arsenopyrite in each ledge has a homogenous and unique chemistry which may be differentiated from the chemistry of arsenopyrite from the other ledges. From the data detailed in this LDA, it could be hypothesised that the relative association of the chemistry data centroids of the arsenopyrite for the ledges is sequentially associated with the corresponding spatial association of these ledges within the deposit, and consequently the emplacement of ore in these ledges is mirrored by progressive changes in arsenopyrite chemistry (Figure 109).

Figure 108. An LDA of the median trace element concentrations of arsenopyrite from 19 locations within the 5 ledges in the Homestake deposit.
Figure 109. The relative median trace element concentrations of arsenopyrite from the ledges in the Homestake deposit represented in a two dimension W-E cross section (see Figure 105A). The size of the spot represents the relative iron-normalized concentration of the particular trace element.
The east to west ledge progression of the samples collected from Homestake is; Main ledge, 11L, 15L, 19L, and 21L. The relatively elevated element concentration regime of arsenopyrite throughout the ledge progression follows the sequence; Co, Mo, Te → Ni, Hg → Cu, Se, Sb (Figure 108). It should be noted that the distribution of Se and Sb in arsenopyrite is broadly reflected in the increased concentrations of these elements in the Homestake Formation within 19 and 21 ledges (Stewart, 2013). The indication that the ledges may be defined by a suite of elements as described in Figure 108 is further reinforced if the trace element chemistry of arsenopyrite is plotted with respect to the arsenopyrite sample positioning within the deposit (Figure 109). The elements Co, Mo, and Te tend to have the greatest concentration in arsenopyrite minerals that are proximal to Main Ledge (especially at the bottom of main ledge) while Cu and Sb show concentrations that are low proximal to Main Ledge and increase as the distance from Main Ledge is increased.

Main Ledge contains the most significant mass of gold throughout the whole deposit; and if it is assumed that Main Ledge is part of a fluid focussing structure, then it may be used to discover if there is a relationship between the chemistry of arsenopyrite and the distance to this significant potential fluid focussing structure. As discussed in section 3.5.2.1.1, the arsenopyrite samples display a relationship between their chemistry and their position within the Homestake Formation, a fact emphasised by approximately linear relationships between selected trace elements in arsenopyrite and their distance from Main Ledge (Figure 110). It is difficult to fully determine how the thirteen deformational events (Caddey et al., 1991) have impacted the Homestake Formation and it should be recognized that the distance from Main Ledge along the Homestake Formation is an approximate calculation of an undeformed formation (determined by measuring the distance between each gold lode in order along the Homestake Formation).
Therefore, it is likely to improve the relationship detailed in this sub-section if, though a more detailed investigation, the size and shape of the undeformed Homestake Formation could be determined.

The relationships detailed in Figure 110 can be combined to provide a graph (Figure 111), that directly relates these relationships to the distance from the hypothesised primary fluid focussing region of the deposit. While this relationship holds good for the Homestake deposit, the obvious implication is that an equivalent relationship or relationships may be used in other areas to identify distances from a primary fluid focussing structure or sources and therefore significantly aid exploration initiatives to locate orebodies.
Figure 111. The median iron-normalized CPS ratio of \((Ni*Mo)/(Se*Sb)\) from arsenopyrite collected in 13 locations plotted against the distance of the sample from Main Ledge, along the Homestake Formation.

It is possible that Tertiary dykes and intrusions focussed around Main Ledge may have led to significant latter fluid flow and remobilization of Phanerozoic material. This would in turn lead to overprinting of the various association patterns of trace elements in arsenopyrite. Originally these intrusions were hypothesised to have been responsible for the primary mineralizing event (Noble, 1950). Now they are recognised as being responsible for a simple, late stage, localized remobilization and overprinting event (Rye, 1974a, Caddey et al., 1991, Stewart, 1997b). This event, which took place in the Tertiary, has led to modest gold remobilization with alteration being constrained to within ten metres of the associated dykes/sills (Caddey et al., 1991, Stewart, 1997a). It should be noted that all Homestake arsenopyrite samples investigated in this theses were collected from outside the observable alteration haloes associated with the Tertiary intrusives (Stewart, 2013). Therefore, it is unlikely that the chemistry of these specific arsenopyrites will reflect the impact of the Tertiary dyke swarms. Additionally, it should be recognized that there may be undiscovered significant fluid conduits in addition to Main Ledge, which are likely to further complicate interpretation. However, until such time as they are
discovered, Main Ledge must continue to be recognised as the most significant fluid focussing structure in the Homestake deposit.

3.5.2.2 Mount Porter Prospect

The Mount Porter Deposit is located approximately 175 km south-southeast of Darwin in the Northern Territory, Australia. Information regarding the deposit and the locations of the samples within the deposit are described in section 2.1.2.1.2 and 3.5.1.1. The Mount Porter diamond core logs and the summarized data can be found in Table 4 and Appendix E-2.1.

The arsenopyrite samples associated with the Mount Porter deposit are sourced from exploration drill cores. Only a few locations within the core have significant gold concentrations which may be considered to be representative of an economic orebody (>1.5 g/t) and associated with an ore zone. The chemistry of the arsenopyrite samples from regions that may be considered to be within the ore zone are compared to the other arsenopyrite samples in Figure 112. Samples from regions of high gold concentration are differentiated from the other arsenopyrites by their relatively elevated CPS data for Co, Zn, Mo, Au, Hg, and Bi. As discussed in section 3.4.1, the high concentrations of Au in arsenopyrite are commonly directly associated with elevated concentrations of gold in the associated mineralized system. It should be recognised that there are only two arsenopyrite samples from the regions of high gold concentrations in this study. Due to this small number of samples, it is quite possible that the chemical composition of these samples may not be representative of other Mt Porter samples associated with elevated gold concentrations.
Figure 112. An LDA of the sample median trace element assemblages of arsenopyrite from Mount Porter, comparing samples in areas of high gold concentration (>1.5 g/t) and those associated with lower gold concentrations (23 samples).

For the purposes of exploration for orebodies, the identification of an ore zone, using arsenopyrite trace element chemistry, is somewhat superfluous, as the concentration of the gold can be easily and accurately measured using fire assay analysis. However, it is possible that the identification of arsenopyrite from orebodies may be used in conjunction with more traditional geochemical exploration techniques. Nevertheless, from the point of view of the hypotheses investigated in this thesis and detailed in this section, it is the arsenopyrite samples from non-orebody regions which are of greater importance for gold deposit exploration. An LDA was performed on the dataset after the samples from the areas of high concentration were removed (Figure 113). In this analysis arsenopyrite samples from areas of medium (1.5-0.75 g/t), low (<0.75 g/t), and below detection limits (<0.1 g/t) gold concentrations are chemically compared. In this analysis it is evident that the arsenopyrite samples from the medium gold concentration group are chemically differentiated from the samples associated with lower gold concentrations by elevated levels of Ag, Au, and Bi in the crystal. These elements are similar to those which have previously defined the arsenopyrite samples from ore zones (Figure 112).
Figure 113. An LDA of the sample median trace element assemblages of arsenopyrite located in non-orebody locations taken from Mount Porter (21 samples).

It is expected that the arsenopyrite samples from areas of low and undetectable gold concentrations have similar chemistries (Figure 113). An LDA was performed on the dataset containing samples from the low and below detection limit gold groups (Figure 114), to determine the slight chemical differences between these two groups. The arsenopyrite samples associated with observable gold concentrations are characterised by
a relatively higher concentration of Zn, Hg, Te, Au, Tl, and Bi in arsenopyrite. Again, an elevated concentration of Au and Bi in arsenopyrite is an indicator of increased gold in the whole rock. It is apparent from the three iterative LDA’s (Figure 112 to Figure 114) that the arsenopyrite samples which are associated with the higher concentrations of whole rock gold appear to be enriched in Au and Bi relative to their generalized whole rock gold concentration.

**Figure 114.** An LDA of the median trace element assemblages of arsenopyrite located in areas of low or below detection limits gold concentrations in Mount Porter (19 samples).

The early identification of an area which is barren of any appreciable gold concentration is also of importance for the exploration of a gold deposit. The ability to define such areas may be achieved by reference to the inter-element association patterns that have been plotted as an LDA in Figure 113 or by equivalent patterns that reflect the specific chemistry of the arsenopyrite discovered during the exploration phase in any other specific area. With specific reference to Mount Porter, the arsenopyrite samples from regions where the gold concentration is below the detection limits of fire assay, are relatively abundant in Co, Ni, Mo, Se, and Sb. This suite of elements is associated with
samples from lower gold concentration regions (Figure 113 and Figure 114). By relating the positioning of the arsenopyrite samples with the relative concentrations of these elements it may be possible to discover barren regions (high Co, Ni, Mo, Se, and Sb) and areas which have increasing Au concentration (low Co, Ni, Mo, Se, and Sb, high Au and Bi).

3.5.2.3 Boorara Deposit

As previously detailed in sections 2.1.2.1.3 and 3.5.1.2, multiple samples have been collected from exploration diamond drill cores representing the Boorara deposit. Mining has been undertaken at this deposit yielding approximately 30,700 oz of gold. The deposit has a probable reserve if 90,000 oz, giving the total endowment of this deposit of approximately 120,700 oz. Exploration drilling regimes have been implemented in a systematic drill pattern within the general area of this deposit and several of arsenopyrite samples have been collected from three cores in the deposit and the surrounding exploration areas.

Information pertaining to the gold concentration in various areas throughout the drill core (representative of the whole deposit) (Appendix E-2.1) has been used to develop a graph in which the fire assayed gold concentrations are plotted in relation iron-normalized CPS gold data for individual arsenopyrites collected from the equivalent core positions (Figure 115). It should be noted that Figure 115 demonstrates that the iron-normalized CPS of Au in arsenopyrite is a close approximation of the whole rock gold concentration.
The gold concentrations of the 1 m intervals of the B7 and B10 drill core are presented by the connected blue lines. The red dots are the relative iron-normalized Au CPS (multiplied by $10^6$ for ease of observation) of arsenopyrite samples taken from relevant locations within the core logs (9 arsenopyrite samples).

The relationship between the trace element chemistry of arsenopyrite and the whole rock gold concentration is however more complicated and consequently, in order to have a clearer understanding of this relationship, the relative concentration of gold within the core sections associated with the equivalent arsenopyrite sample is subdivided into three categories of gold grade; low (<0.75 g/t), medium (0.75-1.5 g/t) and high (>1.5 g/t). This interpretational approach is analogous to that used in the interpretation of the Mount Porter data. In an LDA performed on the sample median trace element assemblages of arsenopyrite from these groups (Figure 116) it is evident that they display significant differences in their trace element chemistry, with arsenopyrite samples within the orebody zone being defined by relatively high concentrations of Co, Ni, Cu, Ag, and Pb. The Boorara deposit is a low grade system and as such it was not possible to determine the
arsenopyrite trace element chemistry of sample associated with high grade ore zones (> 6 g/t Au).

**Figure 116.** An LDA of the median trace element assemblages of arsenopyrite samples from the B7 and B10 diamond drill cores. The groups are defined by the relative concentration of gold within the core section associated with the arsenopyrite sample (9 samples).

Even though it is obvious that the arsenopyrite samples from areas of high gold concentration (>1.5 g/t Au) are significantly chemically different from those in rocks with a lower gold concentration (Figure 116), it is still important to understand the differences between these two groups if the data are to be used effectively to aid exploration.
protocols. An LDA for the arsenopyrite samples from areas of gold concentration lower than 1.5 g/t (classified as potentially not belonging to an orebody) is detailed on Figure 117. Even within this diagram, it is evident that the arsenopyrite samples from regions of higher gold concentrations are defined by relatively increased concentrations of Co, Ni, Cu, Zn, Ag, Au, Tl, and Pb. The elevated concentrations of Co, Zn, and Au in arsenopyrite are analogous to the equivalent samples from Mount Porter, which are located in regions of high gold concentration (section 3.5.2.2). Potentially the elevated concentrations of these elements in this area, or a similar suite of elements that would indicate gold mineralization in another area, may be indicative of arsenopyrite located in regions of significant gold concentration and could therefore be used to potentially identify the geographical position of an ore zone within a more extensive area.

Figure 117. An LDA of the median trace element assemblages of arsenopyrite samples from areas of high gold concentration (>1.5 g/t) and those from regions of lower gold concentrations (0-1.5 g/t) within Boorara (9 samples).

