

The petrography and geochemistry of pyrite-hosted
orogenic gold deposits in the Grampian Terrane of
north-west Ireland and Scotland

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Declaration of authorship

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James Phillip Stratford

“Vision is the art of seeing things invisible”

Jonathan Swift (1667-1745)

Abstract

The Neoproterozoic-Cambrian Dalradian Supergroup of north-west Ireland and central Scotland accommodates vein-hosted gold deposits associated with uplift and deformation during the Ordovician Grampian arc-continent collision event (475-460 Ma) of the Palaeozoic Caledonian Orogenic Cycle (475-405 Ma). The Grampian Terrane hosting these strata was subjected to regional greenschist to amphibolite facies metamorphic conditions which enabled protracted Au and trace element mobility, and the generation of auriferous vein networks. This thesis has sought to discover the extent of this mobility across the orogen and the preservation of Au signatures, feasible sources of Au in north-west Ireland, and the relationship between Au emplacement, deformation and metamorphism associated with orogenesis. Gold occurrences are examined from the deposit to regional-scale.

Reflected light microscopy, Scanning Electron Microscopy (SEM), Energy-Dispersive X-Ray Spectroscopy (EDS/EDX) and Laser Ablation Inductively Coupled Plasma – Mass Spectroscopy (LA ICP-MS) analyses are conducted on vein and wall-rock samples from four vein-hosted Au deposits and occurrences (Curraghinalt and Cavanacaw, Sperrins Inlier; Cloonacool, Ox Mountains Central Inlier; Cononish, SW Scotland) along with samples from potential source stratigraphy within the Appin Group (Blair Atholl Subgroup, north Donegal) and Argyll Group (Easdale Subgroup, Slieve League Peninsula of west Donegal).

LA ICP-MS analyses of pyrite (spot analyses, n=530; raster element mapping) and pyrrhotite (spot analyses, n=50) have revealed that Au and trace elements were mobile throughout the evolution of the Grampian orogen, from the earliest stages of deformation-fabric development to relatively late timing associated with orogenic collapse, and that the Blair Atholl Subgroup (Appin Group) and Easdale Subgroup (Argyll Group) present viable sources of Au and associated metals. Mobility was facilitated by dehydration reactions at the greenschist-amphibolite facies transition, during collision of the incumbent arc with the Laurentian margin. At the largest deposit on the island of Ireland, Curraghinalt, Au is not genetically associated with the growth of pyrite and is derived from an external source, likely related to dehydration of the Laurentian margin and fluid mixing. Episodic rupture caused by decompression and seismic pumping is likely to have facilitated the injection of fluids into pathways (structural weaknesses), with phase separation mechanisms (including fluctuations in fO_2 and pH) and fluid-rock interactions aiding the localised precipitation of sulphide and Au. Implications for exploration vectoring are included in this thesis.

Chapter summary

This study has focused on elucidating the evolution of orogenic deposits and prospects in north-west Ireland through examination of sulphide phases, principally pyrite, using high-precision microanalytical techniques, while also considering the wider regional context through a comparison with data acquired from the Cononish deposit in Scotland. Work is initially constrained within the most developed deposit, Curraghinalt, in the Sperrin Mountains of County Tyrone, Northern Ireland, before widening the scope of the study to the regional scale.

Chapter One introduces the background to the study and research questions, while *Chapter Two* provides information on specific objectives and research parameters. *Chapter Three*, a review of the literature, gives an overview of the characteristics which define the orogenic class of gold deposits, specifically focusing on the unifying factors of plate tectonics, metamorphism and gold mobility. This introduction also summarises the exploration history of the trend for gold: the economic context to this thesis. *Chapter Four* principally concerns microanalytical techniques selected to determine the trace element geochemistry of sulphide minerals, a central tenet to this study (e.g. Scanning Electron Microscopy and Laser Ablation Inductively Coupled Plasma - Mass Spectroscopy or LA ICP-MS); results are presented of a ‘proof of concept’ study which tests the hypothesis of trace element zonation within a sample of regional pyrite from Dalradian stratigraphy close to Lochranza on the Isle of Arran, Scotland.

Chapter Five presents the results of a deposit-scale study focused entirely on the largest known orogeny-associated gold deposit within the terrane, Curraghinalt in County Tyrone, Northern Ireland, stratigraphically constrained within the Sperrin Mountains Inlier of the Dalradian Supergroup. A revised chemically-supported paragenesis of the deposit is presented, results providing insight into the mobility of metals and emplacement in the context of the local and regional deformation history. *Chapter Six* considers implementation

of geochemical methods and system dynamics in a greenfields exploration context at Cloonacool, County Sligo, within the Ox Mountains Central Inlier. In *Chapter Seven*, findings are presented of a regional study focused on a potential source of gold in north-west Ireland, testing the hypothesis that carbonaceous shale units within Appin and Argyll Group stratigraphy of the Dalradian Supergroup were a sink for gold and associated trace elements. Analyses of Au-associated pyrite from the Cononish deposit hosted by contiguous stratigraphy in Scotland and a limited dataset from the Cavanacaw deposit in the Sperrin Mountains are presented in *Chapter Eight* to examine regional variations, extending the picture to the scale of the emerging belt. *Chapter Nine* asks what the implications of findings may be for gold exploration, while *Chapter Ten* seeks to resolve research questions in the context of deposit and regional-scale mechanisms. A summary of principle conclusions is provided in *Chapter Eleven*.

This thesis provides new information on the genesis of vein-hosted gold deposits in the region and builds on diligent work pursued by numerous authors with an interest in orogenic systems and Irish and Scottish vein-hosted gold over several decades. Deposit- and regional- scale geochemical interpretations provided may prove useful for prospectors with an interest in the region, and in comparable orogenic terranes.