It is evident from the observations of the previous LDA’s in this sub-section that Cu, Zn, Au, and Pb appear to be consistently present at elevated concentrations in arsenopyrite from regions of higher gold concentration. Conversely, arsenopyrite from regions of
lower gold concentration appears to be consistently enriched in both Te and Bi. Of these elements it is apparent that there is a strong relationship between the Au/Bi ratio in arsenopyrite collected from non-orebody locations and the whole rock gold concentration (Figure 118 A and B). This relationship can be classed as either linear or logarithmic. Unfortunately, because of the limited number of samples available for analysis it is not possible to determine which one of these trends is the more appropriate. Nonetheless, an antipathetic relationship exists between gold concentration and the level of bismuth in arsenopyrite and this trend could therefore be used to indicate relative position of the arsenopyrite sample to the main orebody.

![Graph showing linear and logarithmic regression lines for the Boorara Au/Bi relationship.]

**Figure 118.** The median Au/Bi relationship of arsenopyrite samples taken from the Boorara deposit with respect to the whole rock concentration.

In regions where gold is precipitating elements that have a similar Lewis character to gold will also be removed from solution. These elements will form discrete mineral phases or adhere to the surface of other minerals during precipitation. Gold is strongly complexed by bisulfide ions and has a soft Lewis acidity, like many of the chalcophile elements. While gold is technically a siderophile element (mostly because it does not form sulfide
minerals and may alloy with other metals) it can be considered to have more in common with chalcophile elements than siderophile elements. Thus, it would be expected that during gold precipitation, as bisulfide complexes become destabilized, other chalcophile elements will also be removed from solution. As the concentration of gold in the whole rock increases, the relationship between the most abundant siderophile and chalcophile elements change in a regular fashion (Figure 119). This relationship demonstrates the change in the concentrations of the most abundant siderophile and chalcophile elements (Ni/Sb), with respect to whole rock gold concentration. It is unfortunate that there is a significant gap in the data with arsenopyrite samples missing from areas where the gold whole rock concentrations range from 0.5 to 0.1 g/t. Under these circumstances it is possible to use an exponential fit to the data reflecting the precipitation of the analytes involved with respect to their actual solubility in the fluid from which they are being deposited (Figure 119 A and B). Obviously it would be experimentally more valid if it were possible to have samples of arsenopyrite that represented the later stages of gold precipitation (lower concentrations of gold), however, this was not possible as no relevant core samples were available for these concentrations. Nevertheless, the general principle of the association of these analytes is still valid, i.e. the higher antimony concentrations indicating the higher gold in host rock.

When the hydrothermal fluid precipitates gold, the sulfide complexes are destabilized. This destabilization will result in other chalcophile elements becoming precipitated in the same locality. These siderophile and chalcophile elements do not form their own discrete mineral phases (because their concentration in solution is too dilute). Instead these elements will precipitate onto the surface of minerals (mostly sulfide minerals) during the growth of these minerals. In areas of high bisulfide destabilization (higher whole-rock gold concentration) elements reliant on sulfur complexation (chalcophile elements) will
precipitate from solution and be present as trace elements in arsenopyrite. The concentration of these elements in arsenopyrite will be greater than in those areas where bisulfide destabilization (lower gold concentration) is less significant.

Figure 119. The sample median siderophile/chalcophile relationship of arsenopyrite samples collected from the Boorara drill cores with respect to the whole rock concentration (7 samples).
4.0 MERCURY ISOTOPE ANALYSIS

4.1 Introduction

The primary objective of this thesis was to investigate and understand the trace element chemistry of arsenopyrite and establish if changes in inter-element association patterns of analytes in this mineral could be used to assist in the discovery of buried and blind orogenic gold deposits. However, an additional secondary objective was also investigated. This secondary objective was based on an original theory by Watling 1972 in which he attempted to relate the distribution of specific mercury compounds to the geographical distribution of Cu/Pb/Zn mineralization in the Keel prospect, County Longford, Ireland. Watling’s theory hypothesised that mercury present in the original ore forming fluids, would migrate away from the main ore zone during mineral emplacement, precipitating to form discrete haloes of specific compounds and compound mixtures away from the ore zone. The initial studies to identify mercury compound halos were undertaken in Ireland (Watling, 1972, Watling et al., 1972, Watling, 1974) with the work indicating that sulfide mercury compounds were primarily represented in the rocks closely associated with primary mineralization. However, at that time it was not possible to determine the concentrations of mercury compounds below parts per million levels, or to have the ability to identify mercury isotopic inter-relationships. This latter aspect is of significance as it can be hypothesised that a relative increase in lighter mercury isotopes would occur distal to an orebody. If the isotopic fractionation could be observed and quantified then it might be possible to use mercury isotope ratios of material taken from drill cores within a mineralized area to triangulate back to the centre of mineralization. This was not possible in the 1970’s due to lack of appropriate instrumentation.

However, with the development of ICP-MS technology, the ability to determine mercury isotope ratios to a very high level of precision also makes it theoretically possible to
design and undertake an experiment to determine not only the presence of low level mercury compounds but also to determine the isotope ratios of these compounds in rocks. In this chapter the experimentation associated with the development of an ICP-MS based system to identify mercury compounds and their specific mercury isotope ratios, as a novel gold exploration protocol, was investigated. Experimentation focussed on a proof of concept to determine if mercury compounds could in fact be identified using ICP-MS based equipment and also if the stable isotopes of Hg varied significantly within a deposit. The experimentation was designed as proof of concept only because the ICP-MS available to the study was based around a quadrupole mass filter while in order to have adequate precision to determine mercury isotope ratios to the required level it would ultimately be necessary to use a multicollector system or equivalent.

4.1.1 General Background

Mercury is present in significant quantities in a variety of settings related to gold and base metal deposition and can be trapped interstitially as elemental mercury within ore forming minerals. Consequently, some hydrothermal deposits (rich in Hg) may be discovered by measuring the concentration of mercury vapour present in the overlying regolith (Warren, 1966, Kelley, 2006). Elemental mercury released during hydrothermal activity, base metal deposition or gold deposition may travel significant distances from the primary depositional site by migration through fractures, fissures and permeable host rocks (McCarthy, 1972). Consequently, mercury is used as a pathfinder element (commonly in association with Sb, Te, and Au) in the exploration for hot-spring, Carlin, Mississippi Valley, and orogenic style gold deposits. Additionally, supergene alteration and/or bacterial reaction with sulfide minerals may allow mercury to be released from these minerals and to escape into the overlying regolith where it can be concentrated and give rise to a “secondary” halo. Traditional exploration geochemists have either used relative
concentrations of the mercury trapped in rocks and soils, or the mercury volatilizing into the air as an indication of sub-cropping mineralization (Lentz, 2005). Unfortunately, because of significant natural variations in the concentration of mercury in these media (usually associated with increases in bacterial activity) it is extremely difficult to interpret “mercury halo” information and to relate it specifically to a mineralizing event (McCarthy, 1972). However, the presence of specific compounds of mercury could significantly improve the use of mercury data as the presence of mercury sulfide would certainly indicate increased sulfide ion activity in the area.

4.1.2 Mercury in Gold Deposits

Mercury is extremely volatile and can be transported either in the vapour (elemental) state or as soluble species in hydrothermal fluids where it can be complexed with both bisulfide and chloride anions (Varekamp and Buseck, 1984). As such mercury has the potential to be present as various compounds in gold deposits. These mercury compounds need not form discrete mineral phases but may be present as interstitial inclusions in mineral lattices, trapped in pores and fluid inclusions, or adhering to the surface of minerals. In addition, due to its chalcophilic nature, mercury may be present in sulfide species as a trace or ultra-trace element.

The investigation detailed in this thesis will concentrate on the release characteristics of four relevant mercury compounds (Hg, HgO, HgS, HgCl$_2$, and HgSO$_4$) that are expected to be associated with mineralizing events (Watling et al., 1972). The relative abundance of these compounds also represents different hydrothermal and supergene processes associated with the emplacement and enrichment of an orogenic gold deposit. As such, an understanding of the concentration and mercury isotopic assemblages of these compounds could be used for exploration purposes. In orogenic gold deposits it is
possible that gold-amalgam (AuHg_x) may also be present in the core of gold deposits and under these circumstances is commonly associated with mercury rich free gold. The main investigation of this thesis is however associated with exploration for an orebody and consequently release characteristics of mercury from gold-amalgam have not been investigated. Additionally, it is not expected that, if gold-amalgam was present in the samples, it would be apparent on traces as the mineral will only start releasing mercury near the melting point of gold (1063 °C) which is above the maximum compound release temperature investigated in this thesis.

4.1.2.1 Native Mercury

Native mercury (Hg_0) is a liquid at room temperature and may be found in trace quantities in some hydrothermal systems, with some base metal systems containing significant concentrations of this element (Ozerova, 1971). Elemental mercury is highly volatile and typically can only be found distal to orebodies in mineralized systems due to its high vapour pressure. Usually the mercury is trapped in fluid inclusions or trapped within mineral phases. Native mercury is easily volatilized and removed from the initial depositional site during subsequent heating and deformational events.

4.1.2.2 Mercuric Chloride

Mercury is typically transported as bisulfide complexes but, similar to gold (section 1.3.1), may also be transported as a chloride complex in various hydrothermal systems. Mercury may also be transported by other halides, however, chloride is by far the most ubiquitous and the most likely to be present in concentrations high enough to lead to complexation. In many orogenic gold deposits, chloride salts are trapped in fluid inclusions, and it is the relative abundance of chloride anions in fluid inclusion which are used as a measure of the salinity of the hydrothermal fluid (Wilkinson, 2001). Mercury is
usually associated with chlorine in these inclusions and it is therefore possible that mercury is present as an HgCl$_2$ inorganic compound in these structures.

4.1.2.3 Mercuric Oxide

Mercuric oxide is unlikely to be formed during gold mineralization in orogenic gold deposits as the oxidising conditions of the fluid, necessary to form mercuric oxide, would have precipitated it much earlier during hydrothermal fluid ascension. The presence of HgO in the depositional area may however be an indicator of the redox potential of the depositional environment and suggest an environment which is most likely barren in gold. However, mercuric oxide may be formed by later supergene oxidation of native mercury and therefore, care must be taken with the interpretation of HgO data.

4.1.2.4 Mercuric Sulfate

Mercuric sulfate is also unlikely to be found in most hydrothermal gold systems as the oxygen fugacity of such a system would have to be extremely high and consequently the transportation potential for chalcophile elements under this environment would be significantly reduced. Therefore it is unlikely that under such conditions significant gold or base metal mineralization would occur. Nonetheless, oxidation of mercuric sulfide will result in sulfate (HgSO$_4$) or basic sulfate (HgSO$_4$.2HgO) formation as will the combination of the sulfate anion with elemental mercury in areas of post-depositional sub-aerial oxidation, and the isotopic signature of the original mercuric species should be maintained in the secondary mercuric sulfate species.

4.1.2.5 Mercury Sulfide

Mercury is transported by sulfide ligands and is a strongly chalcophilic element. However, the presence of cinnabar (HgS) in orogenic terranes is rare, but it is perhaps the
only mercury compound that has the potential to crystallize and form a discrete mineral phase in gold deposits. Cinnabar may be present as inclusions within other sulfide minerals and may be formed by the exsolution of sulfides at grain boundaries or in cracks. In addition, mercury sulfide will precipitate synchronously with many of the other sulfide mineral species in the system and will not precipitate as far away from the primary mineralization site as some of the other mercury compounds. Therefore, as mercury sulfide can only be formed in association with the hydrothermal fluid, the mercury isotopic ratios within mercury sulfide throughout a deposit will reflect the thermal and chemical processes occurring during sulfide mineral deposition at the site of specific sample collection. It is likely that HgS will travel beyond the depositional zone for gold, and as such, will form an extremely useful halo compound for the identification and delineation of an orebody. In addition, the isotopic signature should theoretically be biased towards the lighter mercury isotopes the more distal its deposition is to the original orebody and as such relative variations in the isotope ratio of mercury in HgS and HgCl2 could be used to triangulate the location of the original orebody.