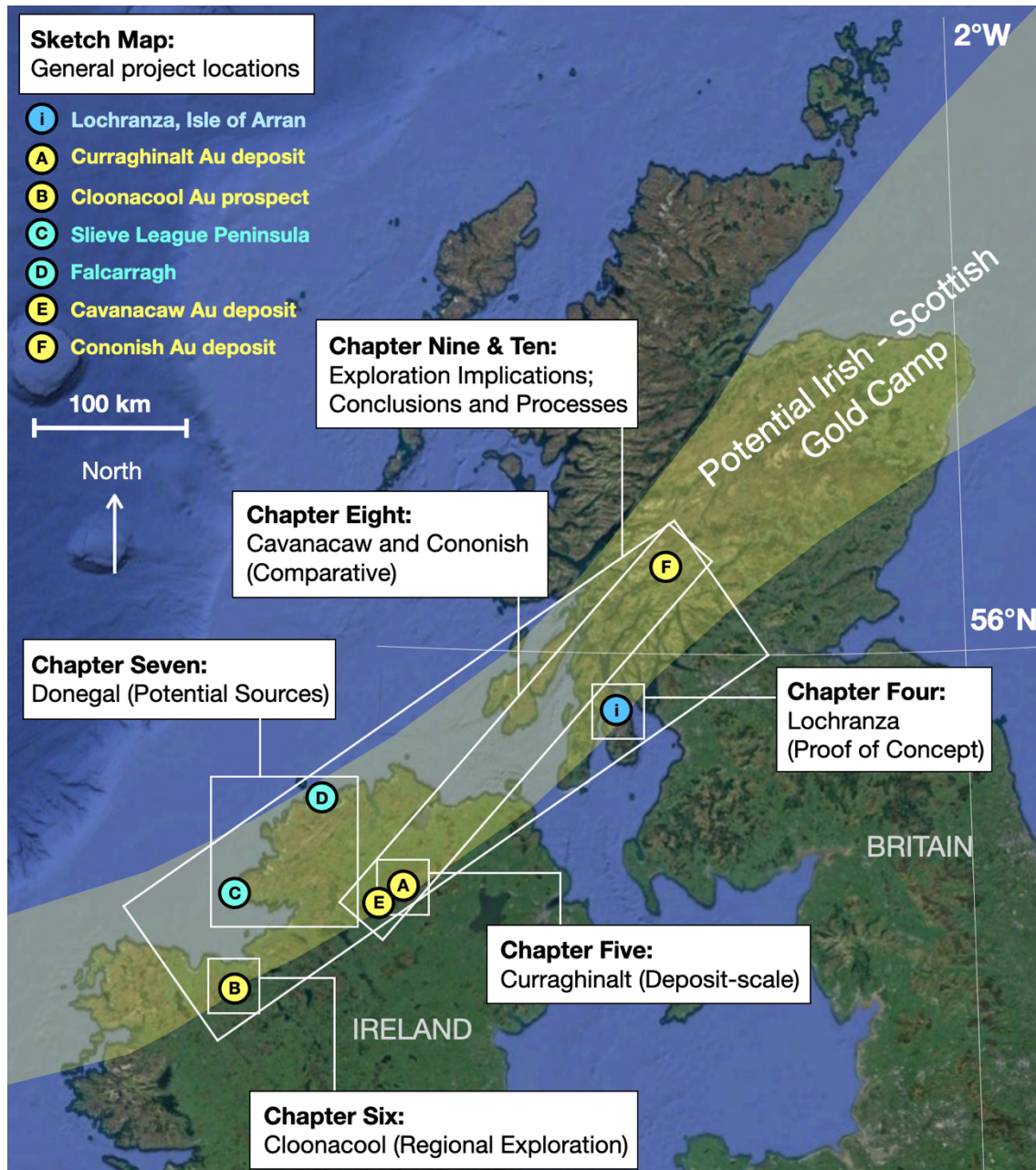


Figure i. Geographic reference map showing localities of interest to this thesis and scales covered within chapters. Base map: Landsat / Copernicus (Google Earth imagery). The area designated as 'Potential Irish-Scottish Gold Camp' is for illustrative purposes only, and serves to broadly indicate the region within which vein-hosted gold occurrences have been discovered and exploration is active.