4.1.3 Mercury Isotopes

Mercury has seven naturally occurring stable isotopes with a range of 8 atomic mass units (\(^{196}\text{Hg},^{198}\text{Hg},^{199}\text{Hg},^{200}\text{Hg},^{201}\text{Hg},^{202}\text{Hg}, \text{and}\ {204}\text{Hg}\)). The natural abundances of these isotopes are detailed in Table 19. This large range in isotopic mass has the potential to facilitate the use of mercury to determine fractionation effects during the formation of the primary mercury halo associated with hydrothermal mineral deposition (Smith, 2005, Blum, 2007). Fractionation is caused by hydrothermal process such a redox, mineral precipitation and boiling reactions and the degree to which fractionation occurs is a result of chemical reactivity, mass, and fugacity of the individual mercury isotopes (Smith, 2005). Fractionation of stable isotopes is associated with the ease of ingress of mercury.
compounds into the surrounding rocks during primary ore emplacement. Under the influence of temperature and pressure gradients, the volatile mercury compounds will migrate away from the centre of the deposit into the surrounding rocks and the relative speed of this migration will depend on the relative molecular mass of the migrating isotope. Heavier isotopes form stronger covalent bonds than lighter isotopes. Therefore, mercury isotopes with a lighter atomic mass will migrate further than the heavier isotopes, as the lighter isotopes will remain in solution for longer (Smith 2005). Each of the mercury compounds should experience this fractionation effect of the mercury stable isotopes. The degree of fractionation will be dependent on the compound and the physicochemical conditions of the depositional environment. The process of fractionation will become more pronounced the longer the hydrothermal system is active. Many gold depositional systems are active for many thousands, if not millions of years, potentially leading to the formation of an isotopic halo around the deposit, analogous to an alteration halo (Bierlein, 2000). Later orogenic activity, faulting, and folding, together with any subsequent metamorphic events will complicate the isotopic halo distribution pattern. However, if the primary mercury distribution pattern can be identified, it is theoretically possible to use these types of isotopic anomalies to identify the original depositional position of orebodies.

Table 19. *The natural abundances of the seven mercury isotopes.*

<table>
<thead>
<tr>
<th>Mercury Isotope</th>
<th>196</th>
<th>198</th>
<th>199</th>
<th>200</th>
<th>201</th>
<th>202</th>
<th>204</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Abundance (%)</td>
<td>0.14</td>
<td>10.0</td>
<td>16.8</td>
<td>23.1</td>
<td>13.2</td>
<td>29.8</td>
<td>6.9</td>
</tr>
</tbody>
</table>

4.1.4 Research Objective

The objective of the research detailed in this chapter is to identify relevant mercury compounds and to determine if their isotopic compositions in whole-rock samples may be used to explore for gold orebodies. This objective has been discussed previously in section 1.6.2. However, it became apparent that time constraints would only allow for a
proof of concept to be investigated for separation and identification of compound
distribution and, because it was not possible to access a high resolution multi-collector
ICP-MS, the development of definitive exploration protocols using mercury isotope ratio
distribution would also not be possible. Nonetheless, a preliminary investigation into the
use of a quadrupole based ICP-MS system was undertaken as part of the proof of concept
experimentation detailed in this chapter.

4.1.4.1 Analytical Technique

The determination of the abundance of mercury isotopes and compounds in samples was
achieved by a combination of thermal desorption of mercury from rock samples and the
introduction of the desorbed gases directly into an ICP-MS instrument for final
determination. The compound isotopic assemblages were investigated to determine if any
shifts in isotopic abundance within specific mercury compounds could be related to the
geographical position of the sample within a gold deposit. In the initial stages of this
experiment it was not known if there would be isotopic segregation of mercury isotopes
and if it did occur, how much segregation there would be. Consequently, isotope ratio
work was undertaken as part of the proof of concept but was restricted to a quadrupole
based instrument only.

4.2 Experimental

4.2.1 Instrumentation

The concept of a system to volatilize and measure mercury isotopes is not new, but was
originally investigated by Watling in 1972. At that time ICP-MS had not been developed
and it was not possible either to measure the sub-ppb concentrations present in
background samples (beyond the immediate vicinity of the orebody) or to simply
determine the relative concentrations of mercury isotopes. Currently, ICP-MS devices are
widely used throughout the world and are widely accepted as high precision and accurate analytical instruments. Using multi-collector high resolution ICP-MS it is now possible to measure multiple isotopic masses simultaneously and cheaply and with an accuracy and precision high enough to potentially prove the concept of the objective in this chapter (Becker, 2002). The quadrupole based ICP-MS system available to the author has at best a mercury isotope measurement precision of ±0.5% relative (Jochum, et al., 2006), which was not sufficient in practice to resolve any potential differences in mercury isotope ratios present in the low Hg concentration samples investigated. However, this was not fully appreciated at the beginning of experimentation and only became a serious impediment once the investigation of the data had commenced. Nonetheless, the use of the quadrupole based system proved that in theory it would be possible to attach the compound separation system to a high resolution multi-collector ICP-MS at some later stage and at least investigate if to would be possible to use the greater precision of that instrumentation base to determine any differences in mercury isotope distribution patterns within an orebody.

A thermal cell that heats up the rock sample and directs the mercury vapour into the ICP-MS (Figure 120) is attached in-line with the ICP-MS instrument. A sample boat is placed in an inner tube which is subjected to a programmed heating regime and the vapour generated during the heating program is entrained in an argon purge gas flow and carried into the ICP-MS. The sample introduction system functions by having an argon gas flow transport the mercury vapour, released during the heating cycle, into the ICP-MS. The ICP-MS is operated in continuous signal acquisition mode and at each scan the isotope abundance of the mercury isotopes being released from the heated a sample is recorded. This procedure ensures that the CPS data for each mercury isotope is recorded with respect to release time and associated with the volatilization of different mercury
compounds. While the basic design of the mercury volatilization system did not change over the course of method development the specific design criteria did change.

**Figure 120.** A schematic diagram of the basic concept for the mercury volatilization device connected to an ICP-MS.

Two prototypes (alpha and beta) were constructed to test the project objective that had been first postulated by Watling in 1972. The initial prototype (alpha) was a simple device which was designed chiefly to determine if the release of mercury compounds and their corresponding isotopes could be measured using a connected ICP-MS system. The construction of the beta prototype was commissioned after preliminary experimentation and method development demonstrated this concept was correct and that multiple mercury compounds could be determined and their isotopic signatures measured. The beta prototype was specifically constructed for the purpose of more precisely discriminating between the release curves of the various mercury compounds.

**4.2.1.1 Alpha Prototype**

In the alpha prototype the inner sample tube is made from an 18 mm bore quartz tube of 2 mm wall thickness with one end tapered to an inner diameter of 5 mm (Figure 121).
Figure 121. A) The alpha prototype mercury volatilization device. This image displays the sealed inner sample tube (connected to the ICP-MS out of frame) surrounded by the heating element. The inner tube has a ceramic sample boat containing a multiple compound standard with a thermocouple suspended over the sample boat. B) The alpha prototype mercury volatilization device connected to the ICP-MS. The argon gas inlet is located to the left of the heating area where mercury compounds are volatilized and are purged into the ICP-MS. The ceramic sample boat may be observed in the inner tube, surrounded by the heating element.

The inner sample tube was surrounded a high resistivity wire to act as a heating element. The element and inner tube are then encased in a 25 mm bore quartz tube of 2 mm wall thickness to act as a basic form of insulation and to prevent accidental electric shock. The heating element is connected to an AC regulated power supply (Variac) allowing for the ramping of voltage supplied to the element, resulting in temperature ramping for the system. The tapered end of the inner quartz tube is connected to a 20 cm length of PVC tubing and this is connected to a two-way tap which has one outlet allowing venting of gases to atmosphere and the other, which is connected to the ICP-MS torch, allowing the carrier gases to be introduced directly into the ICP-MS instrument. The 18 mm end of the inner tube is plugged with a rubber bung with two holes drilled into it. One hole contains
a 5 mm diameter glass tube that is connected to the argon supply. This tube acts as the argon gas inlet which allows the inner sample tube to be purged after sample introduction, prior to ICP-MS analysis. A type K thermocouple is inserted into the second hole in the rubber bung and protrudes 10 cm to be in a position where the sample container is later placed. The hole is then sealed using silicone sealant. The thermocouple is connected to an electronic readout to measure the temperature of the sample in real time. The whole system may be operated by connecting the gas inlet to an argon supply and by connecting the tapered end of the inner tube to the ICP-MS torch (Figure 121).

4.2.1.1.1 Alpha Calibration

It was determined that this analysis would require a heating ramp from room temperature up to a temperature of approximately 500 °C which is sufficiently high enough to completely volatilize the range of mercury compounds investigated in the preliminary experiment. It was initially estimated that an analytical run of 10 minutes would allow for this heating ramp to be achievable. This ramp would also be slow enough to allow for almost full purging of relatively lower temperature dissociating mercury compound prior to the volatilization of the next compound of a somewhat higher melting temperature. Voltage increases to the heating element were performed manually; consequently, it was difficult to create a linear and reproducible heating ramp. Following a number of trials, a heating ramp was developed and implemented for the analysis of standards and samples using the alpha prototype (Figure 122). It may be observed from this figure that the ramp is still not linear and was also difficult to reproduce with the manual voltage changes required to continually heat the device. However, it was possible to use the device to prove the concept of mercury compound release.
Figure 122. *The measurement of the temperature within the inner tube of the alpha prototype during the calibration run.*

4.2.1.2 Beta Prototype

The new prototype (beta) required an even and controllable heat distribution that could be semi-automated if reproducible release of mercury compounds were to be achieved. Therefore, the construction of a beta prototype was commissioned to XRF Scientific Ltd. specializing in the construction of heating devices for scientific purposes (Figure 123). The same concepts from the alpha prototype were used and the same 18 mm tapered quartz inner sample tube was used with this new prototype. The quartz inner sample tube was simply inserted into the outer ceramic tube of the beta prototype and connected to the argon gas inlet and ICP-MS outlet in the same fashion as the alpha prototype (Figure 123, B). The beta prototype consisted of a ceramic tube surrounded by a coiled heating element encased in an insulating plaster. This inner tube is contained within a rectangular prism of ceramic insulating bricks to separate the element from the atmosphere. The prism is shielded with a steel mesh to prevent accidental heat damage to the operator. The heating element around the ceramic tube is connected to a programmable variable control unit connected to a display.
Figure 123. A) The beta prototype with the top insulation panel removed to show the insulated heating element wrapped around the ceramic outer tube. Note the cracking of the insulation covering the heating element. B) The beta prototype mercury volatilization device connected to the ICP-MS. The argon gas inlet is located to the left of the heating area where mercury compounds are volatilized and are purged into the ICP-MS.

4.2.1.2.1 Beta Calibration

The heating profile of beta prototype was measured using a fibreglass insulated type-K thermocouple. After several trials it was deemed that the voltage should be increased over time to maintain a linear heating ramp without heating too rapidly. As previously mentioned, achieving a final temperature of 500 °C in a period of 10 minutes was deemed to be ideal to separate the different mercury vapours, after method development of the alpha prototype. A number of heating ramps were attempted until the final heating ramp was created (Figure 124). It may be observed from Figure 124 that the heating ramp developed on the beta prototype is repeatable, and essentially linear.
4.2.1.3 ICP-MS

The ICP-MS used in conjunction with the alpha and beta prototypes is the same ICP-MS instrument used for all experiments in this thesis and is detailed in section 2.2.1.

4.2.2 Samples

The same samples which were used for the LA-ICP-MS analysis of arsenopyrite, were also used for the analysis of mercury isotopes in whole rock samples. However, due to the time constraints only the samples from the Homestake deposit were prepared and analysed for the purpose of investigating mercury isotope fractionation. The specific samples used are described in section 2.1.2.1.1 and were collected by thesis co-supervisor Mr James Stewart during his visits to the Homestake deposit.

4.2.2.1 Preparation

Small rock chips of approximately 10 g were removed from the core material prior to crushing. The chips were selected to be approximately representative of the core section.
as a whole. The 10 g samples were crushed for 10 seconds in a ring-mill and the resulting powder was sieved in order to provide 3 different grain size fractions (>0.2 mm, 0.2-0.1 mm, and <0.1 mm). The samples were then placed into snap lock bags for storage prior to analysis.