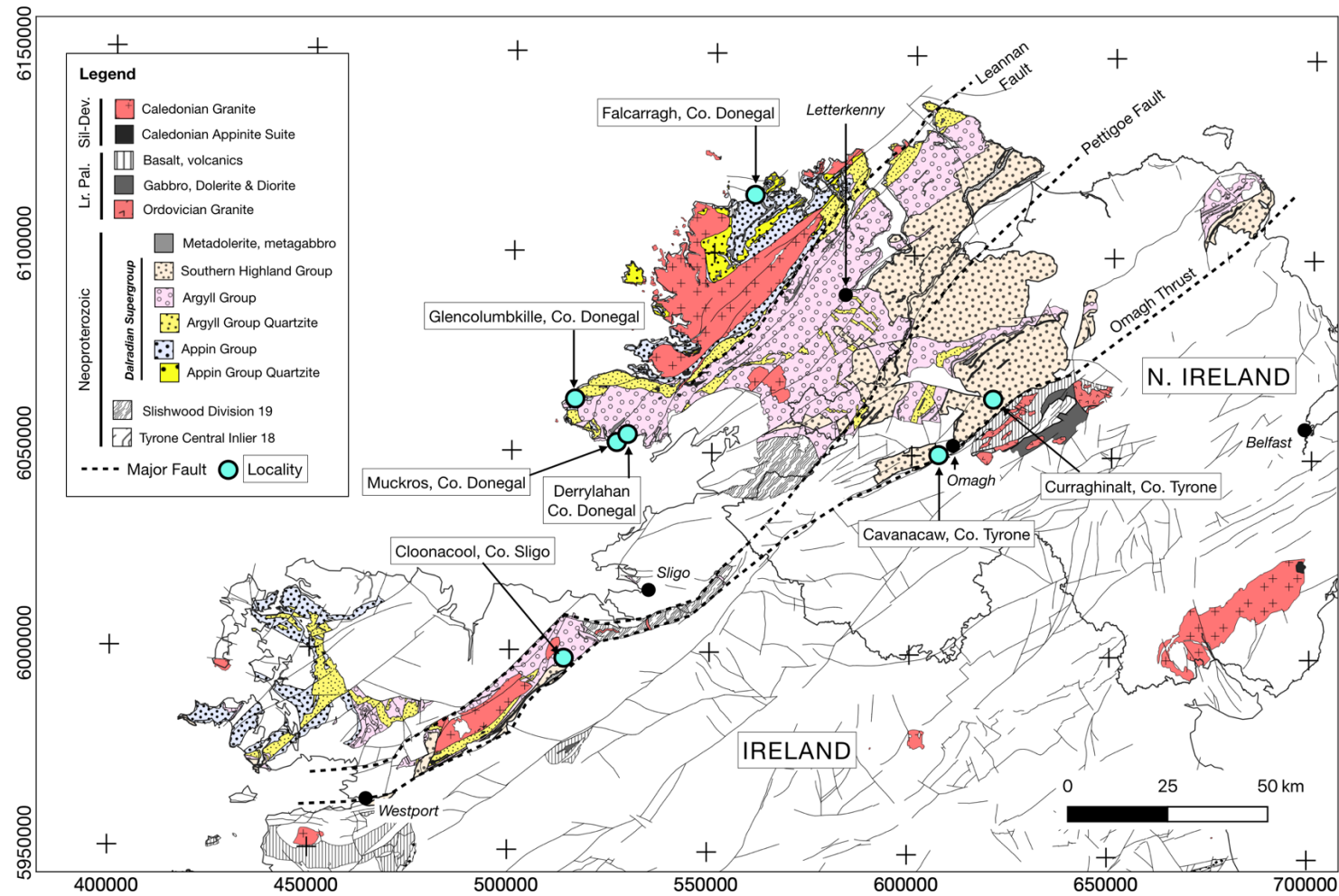


Figure ii. Geological map showing localities of interest to this thesis in north-west Ireland. Co-ordinates are in metres (WGS 84; Zone 29N); relevant geological units and faults are based on the GSI 1:500,000 Bedrock Map of Ireland, with locations of major structures based on Chew et al (2005) and Hutton and Alsop (1996).

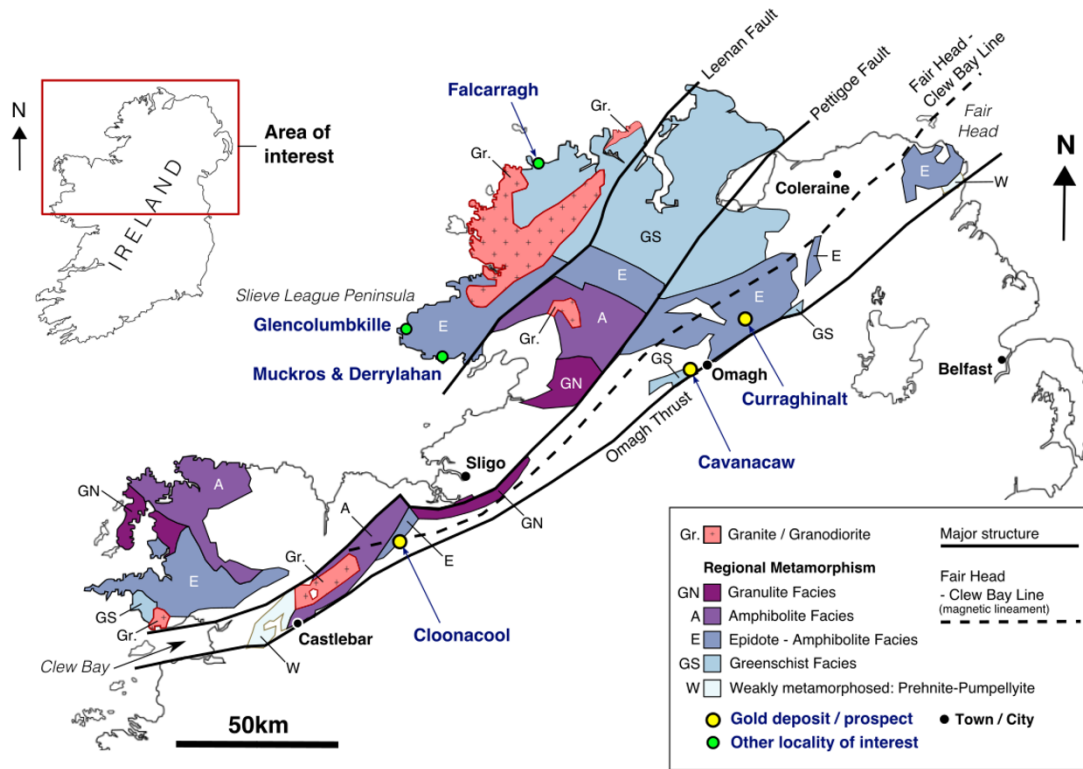


Figure iii. The spatial distribution of regional metamorphic facies in north-west Ireland (north-west of the Omagh Thrust), and the positions of significant granite and granodiorite bodies. Deposits and prospects examined in this thesis, along with other localities of interest in this study are identified, with selected population centres shown as a reference. Major structures of relevance to this study are included in the map, including the position of the Fair Head – Clew Bay Line (FH-CBL) which continues north-east into Scotland as the Highland Boundary Fault (HBF). This schematic interpretation is based on the ‘Compilation Caledonian metamorphic map of Ireland’ by Long et al. (1983) and regional structural information from Chew et al. (2009b). Boundaries and fault positions are approximated; regional metamorphic conditions of stratigraphy on proximal islands are excluded from this map.

Funding and policy context

This study is co-funded by Science Foundation Ireland (SFI) under research grant number 13/RC/2092, the European Regional Development Fund, and industry partners (see *‘Project Contributors’*). The Irish Centre for Research in Applied Geosciences (iCRAG) is an SFI research centre which includes geoscience researchers from universities and institutes across Ireland: Trinity College Dublin (TCD), University College Dublin (UCD), University College Cork (UCC), National University of Ireland (NUI) Galway, the Dublin Institute for Advanced Studies (DIAS), NUI Maynooth and Dublin City University (DCU), along with partner government agencies Teagasc (the Agriculture and Food Development Authority) and Geological Survey Ireland (GSI). The Centre seeks geoscientific solutions to defined ‘challenges’ in the Irish and global environment and economy through targeted research, and to inform society of findings through outreach events and educational programmes. These challenges, informed by societal needs, public policy and the United Nations Sustainable Development Goals (UN SDGs), are seven categories of research which include the ‘supply of raw materials’, ‘safeguarding the geomarine environment’, ‘securing and protecting groundwater resources’, ‘energy security’, ‘protection from Earth’s hazards’, ‘public perception and understanding’ and ‘enabling methodologies’. This study is a constituent project of the first of these, a component of which is a focus on the diversification of the Irish minerals sector and the provision of advanced models for the development of new projects.

This petrographic and geochemical study seeks to enhance our understanding of the prospectivity of Dalradian Supergroup strata for vein-hosted gold deposits. Improved models of deposit evolution and metal emplacement in the context of regional and localised deformation may have the effect of de-risking exploration activities and stimulating growth in the exploration sector.

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Glossary of common abbreviations

ARIS	Aerosol Rapid Introduction System
BC-	Cloonacool sample prefix
BCR-2G	Basalt Glass Mounted Reference Material (USGS)
B-SEM	Backscattered Scanning Electron Microscope/Microscopy
CMA	Centre for Microscopy and Analysis
Cp	Chalcopyrite
CT-	Curraghinalt sample prefix
CS-	Cononish sample prefix
CW-	Cavanacaw sample prefix
DCCAE	Department of Climate Change Action and the Environment (prior to 2020)
DECC	Department of Environment, Climate and Communications (2020-)
DR-	Derrylahan sample prefix
ECE	Energy Critical Element
EDS/EDX	Energy Dispersive X-ray Spectroscopy
EMD	Exploration and Mining Division
FC-	Falcarragh sample prefix
FE-SEM	Field Emission Scanning Electron Microscope
FH-CBL	Fair Head - Clew Bay Line
GC-	Glencolumbkille sample prefix
GGF	Great Glen Fault
GSI	Geological Survey Ireland
GSNI	Geological Survey of Northern Ireland
HBF	Highland Boundary Fault
iCRAG	The Irish Centre for Research in Applied Geosciences
IP	Induced Polarisation (geophysical survey)

LA ICP-MS	Laser Ablation Inductively Coupled Plasma - Mass Spectrometry
LOD	Limit Of Detection
Ltd.	Limited Liability Company
MASS-1	Synthetic Polymetal Sulphide Pressed Powder Reference Material (USGS)
MK-	Muckros sample prefix
NI	Northern Ireland
Ni 43-101	National Instrument, Standards of Disclosure for Mineral Projects, Canada
NIST	National Institute of Standards and Technology (US) (Reference Materials)
PDAC	Prospectors' and Developers' Association of Canada
p.l.c.	Public Limited Company
Po	Pyrrhotite
Py _(n)	Pyrite generation
RL	Reflected light
SEG	Society of Economic Geologists
SEM	Scanning Electron Microscope/Microscopy
SFI	Science Foundation Ireland
SGA	Society for Geology Applied to Mineral Deposits
SGD	Sustainable Development Goal (United Nations)
SIMS	Secondary Ion Mass Spectrometer/Spectrometry
TCD	Trinity College Dublin
TIC	Tyrone Igneous Complex
TL	Transmitted Light
UCD	University College Dublin
UQAC	University of Québec at Chicoutimi (Canada)
USGS	United States Geological Survey
VMS	Volcanogenic Massive Sulphide

Chapter One: Introduction

This thesis concerns three central questions:

(i) what is the extent of gold mobility and associated trace elements within the Grampian orogeny in Ireland and Scotland ?

(to include - to what extent are orogenic Au signatures preserved in pyrite?)

(ii) what is the source of gold in north-west Ireland?

(to include - is pyrite a source of gold?)

and (iii) what is the relationship between gold emplacement, deformation and metamorphism?

This project has two additional foci which may prove of interest to stakeholders: augmented understanding of orogenic mineralising systems in a region of active contemporary economic interest, and the acquisition of pathfinder element signatures which may assist in exploration of the emerging gold camp in the Irish-Scottish Caledonides.

Recent international studies (e.g. Steadman and Large, 2016; Steadman et al, 2015; Li et al, 2014; Danyushevsky et al, 2010; Thomas et al, 2011, Large et al, 2009) demonstrate

the potential of advancing techniques in the field of spectroscopy (e.g. Laser Ablation Inductively Coupled Plasma – Mass Spectroscopy or *LA ICP-MS*) to extract qualitative and quantitative trace element data which can be used to characterise and discriminate phases of pyrite, within orogenic gold deposits and across regional trends. Such an approach has not been extensively deployed at the deposit- or regional- scale in north-west Ireland or Scotland to date, where deposits of vein-hosted gold have been discovered which may broadly fit the accepted definition of the *orogenic* class of ore deposits (Rice et al., 2016), an overview of which is provided in *Section 3.2*. Using trace element geochemistry supported by well-constrained petrography, this study seeks to answer the above research questions, and provide practicable insights for exploration.

The temporal and tectonic context to this study is the initial deformational phase of the Caledonian Orogenic Cycle (475-405 Ma), an arc-continent collisional event (and significant mountain-building episode) known as the *Grampian Orogeny* (or ‘Grampian Event’; 475-460 Ma) (Chew et al., 2009b), described in *Section 3.3.i*. Prior to this collision, Ireland and Britain were fragmented and in a vastly different spatial configuration to the present-day. The areas now recognisable as the north-west regions of Ireland and Britain formed part of the coastal margin of the ancient continent of Laurentia which includes the present-day east of North America, while the south-west of Ireland and Britain resided across the Iapetus Ocean as constituents of the micro-continent of Avalonia. A volcanic island arc in the Iapetus, which collided with the Laurentian margin during the Grampian Orogeny is represented in Irish geology by the Tyrone Volcanic Group (TVG) in the north of Ireland and the Lough Nafooe Group in the west.

As geologists, we must transit liberally between several scientific fields in both the *physical* and *chemical* domains, through the lens of *geological time*; the manner in which the topics covered by this treatise have been examined hold steadfast to this approach; in one respect this thesis concerns a series of crustal-scale tectonic and deformational events which took

place over 400 million years ago in the mid-Palaeozoic: it seeks to reveal trace element signatures indicative of metal mobility throughout phases of Grampian deformation, and is in this sense an historical work, retrieving and presenting this geochemical archive. With regards to the genesis of these systems however, research is pursued principally with a view to deriving physical and chemical processes. In order to understand potential source reservoirs, the movement of fluids through the structural weaknesses that are present both through and between rock formations, and the manner in which metals are concentrated as mineral deposits requires acute consideration and explanations. While scientific experimentation and study parameters are restricted to samples constrained by specific geological events, this study is not solely building on the foundation of acquired knowledge from the available rock record representing the evolution of any one deposit or formation through geological time. Fortunately for those with an interest in orogenic gold, this deposit class exhibits a wide temporal and spatial distribution from the Archean to present day, with comparable system characteristics (Goldfarb et al., 2001). This presents an opportunity to contextualise and interpret results with the perspective of broader research of this deposit class. This includes work in ancient orogens and terranes enduring active collisional tectonics.