4.2.3 Standards

Single and multiple compound mercury standards were produced to identify the mercury release curves (referred to as the “volatilization profile”) of compounds and to calculate the relative concentrations of these compounds in samples by the area under the curves. All standards were serially diluted into a <100 μm particle size pulverised silica (SiO₂) that had previously been heated in a muffle furnace at 600 °C for two hours to remove any potential latent mercury adhering to the surface of the silica grains and any mercury present as a mineral species or included inside the grains. The single compound standards simply contained a known quantity of one of the four mercury compounds (native Hg was not used due to its high volatility and health hazards) finely crushed and physically mixed into the silica matrix. The multiple compounds standard contained known masses of all four of the mercury compounds (HgO, HgCl₂, HgS, and HgSO₄) mixed into the silica matrix. The initial standard contained all four compounds with equivalent mercury concentrations. Serial dilution of this “high concentration” standard ensured that all standards contained the same equivalent amount of mercury as an individual compound, in each subsequent standard. A series of standards was made by serial dilution of the original “high concentration” standard to achieve a range of concentrations approximately between 1 and 100 ppm mercury in each compound.

The single compound standards were created to determine the specific temperature range over which each compound would volatilize and to determine the shape of the
volatilization profile. In addition, with later method development and refinement, the standards could be used to determine the concentration of mercury compounds in the samples with a similar matrix. A range of standards for each mercury compound was created by adding each compound to a silica matrix to develop a 4,000 ppm standard and from the serial dilution of this standard a 100 and 1 ppm standard were also created.

The multiple compound standards were created to observe the potential interactions and overlap of multiple mercury compounds within a volatilization profile. With later method development and refinement it was possible to more easily differentiate the peaks to reduce overlap and increase precision.

4.2.4 Analytical Methodology

The beta prototype mercury volatilization device had the following settings for achieving the greatest signal to noise ratio and the greatest differentiation between mercury compounds:

- Initial Temperature (room temperature) (t=0 seconds)
- Heat to 200°C at t=60 seconds
- Heat to 350°C at t=120 seconds
- Heat to 500°C at t=180 seconds
- Heat to 550°C at t=240 seconds
- Turn off when temperature reaches 580°C

It should be noted that the heating ramp takes a longer period of time to achieve the desired temperature than the settings indicate. This is due to the insulation of the system creating a significant thermal lag and the voltage of the system being internally regulated (significantly below the mains voltage of 240 V).
The isotopes which were measured using the ICP-MS instrument during the analytical run are detailed in Table 20. It should be noted that the atomic masses 195 and 203 do not correspond to mercury isotopes. The $^{195}\text{Pt}$ mass was included in the final methodology in order to allow the mass spectrometer a short period of time to reset after scanning and prior to the next mass being measured (the start of a new cycle of measurement). Additionally, the 203 AMU coincides with a thallium isotope which was used to observe the volatilization of this element which is commonly trapped in sulfide minerals. The detection of this isotope during the analytical run indicated the thermal degradation of sulfide minerals.

**Table 20.** The isotopes and their natural abundances which are measured every 0.921 seconds in this method.

<table>
<thead>
<tr>
<th>Mass</th>
<th>195Pt</th>
<th>196Hg</th>
<th>198Hg</th>
<th>199Hg</th>
<th>200Hg</th>
<th>201Hg</th>
<th>202Hg</th>
<th>203Tl</th>
<th>204Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>33.8%</td>
<td>0.14%</td>
<td>10.0%</td>
<td>16.8%</td>
<td>23.1%</td>
<td>13.2%</td>
<td>29.8%</td>
<td>29.5%</td>
<td>6.90%</td>
</tr>
</tbody>
</table>

The analysis method includes the analytes listed in Table 20 and has the following characteristics:

- Analytical mode: Time Resolved Analysis
- Isotope dwell time: 0.10 seconds
- Sampling time per single cycle: 0.921 seconds

The nature of mercury volatilization precludes having an easy to use mercury standard designed specifically for ICP-MS tuning and, while no tuning standards were developed, the CPS response of the Argon dimer ($^{40}\text{Ar}^{40}\text{Ar}$) was used to align the plasma torch.

### 4.2.5 Method Development

The initial focus of the method development was to produce a semi-linear heating ramp which could be replicated, and which would encompass the temperatures necessary for the volatilization of the four common mercury compounds of interest (HgS, HgCl$_2$, HgO
and HgSO\textsubscript{4}). For the alpha prototype, a Variac was used to set the voltage of the heating element. The first heating ramps consisted of setting the Variac to a given voltage and simply allowing the element heat up. The heat of the system is measured in the centre of the inner tube with a type K thermocouple. The inner tube was calculated to have a volume of approximately 200 mL. The argon gas flow was set to 0.5 L\text{min}^{-1} as this flow rate would allow the inner tube to be relatively rapidly purged, and to ensure that mercury from the volatilized mercury compounds was efficiently flushed into the plasma. This gas flow was not changed throughout all experimental procedures. The various voltages and their associated heating ramps are detailed in Figure 125. Initial observation clearly demonstrates that none of the voltage settings produce a heating ramp which is linear. The low voltages do not reach a high enough temperature to volatilize mercury from HgSO\textsubscript{4}, and the high voltages heat the sample too rapidly to achieve good compound separation. It is evident that the simple setting of a single voltage to the heating element is insufficient for the needs of this experiment.

![Variac Voltage Comparisons](image)

**Figure 125.** The temperature of the inner tube of the alpha prototype over time for various heating element voltages.
To generate a linear heating ramp, suitable for the needs of the experiment, it is clear that the voltage of the heating element needs to be adjusted over the course of the analytical run. By slowly increasing the voltage, a semi-linear heating ramp of 10 minutes duration was achieved (Figure 126). The heating ramp detailed in Figure 126 demonstrates that by regularly increasing the voltage during the analytical run (5 V every 60 seconds); semi-linearity may be achieved. However, while the heating ramp displayed in Figure 126 is considerably more linear than the ramps observed in Figure 125, it is still not completely linear. Thus, it was deemed that the manual manipulation of the Variac was a limiting factor in creating a precise heating ramp appropriate for the experiment.

![Multi-Volatge Heating Ramp](image)

\[ y = 1.4858x + 97.079 \]
\[ R^2 = 0.9374 \]

**Figure 126.** A heating ramp developed by changing the voltage of the heating element. The initial voltage is 20V for the first 60 seconds, and the voltage is increased by 5V every 60 seconds.

The multiple compounds standard was run under the conditions developed for the production of Figure 126 to determine if this heating ramp could be used to adequately separate the volatilization peaks of the mercury compounds (Figure 127). This image represents the four mercury compounds present in the same standard, and each of the components singularly in their own standards and as can be seen from this figure it was
not possible to resolve the compound mixture adequately under this heating system. The inability to replicate the heating ramp justified the construction of a controlled heating device (beta prototype).

![Multiple Compounds Standard Comparisons](image)

**Figure 127.** The CPS of the $^{202}$Hg isotope collected from three separate ICP-MS analyses of the 1 ppm multiple compounds standard.

The beta prototype required further minor development in order to create a reproducible and stable heating ramp that could achieve a specific temperature at set intervals. The heating ramps and the instrument conditions attempts are detailed in Appendix E-1.7. The final heating ramp achieved linearity and reached a final temperature of 500 °C over 10 minutes (Figure 124). Even with this improved final control possible, differentiation of the compound peaks could still not completely be achieved (Figure 128). However, for the preliminary set of investigative experiments detailed in this thesis, it was decided to use the developed parameters as time restraints precluded an in depth investigation into the further development of another, more advanced, heating apparatus.
Figure 128. The CPS of the $^{202}$Hg isotope for the four the 1 ppm single compound standards (dashed lines) measured during separate analytical runs. The solid red line represents the cumulative total of the single compound standards. The solid black line represents the CPS of the 1ppm multiple compounds standard.

One modification of the heating apparatus was undertaken to ensure that the physical specifications of the device holding the sample inside the heating tube was optimized to ensure minimal thermal lag and optimum gas flow across the surface of the sample. The samples were initially housed in a ceramic boat of approximately 8.5 g mass. This housing was selected due to its large volume which is able to contain a mass of sample material in excess of 2 g. It was initially hypothesised that a large amount of material (approximately 2 g) would be required to provide a mass of sample containing a mass of mercury significantly above the detection limit of the analytical equipment. After preliminary investigations into the establishment of an analytical protocol, using volatilization of samples and standards from the ceramic boat, it was determined that the high heat capacity of the boat was causing a significant thermal lag between determined and actual temperatures in the sample and was therefore a hindrance to the reproducible
release of mercury from the sample and to the resolution of mercury peaks. In addition, it was determined that less than a gram of material was required for analyses. Therefore, a new sample boat with a lower mass and lower thermal insulation was required. A new sample boat was constructed from approximately 400 mg of tantalum foil. The Ta foil sample boat had a much lower mass, heat capacity and depth than the ceramic boat. All of these factors led to the volatilization of mercury compounds from the sample at a faster rate with minimum thermal differences between the boat and the sample (Figure 129).

![Sample Boat Comparison](image)

**Figure 129.** A comparison of the $^{202}\text{Hg}$ isotope CPS data for 1 ppm multi-compound standards mounted in a boat made of Ta foil (11.1 mg sample mass) and a ceramic boat (12.6mg sample mass) using the heating ramp displayed in Figure 126.

As stated previously, complete separation of the specific mercury compound peaks within the multiple compounds standard was still not fully achieved (Figure 128). Nonetheless, it was considered appropriate to determine if natural samples could be analysed using this system to indicate whether or not mercury compounds could seen to be present before attempting what would necessarily be an extremely detailed investigation into the optimization of equipment only to discover that no peaks could be observed in natural samples.
4.2.6 Procedure

4.2.6.1 Sample Preparation

As previously discussed in section 4.2.2, the sections of core and rock material were collected by Mr James Stewart from the Homestake deposit. Rock material containing significant veining or sulfidation was identified and marked following visual inspection. These marked sections were removed from the rock by excision using a diamond saw or geological hammer. Following this, the samples were collected and placed in a ring mill where they were ground for approximately 3 seconds. The sample was then recovered and sieved into three size fractions >200 µm, 200-100 µm, and <100 µm. It was only the material in the <100 µm size fraction which was used for analysis.

4.2.6.2 Standard Preparation

Two sets of standards were developed for this experiment. A set of mercury multi-compound standards, and a set of mercury single compound standards, both sets of standards used reagent quality Hg compounds; HgO, HgSO₄, HgCl₂, and HgS, mixed with a matrix comprising of silica. The silica was heated to a temperature of 600 °C for a period of no less than two hours to remove mercury, the silica was then stored in a sealed container.

4.2.6.2.1 Single Compound Standards

Each of the reagent quality mercury compounds was separately ground into a fine powder using an agate mortar and pestle. The grinding was undertaken in a fume hood to reduce the potential for the mercury compound powders to contaminate the laboratory and also to reduce the health hazard associated with grinding mercury compounds.
A mass of the specific mercury compound, equivalent to a total mass of 100 mg mercury (weighed to four decimal places), was added to 25 g silica (weighed to four decimal places) and transferred to a 120 mL PPE tube into which four steel ball bearings had been placed. This standard was mixed continuously for a period of two days using a bottle roller operating at 30 revolutions per minute (rpm). This created a stock standard with a concentration of approximately 4,000 ppm (accurately known) of mercury in a silica matrix. An approximate 0.625 g portion (accurately weighed to four decimal places) of the 4000 ppm stock standard was added to a 120 mL pre-weighed PPE tube. Silica powder was added to create a final mass of approximately 25 g (accurately weighed to four decimal places). This created a set of approximately 100 ppm standards for each of the mercury compounds used (Table 21).

Table 21. The concentration of each of the single compound standards calculated from the masses of the mercury compounds and the silica diluent.