Chapter Two: Objectives and research parameters

2.1. Overview

In order to realise the aims set out in afore-stated research questions, it was necessary to establish a series of constrained and achievable objectives. This process was undertaken early during the course of this research, and the following five were instituted:

- (i) the elucidation of trace-element signatures within well-defined and tested sulphide paragenetic sequences, for orogeny-associated vein-hosted deposits in north-west Ireland and access permitting, stratigraphically contiguous formations in central Scotland;
- (ii) constraints on the source and relative timing of vein-hosted orogenic Au with respect to deformation events;
- (iii) resolution of local and regional deposit relationships;

- (iv) clarification of element mobility within hydrothermal fluids across metamorphic gradients associated with the orogeny, to include assessments of the role of metamorphism on regional gold emplacement;
- (v) presentation of practical geochemical vectors for mineral exploration if attainable.

2.2. Scale and an integrated approach

A central consideration in the design of this project, in terms of its scope, was that of *scale*. It was realised at an early stage that conducting microanalytical research at the scale of individual grains of pyrite, with the ambition of determining deposit- to regional- scale, useful, scientifically rigorous findings, presents an inherent dilemma. Would findings from microscopic studies be applicable at the desired scales? Would the results from individual deposits be representative of trends in orogeny-associated vein-hosted systems across the Irish-Scottish Dalradian Supergroup? Groves et al. (2003) also reflected on such issues; observing that many contemporary studies in orogenic systems research had a tendency to present the results of advanced analytical experiments restricted to the micro-scale, with extrapolated interpretations having in their view, limited applicability at the regional scale in terms of understanding processes or benefits to exploration. They recommended an integrated approach, making use of structural and field-based methods before more sophisticated techniques are invoked, and amalgamation of deposit- and province- scale research. Their stated preference is for single teams with continuity of knowledge to present integrated findings. Some of their requests lie outside the parameters of this study, however, concerns raised have served as useful reference points in formulating the review of available literature and the approach taken to sampling and the design of micro-analytical work, e.g.

reinforcing the need for petrographic constraints. Additional recommendations made by Groves et al. (2003) include research into background concentrations of gold at the regional scale, determination of the processes by which gold is mobilised during hydrothermal events (including overprinting and remobilisation), improved dating and the development of robust four-dimensional models, augmented constraints on the source of carrier fluids across metamorphic belts, and the development of tools which may allow the overlay of integrated chemical, geological and geophysical datasets onto palaeocontinent-scale reconstructions.

Such ideas proposed by Groves et al. (2003) assist in addressing concerns raised by Moritz (2000), who observe a lack of consensus with regards to ore genesis in orogenic systems which they ascribe to over-simplification and super-imposition of broad genetic models onto complex deformation zones; it is noted that economic geologists have a tendency to hypothesise deep origins for deposits where high-temperature metamorphism is recorded, or in the case of models for vein-hosted deposits generally, inferring a relationship to proximal intrusions where this may not be geologically supported. Such considerations are also taken into account in this study.

2.3. Terminology

The classification of *orogenic gold deposits*, given their wide spatial and temporal distribution, is a departure from historical provincial terminology (e.g. ‘Homestake-type’) which had focused the attention of researchers on existing, well-defined existing deposit- or province-scale models and how subject localities compared or contrasted (Groves et al., 1998). In recognising a commonality in mineral and fluid characteristics, most importantly that metamorphism and plate tectonics are the driving forces behind the formation of systems, the orogenic model allows for localised variations (e.g. the involvement of

magmatism) and precludes the need to dwell on local idiosyncrasies with regards to their overall classification.

2.4. Parameters

It was considered in the development of study parameters to accept the recommendations of previous workers including Groves et al. (2003) and Moritz (2000) where appropriate to resolving research questions; the following protocols were implemented:

- (i) at individual deposits, sampling would be as representative as access allowed, this would include samples of sulphide-bearing veins, vein- wall-rock interfaces, and wall-rock samples deemed to be barren;
- (ii) that research would be conducted in the full context of previously conducted work on localised and regional structure, along with petrographic and geophysical studies where available;
- (iii) that the scope of this study would extend beyond that of a single deposit to include regional prospects, access-permitting;
- (iv) that initial geochemical test-work would be conducted on samples of distal regional pyrite to establish optimal working parameters;
- (v) that reconnaissance in the field would include as wide an area as feasible at an early stage to establish stratigraphic and spatial parameters to the study;

and (vi) that geochemical analyses on target grains would be conducted (preferably) once petrographic constraints had been established.

It was determined, based on review of concerns in the research community in tackling ore systems in active and ancient orogens, that the design of this study required integration of previous work at the deposit- and regional- scale, and that work ought to be targeted rather than systematic, cognisant of ensuring robust petrographic support before proceeding to advanced micro-analytical stages. This study would not seek conformity with existing models or classes, recognising the breadth and scope provided in the orogenic model of deposits forming in accumulated terranes in collisional deformation zones. The term '*orogeny-associated*' is used routinely throughout this thesis, where appropriate, to avoid the suggestion that systems within this province conform exactly to those discovered in distal orogenic terranes (e.g. the American Cordillera, the West African Birimian, or the Otago province of New Zealand).