<table>
<thead>
<tr>
<th>Standard</th>
<th>HgO</th>
<th>HgS</th>
<th>HgCl₂</th>
<th>HgSO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stock Standard</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compound (g)</td>
<td>0.1186</td>
<td>0.142</td>
<td>0.1301</td>
<td>0.1465</td>
</tr>
<tr>
<td>Silica (g)</td>
<td>24.934</td>
<td>25.0722</td>
<td>24.9077</td>
<td>24.8410</td>
</tr>
<tr>
<td>Concentration (ppm)</td>
<td>4384</td>
<td>4855</td>
<td>3839</td>
<td>3964</td>
</tr>
<tr>
<td>100ppm Standard</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stock STD (g)</td>
<td>0.6303</td>
<td>0.6258</td>
<td>0.6273</td>
<td>0.6245</td>
</tr>
<tr>
<td>Silica (g)</td>
<td>25.2157</td>
<td>24.3797</td>
<td>24.3722</td>
<td>24.4505</td>
</tr>
<tr>
<td>Concentration (ppm)</td>
<td>107</td>
<td>122</td>
<td>96</td>
<td>99</td>
</tr>
</tbody>
</table>

4.2.6.2.2 Multiple Compounds Standards

A specific mass of each of HgO, HgCl₂, HgS, and HgSO₄ was transferred into a 120 mL PPE tube and an additional mass of pre-heated silica was added to produce a final mass of approximately 25 g accurately weighed to four decimal places. The final concentration of mercury in the standard for each compound was approximately 4,000 ppm. Four steel ball bearings were added to this mixture and it was mixed continuously for a period of two days in a bottle roller operating at 30 rpm. Following this a 0.625 g portion of the stock standard was added to a new pre-weighed 120 mL PPE tube. Silica was added to
this tube to create a final mass of 25 g. This dilution created a standard with a concentration of approximately 100 ppm mercury for each compound. Using a similar method, a series of standards was created to have concentrations as detailed in Table 22. Only the 1 ppm standard was used in experiments for the analysis of rock samples. This standard was created by adding a 0.25 g portion of the 100 ppm standard to a pre-weighed 120 mL PPE tube and adding silica to bring the mass of the standard to 25 g.

Table 22. Concentrations of Hg in each of the compounds in the multi compounds standard.

<table>
<thead>
<tr>
<th>Approximate Standard Hg Concentration</th>
<th>Mercury Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HgO</td>
</tr>
<tr>
<td>20 ppm</td>
<td>20.7</td>
</tr>
<tr>
<td>10 ppm</td>
<td>10.5</td>
</tr>
<tr>
<td>5 ppm</td>
<td>4.96</td>
</tr>
<tr>
<td>2 ppm</td>
<td>2.11</td>
</tr>
<tr>
<td>1 ppm</td>
<td>1.04</td>
</tr>
</tbody>
</table>

4.2.6.3 Mercury Volatilization ICP-MS Analysis

The analytical system was set up with the beta prototype connected to the ICP-MS and the tap from the mercury volatilization device to the ICP-MS (Figure 123 B) was switched on to allow argon to pass through the heating chamber into the plasma. The system was purged with high purity argon for a period of 30 seconds. The plasma was switched on with argon running through the cell and left to stabilize for 5 minutes. The ICP-MS was then tuned to the argon dimer (\textsuperscript{40}\text{Ar}-\textsuperscript{40}\text{Ar} (m/z 80)) to ensure that the greatest signal was being received from the ICP to the MS, following this the argon flow was diverted and exhausted into the atmosphere. A known mass of the 1 ppm multiple compounds standard was placed into the sample boat and the powder smoothed to ensure that it was distributed evenly along the length of the boat. The boat was then introduced into the inner quartz tube to a depth of 5 cm and the rubber plug, with the thermocouple and gas inlet attached, was inserted into the rear of the inner furnace tube in order to create a seal. The inner tube
was purged with argon gas at a rate of 0.5 L/min⁻¹. After thirty seconds of purging the tap connecting the inner furnace tube to the plasma was opened to allow gas flow from the inner tube into the plasma. The ICP-MS data acquisition method was engaged, (as detailed in section 4.2.4) and after 15 seconds of acquisition the heating ramp was also engaged (Figure 124). After a period of 585 seconds had elapsed the data acquisition method and heating ramp both ceased. At this point the tap connecting the inner tube to the plasma was closed, allowing the argon gas to vent into the atmosphere and preventing any other gases from entering the plasma. The insulating cover of the heating device was removed and the heater cooled to room temperature using compressed air. The rubber plug was removed from the inner tube and the sample boat removed. All additional samples were analysed in a similar manner.

4.2.7 Data Analysis

The CPS data for all of the isotopes are plotted against time to create a line graph representing the volatilization profile for the various mercury compounds within the sample (Figure 130). Peak shape and release characteristics with respect to time are visually identified and recorded. As observed in Figure 130, the identification of peaks may be complicated due to overprinting of release curves from other mercury compounds. The peak positioning is compared to the graphs of the multiple compounds standard analysed at the beginning of the analytical run (similar to Figure 128). From this comparison the peaks are related to mercury compounds and the height of the peak is recorded. The relative CPS response for each of the Hg isotopes was also recorded. The isotope CPS responses are then used to calculate isotopic ratios for each of the observable mercury compounds within the sample.
Figure 130. An example of the CPS data for nine isotopes during the volatilization of the sample (data for sample 14B3 is displayed in this figure).

The mercury release curve represents the product of both the mass and concentration of the individual mercury compound within the standard and by comparison of peak heights can theoretically be used to give an approximate concentration of an equivalent individual compound within analysed samples. However, a slight modification to this approach was adopted when calculating the isotope ratios of the various mercury compounds, analytical data accumulated during the period of time representing approximately the area represented within the half width of the peak is selected. Within this period of time, representing the thermal release of each compound, a series of CPS data point ratios are calculated for each data acquisition interval (0.921 seconds). The isotope ratios are displayed graphically to determine if any systematic isotope ratio changes are occurring within the period represented by the peak half width. The half width interval will be the period over which the greatest release of individual mercury compounds will occur and as such should provide the most precise data and be relatively free of overlap from the release of other mercury compounds. This situation should therefore allow for the best
possible indication of any changes from the natural abundance isotope pattern of mercury to be observed in individual mercury compounds released from natural samples.

4.3 Results and Discussion

The aim of the research detailed in this chapter was both to determine if the fractionation of mercury compounds within a gold deposit could be observed and if so could their interrelationships be used for exploration purposes, and to determine if it was possible to see differences in mercury isotope patterns for each of these compounds with respect to distance from mineralization. However, as stated earlier, the development of the thermal ramp device took considerably longer than planned and consequently it was only possible to undertake a proof of concept study into the potential of using variations in the melting appoints of the compounds investigated to separate mercury compounds from one another. However, even after experimentation with various prototypes, while it was possible to identify mercury release from various compounds, compound separation was still not sufficiently good to obtain background resolution of peaks and will require further investigation and thermal ramp development prior to any potential real world application. Furthermore, the precision of the mercury isotope ratio measurements was not good enough to determine other than gross differences in isotope abundance and to be effective will require coupling of the thermal desorption device to a multi-collector ICP-MS or equivalent. Nonetheless, the work undertaken confirmed that mercury compound identification was possible using ICP-MS has laid the foundation of a future more detailed study and is therefore evaluated in the following section.

4.3.1 Compound Separation and Identification

The issues associated with developing a prototype mercury compound volatilization system to introduce volatilized mercury compounds into the ICP-MS, has been discussed
in the method development section (section 4.2.5). One of the most significant issues discussed in that section was the separation of the mercury compound peaks.

4.3.1.1 Mercury Standards

Mercury compound standards were created with the intent to analyse them at the beginning of an analytical run to facilitate in the calculation of the concentration of the individual mercury compounds within the rock samples. It was envisaged that these multiple compounds standards, at various but specific concentrations, could be used to create a calibration curve that would be used for calculating sample concentrations. The calculated concentrations from the calibration curve would not be an accurate concentration of the compounds in the sample, due to some mercury compounds being trapped within the rock and potentially unavailable for volatilization. However, it was deemed as being a best practice approach and valid in relative terms.

Single mercury compounds will volatilize over various temperature ranges during the heating regime depending on their physical chemical characteristics. Consequently, in order to determine at which temperature the compounds volatilize, a series of single compound standards were volatilized individually and their ICP-MS response (for $^{202}\text{Hg}$) was documented. Analysis was repeated three times and a mean mercury release curve for the data was developed (Figure 131). From this figure it can be determined that using the equipment developed, the peak volatilization of mercury from individual compounds occurred at the following temperatures and times during the heating run:

1. $\text{HgCl}_2$ volatilizes at 180±7 seconds coinciding with a temperature of 179±10 °C
2. $\text{HgS}$ volatilizes at 210±8 seconds coinciding with a temperature of 210±11 °C
3. $\text{HgO}$ volatilizes at 289±11 seconds coinciding with a temperature of 289±13 °C
4. HgSO₄ volatilizes with two significant peaks at 333±12 and 405±12 seconds coinciding with the temperatures of 329±9 and 391±9 °C

The melting temperature of the first three mercury compounds are as follows (Weast, 1971):

1. HgCl₂ melts at a temperature of 276 °C
2. HgS melts at a temperature of 334 °C
3. HgO melts at a temperature of 500 °C
4. HgSO₄ decomposes

Therefore, the data implies that mercury is being removed from these compounds at temperatures significantly below their melting point. This temperature discrepancy can be logically attributed to the positioning of the thermocouple in the sample which may be in a region within the tube that is significantly cooler than the area where the sample material is contained. Additionally, the fact that mercury is being continuously removed from the sample in the argon purge means that no thermal equilibrium is possible and the thermal release curves obtained therefore represent variations in the temperature vs. partial vapour pressure curve of the melting profile of the specific compound under non-equilibrium conditions and are not an indication of true melting temperature. Under these circumstances mercury release and compound breakdown will occur at lower temperatures than the compound’s actual melting points and result in a release curve that peaks at a temperature considerably below the established melting point of the compound itself. Providing the thermal ramp is reproducible from sample to sample, this discrepancy will have no significant effect on data interpretation.
The identification of the release characteristics of mercury from the individual compounds, using data for the individual compound peaks, assists in the identification of the compounds peaks in the samples as the mercury release patterns from samples are far more complex than for individual compounds. It may be observed in Figure 131 that the multiple compounds standard approximately follows the sum of the single compound standards. The slight differences between the release characteristics of the peaks between the multiple and single compound standards may be attributed to the difficulty in reproducing the heating curve for each analysis. It may also be apparent from the release curves of samples (Figure 131) that some other practical issues such as multiple peaks for some of the compounds, and the overlapping of peaks during the heating ramp may interfere with interpretation, although if the robustness of the release characteristics can be improved, peak deconstruction software, similar to that used in liquid chromatography, could be employed to achieve this. It may be observed from Figure 131, that HgCl$_2$ and HgSO$_4$ have volatilization profiles with more than one peak. The complex dissociation pattern for HgCl$_2$ is unexpected and may suggest the presence of impurities or
stoichiometric changes in composition as the temperature increases. However, both of these explanations are unlikely and it is probably more likely that the compound itself is being heated at different rates because of positioning within the heating zone, a situation that has to be addressed before accurate data can be obtained. The mercury release pattern of HgSO$_4$ is also complex, but in this case, it is probable that the multiple peaks are an indication of both the positioning of the sample in the heating zone and mercury release from mercuric sulfate itself as stoichiometric changes occur during the course of its breakdown to mercuric oxide (HgO). Nonetheless, it is essential to ensure that the reason for any complex mercury release pattern observed during the heating of specific compounds is identified before final use of the technique in field trials.

The overlapping of peaks from the analysis of multiple compounds standards may be observed in Figure 128 and Figure 131. These overlapping peaks make it difficult to determine the compound responsible for the presence of mercury at a given temperature. This is a direct result of the heating ramp not being at a sufficiently slow speed to fully separate the HgCl$_2$/HgS and HgO/HgSO$_4$ peaks. Any final heating ramp would need to be designed to rapidly heat the inner tube to 150 °C (as the temperature region 25-150 °C does not correspond with the volatilization of any mercury compounds that are likely to be present in the crushed rock samples), and then to slowly increase in temperature until a final temperature of 550 °C is reached. This proposed heating ramp was not achieved in this project due to the previously mentioned time and instrumental constraints.

4.3.1.1.1 Calibration Standards

Because the masses of calibration standards and samples will always differ, it is necessary to calculate data based on CPS per microgram of mercury. An example of this calculation is given in Table 23. In addition, there appeared to be differences in the CPS for equivalent
masses of mercury released from different compounds. Consequently the CPS per milligram of mercury was calculated for each mercury compound. The CPS corresponding to the major peak height was used to approximate the concentration of mercury in that compound. The $^{202}\text{Hg}$ CPS response for each compound was divided by the mass of material to create a CPS/compound mass ratio (Table 23). The concentrations of mercury compounds are calculated in section 4.3.1.2 on the basis of this procedure.