Chapter Three: Literature review and exploration context

3.1. Gold chemical and mineralogical characteristics

Gold, named by the Anglo-Saxons and with the element abbreviation ‘Au’ from the Latin ‘*aurum*’, has an atomic number of 79 and is a member of Group IB of the periodic table system. While considered a transition metal, gold exhibits unique electronic properties. Gold has an atomic mass of 196.967 u, a specific gravity of 19.32 (at 20 °C), a melting point of 1,064.18 °C and a boiling point of 2,836°C (Boyle, 1979; Royal Society of Chemistry, 2020a). The nucleus of a gold atom comprises 79 protons and 118 neutrons, with 79 electrons occupying available electron shells (Boyle, 1979). Its only stable isotope, ^{197}Au , is known as a ‘Mössbauer nucleus’, permitting the resonance absorption of gamma rays, and is estimated to have a half-life of 3×10^{16} years; additional artificial radioisotopes are known with half-lives < 185 days (Strominger et al, 1958 in Boyle, 1979) including ^{198}Au , which has a half-life of 2.695 days (Royal Society of Chemistry, 2020a). Gold is yellow in colour and is a highly malleable metal. It is considered the most ‘noble’ metal due to its high resistance to corrosion, making it a valuable material in art and jewellery (Schmidbaur et al., 2005). Its high electrical and thermal conductivity make it a metal of key interest to the electronics industry. Colloids or nano-particles of gold are of interest to those engaged in technological

endeavours applicable to a variety of fields: e.g. in the control of pollution, processing of chemicals, fuel cells (Corti et al., 2002) and developing medical applications such as cancer imaging, therapy and drug delivery (Cai et al., 2008).

The average abundance of gold in the Earth's crust is 0.004 ppm (4 parts per billion) (Greenwood and Earnshaw, 2012) while in sea-water, estimates of gold concentration vary from 1 – 4,000 ppt (parts per trillion) (Yannopoulos, 2012). In schists, of interest to this study, gold has a mean natural abundance of 18.6 ppb (0.0186 ppm) (based on 1,969 samples in a study by Boyle, 1979); for amphibolites and greenstones this falls to 7.1 ppb (0.0071 ppm; n=425) (Boyle, 1979). Gold abundances are also provided by Boyle (1979) for a population of shale, mudstone, siltstone and argillite (avg., 8 ppb or 0.008 ppm; n=1,356) and of sulphidic-schist, pyritic greywacke, pyritic black shale and pyritic tuff which show a mean Au abundance two orders of magnitude higher, albeit for a limited dataset (avg., 132 ppb or 0.132 ppm; n=19). Mineralogically, gold is found in nature principally as native gold (Figure 3.1), or within tellurides (Boyle, 1979). Native gold forms as parallel groups of



Figure 3.1. A specimen of native gold (Lavinsky, 2020; no scale provided).

octahedra, dodecahedra and cubes [111], commonly forming reticulated aggregates and dendritic assemblages (Anthony et al., 2015; Webmineral, 2012). It has a molecular weight of 196.97 grams, a hardness of 2.5-3 (it can be scratched with a finger-nail), and a density of $16 - 19.3 \text{ g/cm}^3$. It has a hackly, arborescent, spongy or platy habit, may form rounded nuggets or flakes, and has a characteristic metallic lustre. Gold is non-magnetic and non-fluorescent. Optically it may appear yellow (pure), orange, yellow-white, or a reddish-white (impure). Gold purity is often expressed (e.g. in mineralogy, the metallurgy of gold bullion) in terms of fineness in parts per thousand (e.g. 820 ‰): impure native gold typically contains a proportion of Ag, Cu and Fe, along with minor trace elements. Examples of auriferous telluride minerals include pure gold telluride (calaverite, AuTe_2) and gold-silver telluride (e.g. petzite, Ag_3AuTe_2) (Boyle, 1979).

Gold exhibits a range of oxidation states (I to VII); the principle states of chemically-bound gold in fluids which occur in nature are trivalent, as auric gold (Au^{III}), or monovalent as aurous gold (Au^{I}) (Pokrovski et al., 2014). Aurous gold (Au^{I}) is the dominant oxidation state in hydrothermal fluids and silicate melts, while Au^{III} is only stable in oxidising surface environments. The most important carriers of gold in hydrothermal fluids with elevated temperatures, explored in this study, are hydroxide (OH^-), chloride (Cl^-) and hydrogen sulphide (HS^-) complexes.

3.2. Orogenic gold deposits

3.2.i. Characteristics and classification

Orogenic gold deposits are a constrained class of quartz-carbonate vein-hosted ('lode') gold system, along with associated placers (Goldfarb et al., 2001; Groves et al., 2003), which have a wide temporal and spatial distribution. Deposits in this class are thought to account for

over one billion ounces of gold in terms of produced and estimated ounces worldwide and are hence significant in terms of global resources. Goldfarb et al. (2001) identify key characteristics which distinguish them from other classes such as epithermal deposits, porphyries and volcanogenic massive sulphide deposits (VMS). They are hosted by deformed, variably metamorphosed host rocks, often at greenschist facies, generally exhibiting low sulphide volumes, carbonate-sulphide $\pm$ sericite $\pm$ chlorite alteration, are transported by low salinity, CO₂-rich ore fluids with $\delta^{18}\text{O}$ values of 5-10 ‰ and have a spatial association with large-scale compressional or transpressional structures. Orogenic gold deposits accumulate in deformed crustal blocks, proximal to major tectonic boundaries and structures. Most in the 'orogenic' class are recognised as being post-orogenic with respect to the tectonic deformation of host rocks, however are considered syn-orogenic in relation to deep-crustal thermal processes relating to subduction (Groves et al., 1998). They tend to comprise abundant quartz-carbonate veins, and form at upper to mid-crustal pressures (1-5 kbar) and temperatures (200-500 °C). Orogenic gold deposits may be sub-classified by formation depth: as epizonal (<6km), mesozonal (6-12km) or hypozonal (>12km) (Figure 3.2); in epizonal systems Au tends to have an association with Sb, for mesozonal deposits a Au-As-Te signature is common, while at hypozonal formation depths, Au is most commonly related to abundances of As (Goldfarb et al., 2001; Groves et al., 1998). The term 'orogenic gold deposits' itself was first proposed by Groves et al. (1998), and derived from a recognition that a clear grouping of deposits have a unifying association with tectonic processes at a range of depths. Many of these had been classed previously as 'mesothermal', a term which was judged to be inappropriate in its use with respect to its original definition and a source of confusion for the researcher or prospector (Groves et al., 1998). The term 'mesothermal', as defined by Waldemar Lindgren in 1933 (Moritz, 2000), was applicable specifically to vein-hosted deposits formed at depths of between 1.2 and 3.6 km. The use of the term had subsequently expanded to include deposits beyond this range in a variety of

formation depths, and was determined by Groves et al (1998) as being more appropriately applied to either Carlin-type deposits or skarns. Their superseding designation, ‘orogenic gold deposits’, was conceived as an attempt to alleviate confusion by providing a straightforward acknowledgement of the formation of gold deposits as a constituent component of orogenesis, rather than simply defining them by depth (often incorrectly), or over-complicating the issue with a multitude of sub-divisions attributed by district-scale characteristics (Robert et al., 1997).