**Table 23.** The CPS response for $^{202}\text{Hg}$ during the measurement of the 1 ppm multiple compounds standard. From the mass (5.2 mg) and concentrations of the compounds in the standard it is possible to determine the total mass of each compound. From this a CPS to mass ratio is generated.

<table>
<thead>
<tr>
<th>Compound</th>
<th>CPS</th>
<th>Conc. (ppm)</th>
<th>Mass ($\mu$g)</th>
<th>CPS/$\mu$g</th>
</tr>
</thead>
<tbody>
<tr>
<td>HgCl$_2$</td>
<td>4698</td>
<td>1.192</td>
<td>6.20E-03</td>
<td>7.58E+5</td>
</tr>
<tr>
<td>HgS</td>
<td>4068</td>
<td>0.999</td>
<td>5.19E-03</td>
<td>7.83E+5</td>
</tr>
<tr>
<td>HgO</td>
<td>3630</td>
<td>1.038</td>
<td>5.40E-03</td>
<td>6.72E+5</td>
</tr>
<tr>
<td>HgSO$_4$</td>
<td>6161</td>
<td>1.003</td>
<td>5.22E-03</td>
<td>1.18E+6</td>
</tr>
</tbody>
</table>

### 4.3.1.2 Rock Samples

Only the samples which were analysed using the Beta Prototype and the heat ramp described in Figure 124 are discussed in this section. The ten samples investigated in this most recent analytical run consisted of crushed rock samples from the Homestake deposit (see section 2.1.2.1.1 for sample information). These samples were analysed following the analysis of the multiple compounds standard. The CPS/compound mass ratio is applied to the $^{202}\text{Hg}$ CPS response of compounds identified within the samples to ascertain the mass of the compound that has been volatilized from the sample (Table 24). The mass of the compound within the sample is compared to the sample mass to determine the concentration (in parts per billion) of the compounds in the sample (Table 24.). The height of the peaks which were clearly observed above the background was used for the concentration calculations detailed in this table.
Table 24. The calculated concentrations (in parts per billion) of mercury compounds in the ten crushed rock samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Compound Concentration (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HgCl₂</td>
</tr>
<tr>
<td>14B3</td>
<td>1.76</td>
</tr>
<tr>
<td>4546WB1</td>
<td>2.71</td>
</tr>
<tr>
<td>56B1</td>
<td>1.37</td>
</tr>
<tr>
<td>56B2</td>
<td>0.27</td>
</tr>
<tr>
<td>568EC3</td>
<td>2.41</td>
</tr>
<tr>
<td>596E1</td>
<td>3.71</td>
</tr>
<tr>
<td>597B1</td>
<td>4.01</td>
</tr>
<tr>
<td>N17B4</td>
<td>0.96</td>
</tr>
<tr>
<td>N17B5</td>
<td>0.52</td>
</tr>
<tr>
<td>N8A3</td>
<td>3.50</td>
</tr>
</tbody>
</table>

It should be noted that the calculation of the mercury compound concentrations (Table 24) is not an accurate representation of the actual concentration of that specific compound within the sample. It has been previously discussed that as the peaks in the multiple compounds standard and samples overlap, this overlap will artificially increase the mercury isotope CPS response for the compounds which overlap and give incorrect compound concentrations. Therefore, it is not currently possible to accurately ascertain the single compound CPS response using the current heating ramp. Additionally, the sample was crushed but may not have all of the mercury compounds contained within the rock available for volatilization (a percentage of the compounds are still trapped within the rock material). It should also be recognised that the $^{202}$Hg isotope is the most abundant natural isotope of Hg (29.8%), but the relative ratio to other isotopes may change as a result of fractionation. It should be reinforced that the peak height of the $^{202}$Hg CPS response for the compounds in the sample is used as an approximation of concentration. Therefore, the final calculated compound concentration should be used only as an indication.
As discussed previously in section 1.3.1, gold transportation is dominated by sulfide and chloride ligands. The Hg$^{2+}$ cation is a moderately soft Lewis Acid which is able to be transported by both sulfide and chloride ligands (Parr and Pearson, 1983). When mercury is precipitated within a depositional environment some of the mercury may be reduced to Hg$^0$ if the oxidation potential of the fluid is favourable, or possibly some mercury may be volatilized from a compound and recondense as the native element, however, thus far mercury in the elemental state has not been observed in any of the rock samples from the Homestake deposit. This may be attributed to the oxidation potential of the fluids being unfavourable for the formation of Hg$^0$ or may be attributed to mercury having been volatilized during sample preparation and crushing. One other aspect should be considered in that crushing and grinding of rocks is performed in an aerobic environment and the high temperatures involved may facilitate the oxidation of any native mercury present to the oxide. This may be the reason that some samples do appear to have oxide mercury present. These possibilities are theoretical only and will have to be checked in detail in any future study. A significant portion of the mercury within a gold depositional environment will not be reduced and will form compounds with mercury being in the +2 oxidation state. Since Hg$^{2+}$ is complexed with either sulfides or chlorides, it is these anions which are most likely to bind with the mercury cation and form a compound. Therefore, it is unsurprising that HgS and HgCl$_2$ are the dominant mercury compounds observed in rock samples (Table 24).

The calculation of the concentrations of HgS and HgCl$_2$ in rock samples demonstrates that these compounds occur at extremely low levels (<10 ppb) in the Homestake deposit (Table 24) and will not be visible to the naked eye as discrete mineral phases. Additionally mercuric chloride is extremely unlikely to occur as a discrete mineral phase anyway and would more likely be co-entrained within bulk host rock matrices as an adsorbed species.
The mineral cinnabar (HgS) may be formed under epithermal conditions, however, as the Homestake deposit is a mesothermal system, the formation of cinnabar is unlikely and has not been documented in the history of the deposit. Their presence as chemical species within the deposit is still unlikely to be confirmed using conventional microscopy.

The detection of HgO in the rock samples (Table 24) corresponded with two samples from Main Ledge and a sample from 21 Ledge. All of these samples are at a significant depth within the deposit and it is unlikely that these samples would experience supergene oxidation. Therefore, the presence of HgO does not imply the supergene oxidation of elemental mercury for the Homestake deposit, but is most likely the result of oxidation of elemental mercury during and after sample collection and preparation.

The presence of HgSO₄ in some of the samples is likely to be the product of the oxidation of mercury sulfide after deposition. Similar to HgO, the oxidising conditions required for HgSO₄ to form in a hydrothermal environment are not conducive for the transportation of gold. Therefore, HgSO₄ is likely to be the product of the oxidation of HgS or other sulfide minerals with significant mercury concentrations as contaminants in the mineral. There is also the possibility that the observed HgSO₄ is the product of supergene oxidation of sulfide materials. HgS has been observed in all samples analysed and it is possible that this may be the reactant which has experienced oxidation after deposition. The presence of HgSO₄ is attributed to samples from a wide variety of formational depths below sea level; implying that it was associated with a number of lithologies which have not experienced the same degree of supergene oxidation. Therefore, it is unlikely that the HgSO₄ is formed from supergene oxidation of HgS material. The lack of apparent relationship between the presence of HgSO₄ and depth further indicates the likelihood of later oxidation of HgS material, possibly during sampling or crushing.
Samples 56B1 and 56B2 are two sections of rock collected from the ore facings within a few metres of each other in 19 Ledge. These samples have the same lithology and the same relative abundance of sulfides and quartz veins. It is evident from the comparison of the relative concentrations of mercury compounds (Table 24) and the $^{202}\text{Hg}$ CPS response over time (volatilization profile) (Figure 132) that these two samples are significantly different from each other. This may imply that the differences in the mercury compound abundances may be influenced by slight mineralogical differences between the samples. This would further imply that the lithology of the sample has a significant impact on the availability and the relative abundances of these mercury compounds. From this observation it is evident that the samples require a greater investigation into their precursor mineralogy prior to analysis, which may help to develop an understanding of which mineral species are more liable to release mercury compounds. It must be remembered that this is the first time that this type of data has been seen and interpretation attempted. Consequently, it must be stressed that a significant amount more work must be undertaken before all relevant parameters can be investigated to a sufficient level to make interpretation of mercury compound data a logical and robust procedure.

Due to the small database of samples investigated thus far in this thesis, it is not possible to interpret the relevance of the concentrations of the compounds within the samples, and while it could potentially be assumed that the concentrations of the samples detailed in Table 24 are approximately reproducible, it still can be implied with a high degree of certainty that the identification of mercury compounds may be achievable with relatively minor modification of the current instrumentation and methodology. However, careful observation of the peak position and potential overlap must be accounted for in any additional analyses. The overlap of the compound peaks will reduce the accuracy of the compound concentrations. Thus, it is recommended that further development is
undertaken on creating a more reproducible and suitable heating ramp before further detailed studies are undertaken.

Figure 132. The CPS data of the $^{202}\text{Hg}$ isotope for samples 56B1 and 56B2. It should be noted that the heating is stopped after the inner tube reaches 500 °C which coincides with a rapid drop in $^{202}\text{Hg}$ being detected with the ICP-MS at 475 seconds.

The sum of the mercury compounds within the rock samples is approximately a few parts per billion for most of the samples (Table 24). The solution ICP-MS analysis of arsenopyrite demonstrated that the concentration of Hg in arsenopyrite is between 0.5-7 ppm (section 3.2.4 and Appendix E-1.7). The measured concentrations of mercury compounds in rocks, as determined from the volatilization device, are a few orders of magnitude lower than the concentration of mercury contained within arsenopyrite. This could imply that the discrepancy in concentrations may be attributed to the fact that the arsenopyrite is not being broken down during the heating ramp and that a higher temperature is needed to achieve this. Furthermore, the crushed rock samples contain a number of other secondary minerals. Overall, these effects will significantly reduce the
amount of mercury which may be volatilized and subsequently detected using the combined thermal release and ICP-MS measurement technique and will require further investigation prior to establishment of a final analytical protocol for the technique.

The interrelationship between the concentrations of HgS and HgCl$_2$ may be indicative of the localized fluid chemistry. This, in turn, may have applications generating a greater understanding of the fluid chemistry and this interrelationship may be used for exploration purposes. At this stage, analyses have not been repeated with the most recent heating ramp; and as such, it is difficult to assess the reproducibility of the concentrations.

### 4.3.2 Isotope Analysis

Calculation of the relative mercury isotope ratios was performed after the volatilization profile peaks had been identified and the concentration of the volatilized compounds recorded (section 4.3.1). The regions corresponding to the detection of a single mercury compound (an unobstructed peak) were identified and ratios were generated for every full cycle of data acquisition (0.922 seconds). The median of these ratios was used to provide the isotopic ratios of the compounds in both the standards and rock samples. Not all of the possible isotope ratios have been included in this investigation, as some of the ratios were imprecise when low CPS responses for individual isotope masses were recorded.

The isotopic compositions of the single mercury compound standards were initially determined in order to identify any potential interference effects that may arise due to the overlap of compound peaks in the multiple compounds standard. The isotope ratios of the single compound standards were observed in order to cross reference the calculated values to values for the equivalent ratios obtained from the natural abundances of the isotopes and to then be able to relate any changes that may be apparent in compounds...
volatilized from geological samples to actual differences rather than to apparent differences imposed on the isotope ratios by the volatilization process. The isotope ratios calculated over the course of the investigation of the HgCl$_2$ single compound standard, for example, are detailed in Figure 133. As expected, an increase in the precision of the isotope ratios can be observed between 70 and 300 seconds, a time frame corresponding to the volatilization of HgCl$_2$ and consequently to the time at which most mercury was being volatilized.

![Figure 133](image.png)

**Figure 133.** The mercury isotope ratios measured from the volatilization of the HgCl$_2$ 1 ppm single compound standard. The dash black line represents the $^{202}$Hg CPS response during the analytical run (secondary vertical axis).