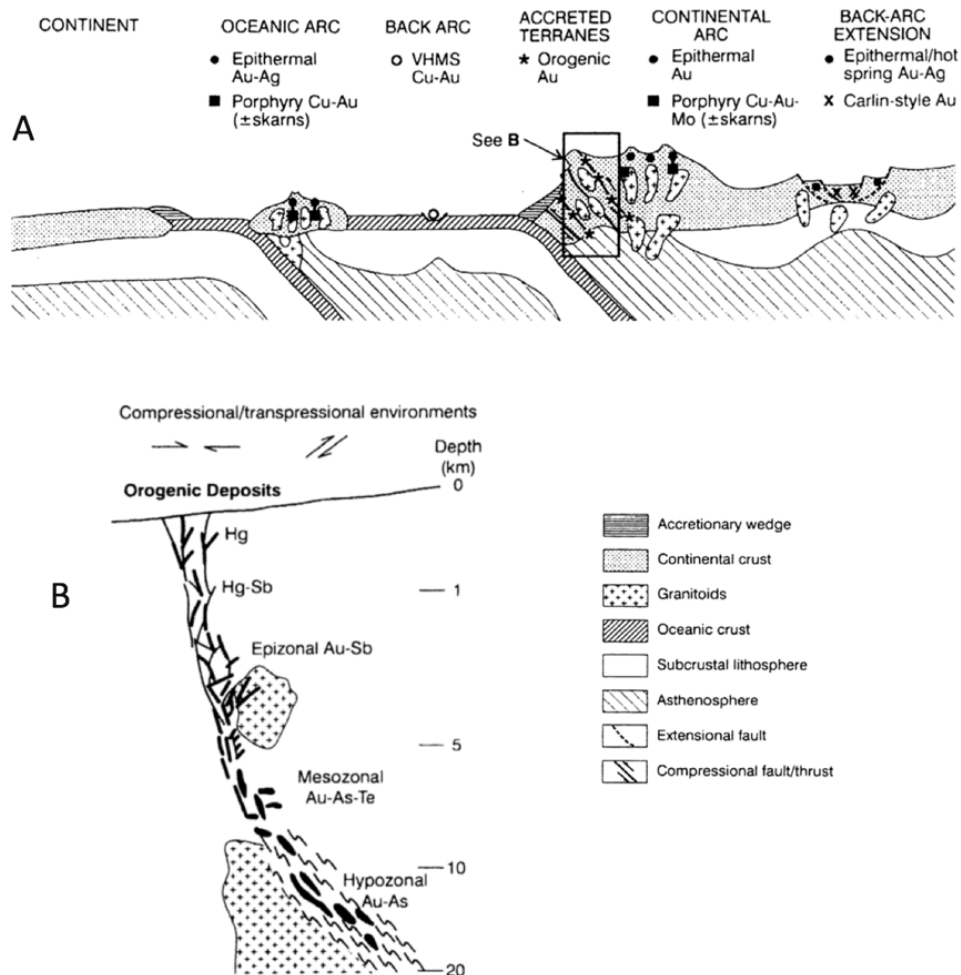


Figure 3.2. (A) Tectonic settings during collisional orogeny, with the position of orogenic Au deposits within accreted terranes indicated; (B) formation depths and typical chemical associations Goldfarb et al. (2001).

Orogenic gold deposits have a wide temporal and spatial distribution and are associated with metamorphic terranes throughout the geological record (Groves et al., 1998). From the Archaean to the Phanerozoic, they have commonly been discovered in greenstone belts (deformed ancient volcano-sedimentary basins), while more recent examples from the Palaeozoic to recent times are found in recognisable accretionary collisional terranes. Type districts from the Archaean include the Birimian Belt in West Africa associated with the Eburnean Orogeny (2,200 – 2,000 Ma) and the Superior Province of Canada (2,690 – 2,630 Ma), while Palaeozoic examples include deposits hosted by the Otago Schists of New Zealand (Jurassic to early Cretaceous) along with the Caledonian-Appalachian belt of interest to this study (Ordovician to early Devonian) (examples of which are presented in Table 3.1).

Province	Vein Age	Metamorphic Events
Kaapvaal Craton, RSA	3200-3604	>3200, 2850
Superior Province, Canada	2720-2670, 2633-2404	2690-2643
Yilgarn Craton, Australia	2750-2685	2690-2660, 2650-2630
Birimian Belt, West Africa	c. 2100	Eburnean Orogeny, 2200 - 2000
Queensland, Australia	408 +/- 30, Late Carb.	Devonian
Otago, New Zealand	Jurassic- Early Cretaceous	Early Jurassic - Early Cretaceous
Shangdong Peninsula, China	Early Cretaceous	Archean (magmatic link)
Russian Far East	135-100	Late Jurassic-Early Cretaceous

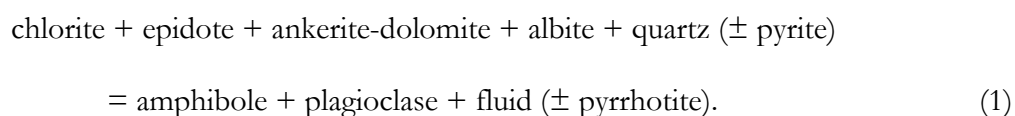
Table 3.1. Examples of orogenic gold provinces indicative of their temporal and spatial distribution (Goldfarb et al., 2017).