The mercury isotope ratios of the other single compound standards were determined and investigated in the same manner as those for the ratios present in HgCl$_2$ (Figure 133). The median isotope ratios of the volatilization peaks, corresponding to each of the single
compound standards, are summarized in Table 25. It may be observed from this table that
the single compounds appear to have similar isotopic ratios to the other compounds
investigated and also to the natural isotopic abundances of mercury. This is further
reinforced by the low relative standard deviation percentage of all of the non-$^{196}$Hg isotope
ratios. The comparatively higher relative standard deviation for the $^{196}$Hg ratios arises
from their lower natural abundance which means that the signal to noise ratio for $^{196}$Hg is
much lower and is more susceptible to random instrument errors. It must be emphasised
that the number of significant figures used in this table for the isotope ratios generated in
this study are purely mathematical and for comparative purposes only; as it is recognised
that the precision of the data generated using a quadrupole based system is probably at
best ±0.2 to ±0.5% relative (Kuisma-Kursula, 2000) and will reflect variations in the third
decimal place only. Isotope ratios have been calculated without calculating and correcting
for mass bias as at this stage of the method development study only precision of the
method is being tested and with the limited number of samples analysed there really is
nothing to be gained in determining mass bias effects and correcting for them.

The multiple compounds standard has significant overlap of the individual mercury
compound peaks making it difficult to determine what influence overlapping may have
on the isotopic ratios of each compound (Figure 134). The data in Figure 134 demonstrate
that during the volatilization of the compounds (150-400 seconds) the isotope ratio
precision stabilizes which is similar to the equivalent situation in the single compound
standards (Figure 133), and is the point at which the most mercury is being released.
Significant, care was taken to ensure that the data used to generate the median isotopic
ratios for the compound have the least possible interferences from overlapping
compounds. However, it is impossible, with the current methodology, to completely
remove the effect of overlapping compounds.
Table 25. The median mercury isotope ratios measured over the half-peak width of the volatilization profile of the 1 ppm single compound standards.

<table>
<thead>
<tr>
<th>Isotopic Ratio</th>
<th>Compound</th>
<th>Natural Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HgCl₂</td>
<td>HgS</td>
</tr>
<tr>
<td>196/198</td>
<td>0.0159</td>
<td>0.0160</td>
</tr>
<tr>
<td>196/202</td>
<td>0.0053</td>
<td>0.0054</td>
</tr>
<tr>
<td>196/204</td>
<td>0.0231</td>
<td>0.0237</td>
</tr>
<tr>
<td>198/202</td>
<td>0.3444</td>
<td>0.3325</td>
</tr>
<tr>
<td>198/204</td>
<td>1.4703</td>
<td>1.4597</td>
</tr>
<tr>
<td>199/202</td>
<td>0.5591</td>
<td>0.5588</td>
</tr>
<tr>
<td>199/204</td>
<td>2.4611</td>
<td>2.4525</td>
</tr>
<tr>
<td>200/202</td>
<td>0.7673</td>
<td>0.7710</td>
</tr>
<tr>
<td>201/202</td>
<td>0.4411</td>
<td>0.4420</td>
</tr>
<tr>
<td>202/204</td>
<td>4.4060</td>
<td>4.3970</td>
</tr>
</tbody>
</table>

The median isotopic ratios of the crushed rock samples previously investigated in section 4.3.1.2, which mostly corresponds to the volatilization peaks of HgCl₂ and HgS, were investigated (Appendix E-1.8). Similar to the investigation of single and multiple compound standards (Figure 133 and Figure 134), the isotope ratios of the samples had low precision because of the extremely low concentrations of the mercury compounds in these samples and the difficulties in identifying and determining exact peak potions (Figure 135).
Figure 134. The mercury isotope ratios measured from the volatilization of the multiple compounds standard, MC STD A. The dashed black line represents the CPS of the $^{202}$Hg isotope measured during the analytical run (secondary vertical axis).

Figure 135. The CPS response of the mercury isotopes during the volatilization and subsequent ICP-MS analysis of sample N17B5. The dotted red line represents the temperature of the sample tube during the heating procedure (secondary vertical axis).
When the data from the isotopic ratios of the rock samples were calculated it was observed that the isotope ratios between samples collected from the same location within the Homestake deposit (for example 56B1 and 56B2) have significantly different ratios for both HgS and HgCl$_2$ (Appendix E-1.8). As stated previously, time constraints associated with this project have meant that the investigation of the samples presented in this chapter have not been replicated using the same heating conditions. It must also be remembered that this investigation was very much a secondary aim of the research detailed in this thesis and as such was undertaken predominantly for interest, and if it showed potential, for future development and investigation only. Therefore, there is uncertainty of the extent to which instrument set-up and tuning for each analytical run will have on the various isotopic ratios and this must be investigated in any future study before any significant claims with respect to isotope ratio variations can be made. Additionally, the concentration of mercury isotopes measured in rock samples are close to the detection limits of the current instrumentation which also negatively impacts on precision. Nevertheless, there is still a significant possibility that the samples have a different mercury isotopic composition and if this were the case then there is the possibility that these differences could be used as guides to potentially mineralized areas. However, at this stage, it is not possible to determine if there is significant mercury isotope fractionation within the Homestake gold deposit.

4.4 Conclusion

It has been demonstrated in section 4.3.1 that the thermal volatilization of mercury compounds gives rise to a CPS profile that is unique for each specific compound investigated in this thesis. The peaks produced from the volatilization of mercury from a multiple compounds standard, while having a significant degree of overlap, are nonetheless distinguishable from each other. Volatilization profiles that correspond to
standard release curves for HgCl$_2$ and HgS have also been identified in crushed rock samples. By measuring the CPS peak height of each compound from the multiple compounds standard, it is possible to create a mechanism for measuring the concentration of compounds within rock samples. Overall, the approximate concentration of the individual mercury compounds may be calculated for rock samples. At this stage, the concentration and distribution of mercury compounds in the samples cannot be related to the sample location within a deposit.

Furthermore, it has been demonstrated in section 4.3.2 that the isotope ratios of the mercury compounds may be measured in standards and samples. The various standard compounds appear to display relatively similar isotopic ratios to each other despite different tuning conditions. The rock samples display a significant variation in mercury isotopic ratios and samples from the same location also appear to have significantly different isotopic assemblages which are not at this stage able to be accurately reproduced. Therefore, it is not possible, at this stage, to identify any geological phenomena which may be related to the isotopic fractionation of mercury in the Homestake deposit.

While it is evident that the current instrumentation and methodology are not sufficiently precise to accurately determine the isotopic ratios of mercury compounds in rock samples, a proof of concept has nevertheless been achieved with both the identification of mercury compounds and their concentration being proven possible. In addition, mercury isotopic ratios may be calculated using data from the volatilization peaks, albeit at this stage with inadequate precision. Ultimately, once both the heating apparatus and its coupling to a multi-collector ICP-MS has been undertaken, this technique will be able to be used as part of a more comprehensive gold exploration protocol.
5.0 CONCLUSION

The aim of the mercury isotope investigation was to achieve a proof of concept for a technique that could provide the basis for an identification of mercury compounds and the generation of quantitative data with respect to the accurate determination of mercury isotope ratios in these compounds that were volatilized from rock samples during a programmed heating run. While this aim was achieved, there was unfortunately insufficient time available for a detailed study to develop the technique further to the point of augmenting the main focus of this thesis; the arsenopyrite-based research. However, the initial research indicated that it was possible to identify mercury compounds present within orebodies, but did not have sufficient precision, using a quadrupole based ICP-MS, to identify mercury isotope haloes. Nonetheless the technique showed considerable promise and should be the subject of future investigations.

The primary aim of this thesis was to develop a methodology for using the trace element distribution patterns in arsenopyrite samples, collected from individual prospect licences, as a potential tool to discover buried and blind gold deposits. This aim was to be achieved by identifying the trace element assemblages in arsenopyrite using Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS). This technique provided high spatial resolution, fast, multi-element analysis of solid sub-millimetre sized samples. These features are essential if a prototype exploration protocol were to be developed and used for the commercial geochemical exploration of gold deposits.

On the basis of the identification and interpretation of trace element data for arsenopyrite, five specific objectives were addressed. These objectives are detailed in section 1.6.1 as:

1. Identifying the resource type
2. Identify the gold deposit type
3. Identify the gold deposit camp

4. Estimate the endowment of a gold deposit

5. Determining variations in the arsenopyrite chemistry within a deposit

A total of 626 individual arsenopyrite samples from 59 gold and 20 non-gold ore deposits were investigated using LA-ICP-MS. By establishing the relative changes in the trace element assemblages within arsenopyrite samples from different geological environments it was possible to identify specific trace element inter-relationships which could be directly correlated with geological parameters, present during the formation of the arsenopyrite crystal and the deposition of the orebody. This study has concluded that it is possible to identify specific geochemical signatures in arsenopyrite which indicate the presence (or otherwise) of gold mineralization. Those geochemical signatures which indicate the presence of gold mineralization can also be used to assist in establishing the proximity of that sample to a gold orebody. It is believed that with further development the protocols detailed in this thesis can lead to significant new innovations in the field of geochemical exploration for gold deposits.

The elements in arsenopyrite which were investigated in this study are those which have a high propensity to replace the lattice forming elements of arsenopyrite; these are the chalcophilic and siderophilic elements. Despite evidence for siderophilic elements replacing iron in the arsenopyrite lattice, it was determined that the counts per second (CPS) data for iron did not change by a significant extent in any of the crystals analysed, largely because there was so much iron in arsenopyrite that any elemental replacement affected the total iron concentration by an insignificant amount. Therefore, it was possible to use the CPS data of iron to normalize the CPS data for all other elements in arsenopyrite. The use of iron CPS data as an internal standard facilitates the application
of the technology internationally and allows inter-comparison of data between laboratories worldwide.

By comparing the relative iron-normalized CPS data of the arsenopyrite samples from the 59 gold deposits investigated in this project, it was possible to differentiate these samples on the basis of their age of formation. In addition, within the Yilgarn it was possible to differentiate samples at the province and camp scale. This study concludes that the trace element differences between samples from different provinces in the Yilgarn (thousands of kilometres distant) are readily apparent, as are the differences between camps (tens to hundreds of kilometres distant). The differences between these trace element assemblages are the result of the differences in the depositional environment between the provinces and camps. These depositional environment differences include: lithology, depth of formation, the hydrothermal fluid source, chemical fugacity, fluid mixing, and the hydrothermal fluid pathways.

The lithology at the site of a gold deposit was demonstrated to have an observable affect on the trace element chemistry of arsenopyrite formed within these deposits. Usually the elements which are present in significant concentrations within host rocks are enhanced in the arsenopyrite crystals and are observable as relatively higher CPS data. This is most likely the result of these elements being leached from the rocks during the interaction of the rocks with the hydrothermal fluid responsible for the precipitation of gold and arsenopyrite. While it could be argued that the differences between the arsenopyrite from the deposits formed at different ages may simply be the product of the different lithologies in which mineral deposition occurred, it has been demonstrated that this aspect does not override the chemical differences caused by variations in the original fluid source which is related to the age of formation. This is most strongly emphasised with reference to the
differences between the chemistries of arsenopyrite from Proterozoic and Archean BIF deposits. It was also observed that within a deposit the trace element assemblages of arsenopyrite were different depending on the nearby local lithology (within a metre of the arsenopyrite crystal). These variations of arsenopyrite chemistry within a deposit were shown to be similar to those observed between the BIF and greenstone deposits, i.e. arsenopyrite formed in dolerite (a greenstone) had a suite of elements that could be used to differentiate it from arsenopyrite formed in a BIF.

Of deposits with the same lithology, it was observed that the depth of deposit formation had an observable impact on the trace element assemblages of the arsenopyrite samples formed from 16 deposits within the Norseman-Wiluna greenstone belt, Yilgarn Craton, Western Australia. The depth of deposit formation influenced the pressure and temperature of the deposit during formation, and as such this significantly influenced the solubility of various elements in the hydrothermal solution, and impacted on the amount of lattice strain experienced by the arsenopyrite crystal.

Arsenopyrite which has been formed in close association with gold mineralization and is present in gold orebodies is useful as an indicator of the potential endowment of a deposit. It was determined that arsenopyrite from 4 giant, 16 intermediate, and 9 small Archean gold deposits were easily differentiated on the basis of the trace element chemistry of the associated arsenopyrite. The discovery and exploitation of giant and supergiant gold deposits is mostly the focus of senior mining companies and as such it is important to correctly identify these large deposits in greenfields exploration regimes, as early false negative results may lead to the abandonment of the tenement. Additionally, it is important to identify less well endowed deposits early in exploration initiatives to minimise wasted expenditures on exploration of lower endowment deposits.
Over 100 arsenopyrite samples were collected from multiple locations at the Homestake, Mount Porter, and Boorara deposits and from the investigation of the trace element assemblages in the arsenopyrite from these deposits it was clearly observed that the trace element assemblages change regularly throughout the deposit. This is the result of the physicochemical evolution of the hydrothermal fluid as it travels away from the primary conduit and disseminates into the country rock and through structural features. The evolution of this hydrothermal fluid may be better understood and used in greenfields or brownfields exploration by detailed investigation of arsenopyrite trace element assemblages. By observing the relative CPS ratios of a number of elements and plotting the positioning of these samples in three dimensions it is possible to identify where fluid conduits and regions of greater gold concentration may be located this information may be used to increase the lifetime and profitability of the deposit.

The trace element chemistry of arsenopyrite formed during gold mineralization is very likely to be significantly different from the chemistry of other arsenopyrites which are formed by different geological processes. Therefore, it is unsurprising that arsenopyrites formed in gold and non-gold depositional environments are easily differentiated from each other. If an arsenopyrite crystal is collected from an exploration licence where hydrothermal activity is indicated, it is possible to identify whether the arsenopyrite is associated with gold or non-gold mineralization. If non-gold mineralization is indicated it is also possible to determine the specific ore-forming elements associated with that deposit.

The primary application of variations in arsenopyrite trace element chemistry is to better identify and discover buried and blind gold deposits, especially those which cannot be economically discovered with current technologies. When arsenopyrite crystals are
collected and analysed the data are initially used to determine if they contain a chemical signature for a gold or non-gold deposit. If it is determined that gold mineralization is present, it may then be necessary for a more in-depth collection and analysis regime to be undertaken to facilitate the possibility of vectoring towards feeder conduits for the mineralization and areas that potentially contain higher gold grades. Once this has been achieved it would then be possible to establish a drilling program to outline the deposit and collect and analyse additional samples from drill core, thus allowing a three dimensional resource distribution map to be constructed. After an orebody has been intersected by drilling, then any arsenopyrite samples formed within this region may be investigated to determine the endowment of the gold deposit, assisting in resource estimation and mine site development.

The significant reduction in economically profitable near-surface orebodies means that in future there will have to be a greater reliance on the discovery of geochemically blind mineral occurrences. An exploration protocol based on the geochemistry of arsenopyrite can address this issue. It is believed that a detailed knowledge of the trace element assemblages and their inter-relationships within arsenopyrite crystals collected during exploration initiatives will expedite the discovery of buried and blind orogenic gold orebodies and considerably assist in their development to profitable mine sites.
6.0 RECOMMENDATIONS

While this study has confirmed that it is possible to use arsenopyrite trace element chemistry as a geochemical exploration tool, a significantly greater cross section of arsenopyrite samples, associated with and unrelated to mineralizing events, should be analysed to provide a better indication of the reproducibility of data within a deposit. In this way it will be possible to more accurately determine the validity of inter-element association patterns and the consequent relationship between arsenopyrite trace element chemistry and geological phenomena.

It is essential that more samples are taken from individual deposits and that these samples are investigated in greater detail. The resulting data will enable a better understanding of the changes in arsenopyrite chemistry within a deposit to be quantified. After this more in-depth investigation, it should be possible to use the more robust inter-relationships between arsenopyrite trace element chemistry and position of samples within a depositional environment as an industry-ready exploration tool to discover gold deposits in greenfields terranes and to better develop brownfields discoveries.

Careful micro-sampling and subsequent acid digestion of arsenopyrite samples should be implemented to provide accurate concentrations of major and trace element in the arsenopyrite matrix. The data from such an experiment will be able to be used to assist in developing cross-calibration curves which relate the iron-normalized CPS data for a particular element to the actual concentration of that element in arsenopyrite. In this way the technique will have more universal application as the data will be based on absolute values rather than simply CPS values which may vary under different instrument setup regimes.
The CPS responses of many elements initially investigated during the method development phase of this research were below the detection limits of the LA-ICP-MS instrumentation used. However, instrumentation is continually being updated and subsequent versions of ICP-MS equipment will invariably be able to determine element concentrations at significantly lower concentrations than currently achievable. Consequently, a watching brief should be maintained on new generations of equipment to ensure that the most relevant is used for analyte determination and simply because an analyte is too dilute to be of significant use now does not mean that it cannot be used in the future.

The statistical techniques used in this thesis were simple ones which required no data processing or smoothing. These simple techniques were used to effectively demonstrate the relationships between groups without significant user bias. A greater range of statistical techniques should be investigated to determine whether other techniques than those applied in this thesis would be appropriate for the identification of better trend definition and interpretation of analytical data. Such additional techniques could be univariate analysis of variance (ANOVA) and multivariate analysis of variance (MANOVA), both of which are able to demonstrate the effect of the analytes on the discrimination of the samples.

Arsenopyrite typically coexists and co-precipitates with pyrite, pyrrhotite, and several other secondary mineral species depending on mineralization style and type. Therefore, for example, it is possible that the differences in trace element chemistry of pyrite and pyrrhotite may be used to determine geological phenomena both on their own and in association with data from the analysis of arsenopyrite. In addition, it may be possible to inter-compare the trace element chemistry of a wide range of minerals, including even
gangue minerals, that are present in deposits to better elucidate elemental interrelationships between mineral species and use these to produce more robust inter-mineral analyte association protocols that can be used to determine the presence or absence of mineralization in an area.

The trace elemental assemblages of arsenopyrite, and possibly other minerals (such as pyrite, chalcopyrite, galena, magnetite, and sphalerite), may be used as an indicator of other hydrothermal metal deposits, more specifically base metal deposits. The protocols developed in the current study could be used for other minerals in base metal deposits to establish if these are useful for indication of mineralized areas and deposits other than gold.

For the purposes of assessing the chemical homogeneity of a mineral and to determine the evolution of a crystal over the period of gold mineralization, arsenopyrite crystals may be investigated using scanning LA-ICP-MS protocols. In addition, it is possible to chemically etch arsenopyrite crystals to better display crystal boundaries and growth patterns. When chemical etching is used in conjunction with scanning LA-ICP-MS then it should be possible to investigate the evolution of the hydrothermal fluid over the course of the mineralization event.

It was briefly discussed in section 3.4.4.2 that the trace element chemistry of arsenopyrite from four deposits indicated that these deposits had a greater gold endowment than was indicated based upon the current assessment of their ore reserves. This observation may be the result of the current state of the geological investigation of these deposits, and as such it is recommended that these deposits (Boorara, Great Fingall, Ora Banda, and
Yilgarn Star) are investigated in detail to ascertain if there are hitherto undiscovered orebodies within the overall mineralization system.

It is recommended that the determination of mercury isotope ratios from multiple mercury compounds be investigated further as time constraints and limited detailed technical development led to the project being curtailed without determining if the isotope ratios of mercury compounds fractionate within a deposit. If the mercury isotope ratios fractionate within and between each of these compounds within a deposit and if this phenomenon is logical, chemically and physically controlled and able to be quantified, then it may be possible to develop exploration protocols relying on variations in the relative distribution of mercury isotopes.

The heating ramp of the mercury volatilization system needs to be modified in order to better separate the mercury compound volatilization profiles. It is recommended that heating of the system is performed in a stepwise manner; the system is heated at an appropriate, but fast rate, to a set temperature and remains at that temperature for a period of time, then the temperature is appropriately increased again and allowed to remain at this temperature for a period of time. This may allow the sequential and complete volatilization of each compound without any interference from other compounds.

The isotope analysis of rock samples demonstrates a large degree of variation between data for samples from the same location. This is more often than not due to the low concentration of mercury compounds in these samples. It is evident that the quadrupole-based mass spectrometer is not able to provide precise data for isotope ratios when the isotopes are present at low concentration. Therefore, the use of a high resolution-multi-
collector ICP-MS should be investigated as in theory it would be ideal in terms of higher sensitivity and significantly improved analytical precision.

It is necessary to construct a redesigned volatilization device which has a much greater sample turnover rate and has significantly reduced thermal lag. This may be achieved by having two heating devices (cells) connected in parallel to the ICP-MS, when one cell is cooling down after an analytical run; the other is connected in-line to the ICP-MS. In addition, each of these heating cells is designed in such a manner as to have minimal thermal lag and a top which is attached to a hinge to allow easy access to the quartz sample tube which will facilitate fast air cooling of the cell.

An investigation needs to be undertaken to produce more reproducible mercury compound standards at low concentration. These standards are at present produced by solid mixing, which is not reproducible at high dilution. Consequently, a method that will allow significantly improved homogenization to be achieved, such as the incorporation and mixing of mercury salts in solution and their subsequent precipitation once mixed, should be investigated. It may also be possible to produce the relevant mercury compound by chemical reaction in the slurry (for example by the reaction of sodium sulfide with mercuric chloride to produce mercuric sulfide). In this way more accurate and homogenous production of standards containing extremely low levels of mercury compounds may be achieved.

The crystal lattice changes associated with the heating of individual mercury compounds should be investigated to determine if changes in crystalline structure are associated with the release of mercury vapour. This may help to better understand the shape of the mercury release curves associated with the volatilization of HgCl₂ and HgSO₄. Any
variation in systematic release of mercury vapour during a heating event could potentially then be related to crystal lattice rearrangement or mercury compound changes associated with new stoichiometric or compound formation could be identified using a dedicated temperature-controlled X-Ray diffraction system (similar to a hot-wire ginear XRD system).

The release of elemental mercury (Hg\textsuperscript{0}) from rocks may be investigated by crushing the samples in a specially designed ring mill which allows the contents of the ring mill to be continuously purged during the grinding process. The expelled gas could either be passed though a silver wool trap, which will capture any elemental mercury for subsequent bulk volatilization, or continuously passed into the ICP-MS. In the former case, following grinding, the wool could then be introduced into an in-line heating device connected to an ICP-MS and heated to release the mercury vapour. In the latter case a continuous release trace for mercury vapour from rocks could be recorded. In both cases, using a multicollector ICP-MS, the isotopic composition of this mercury vapour may also be determined to see if variations occurred throughout the deposit and if these variations could be used to vector exploration to the conduits through which the ore fluids originally flowed.
7.0 REFERENCES


MAY, C. & WATLING, R. J. 2009. A comparison of the use of refractive index (RI) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) for the provenance establishment of glass bottles. *Forensic science, medicine and pathology*, 5, 66-76.


MURPHY, M. 2009. Trace Element Assemblages in Arsenopyrite as an Indicator of Gold Mineralization. Honours, University of Western Australia.


STEWART, J. I. 2009. RE: Personal Communication. Type to MURPHY, M.

STEWART, J. I. 2013. RE: Personal Communication. Type to MURPHY, M.

STEWART, J. I. & WATLING, R. J. 2009. RE: Personal Communication. Type to MURPHY, M.


A-0 APPENDICIES
A-1 Deposit Information
A-1.1 Gold Deposits
   A-1.1.1 Homestake

A. Location of the Homestake deposit within the Black Hills region, South Dakota, USA (Stewart, 2013).
B. The location of the Homestake deposit with respect to the gravity data (greyscale) and magnetic data (red) (Stewart, 2013).
C. The highly deformed Homestake Formation (Stewart, 2013).

D. The view north of the open-cut pit of the Homestake deposit (Stewart, 2013).
E. Arsenopyrite from high grade ore locations within Main Ledge, 15 Ledge, and 19 Ledge from the Homestake deposit. (1) Medium to coarse grained (1-5 mm). (2) Arsenopyrite representing concomitant growth and merging of crystals. (3) Minor arsenopyrite in chlorite-quartz gangue and bands of sulfidic black shale. (4) Coarse (~12 mm) arsenopyrite in BIF. (5) Stressed and reoriented arsenopyrite wrapping around and encapsulated by very coarse garnet. (6) Underground ore face dominated by stratiform pyrrhotite a laminated quartz vein and white, coarse euhedral of arsenopyrite. (7) Ore face showing a thick deformed quartz vein and copious fringing arsenopyrite. (8) Garnet sideroplesite-cummingtonite-chlorite-arsenopyrite ore. (9) An intricate and dismembered band of arsenopyrite with at least 4 grain sizes. (10) Fine, medium, and coarse arsenopyrite in a gangue of chlorite (Stewart, 2013).
A. Longitudinal section of the Mount Porter historic and modern drilling (Stewart, 2013).
A. A diagram of the generalized ore zone stratigraphy of the Boorara deposit (Stewart, 2013).
**A-2 Instrumentation**

**A-2.1 Average Operating Conditions**

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