3.2.ii. Tectonics, metamorphism and fluids

Metamorphism is an integral component driving the release and mobilisation of fluids during collisional orogeny (Cave et al., 2017; Goldfarb et al., 2001; Groves et al., 1998; Groves et al., 2003; Kerrich and Cassidy, 1994; Phillips and Powell, 2010; Pitcairn et al., 2006). Within the Mesozoic Otago schists of New Zealand, an inverse relationship is observed between trace element concentrations (Au, As, Ag, Hg, Mo, Sb and W) and metamorphic grade; pyrite to pyrrhotite reactions associated with prograde metamorphism are considered responsible for the release of As, Ag, Hg and Sb within those systems (Cave et al., 2017; Pitcairn et al., 2006). Whole-rock geochemical analyses of unmetamorphosed, sub-greenschist, greenschist and amphibolite facies samples (n=60) within the Otago and Alpine schists by Pitcairn et al. (2006) provide evidence of element mobility associated with sulphide recrystallisation and metamorphic conditions. Where pressures and temperatures are interpreted as increasing from unmetamorphosed to sub-greenschist facies conditions, As and Sb concentrations within pyrite also show an increase, attributed to localised element remobilisation (this increase was observed in their study for the range of concentrations, but not the average concentrations for those elements). Pyrite recrystallisation between sub-greenschist and greenschist facies is conversely associated with a decrease in the abundance of Sb, along with Au and Hg. The ‘disappearance’ of sulphide minerals with further prograde metamorphism is considered to be the principal cause of metal depletion at higher metamorphic grades: neither pyrite, nor cobaltite, nor galena, nor sphalerite were observed by Pitcairn et al. (2006) within the garnet zone greenschist or amphibolite facies samples in their study, with remaining sulphide (pyrrhotite and rare chalcopyrite) demonstrably devoid of ore-forming elements. Increasing temperature and pressure, a locally derived metamorphic fluid being present, along with redox reactions between the rock and those fluids are interpreted as likely causes of lowered stability of those elements within sulphide minerals; desulphidation

reactions as described herein of pyrite to pyrrhotite during prograde metamorphism leads to element depletion.

Sulphur availability within aqueous fluids contributes to the mobilisation of Au, Au and Hg in transporting complexes (e.g. bisulphide), which migrate along fractures, foliations, or through high-porosity rock pathways (Pitcairn et al., 2006). Phillips (1993) describes how low-salinity, H₂O-CO₂ fluids are released when rocks transition from chlorite-albite-carbonate assemblages to amphibole-plagioclase assemblages at T > 400 °C (Figure 3.3). These fluids may carry Au complexed with S (also Cl), a typical component to such fluids, and may mix with other fluid types at high crustal levels (e.g. magmatic; fluid mixing has been suggested a likely process by Wilkinson (2001) and Parnell et al. (2000) for the Sperrins deposits in Ireland). The distribution of fluids within the lower crust is dependent on where and when fluids were released as a result of metamorphic reactions (Thompson and Connolly, 1992). Phillips and Powell (2010) describes a model for devolatilisation reactions at the greenschist-amphibolite facies transition for meta-basic rocks, which may be broadly described by the following reaction:



They propose that such reactions may result in the release of a large volume of an aqueous fluid (2-5 wt.%), which carries Au to shallow levels where it may precipitate. The composition of this fluid is H₂O-CO₂; at 440-470 °C, X(CO₂) (the concentration of CO₂, defined as the number of moles of CO₂ divided by the total moles of all gasses within the mixture) will be < 0.1, while at temperatures between 500 and 520 °C, this value increases to 0.2-0.3. The volume of fluid will depend on the proportions of participatory minerals such as chlorite, while the H₂S content depends on the presence of pyrite or other sulphides.

Phillips and Powell (2010) however caution that pelitic sequences will likely involve different fluid compositions compared with mafic rocks considered in their study.

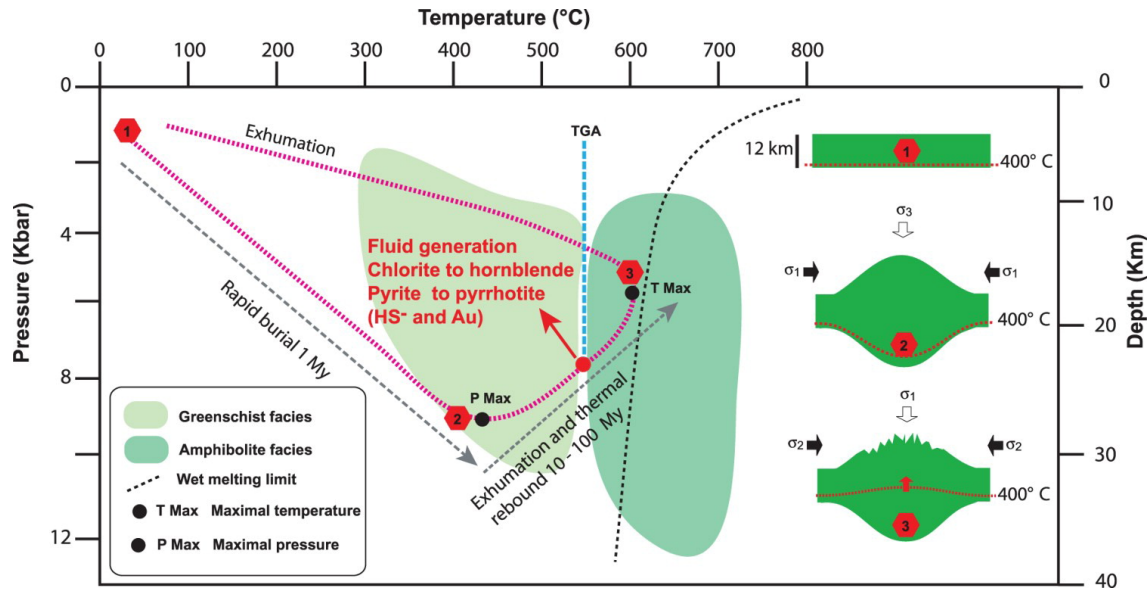


Figure 3.3. P-T-t (pressure-temperature-time) diagram showing an idealised model for the burial and exhumation of seafloor strata and consequent metamorphic fluid generation. Positions 1-3 represent different points in the cycle, from the onset of burial (1) to maximum depths and pressure ($P_{\max}$) (2), before reaching maximum temperature ($T_{\max}$) following the onset of exhumation and thermal rebound (3). Fluid, HS^- and Au are liberated from rocks at the transition from greenschist to amphibolite facies ("TGA") at c. 550 °C. Inset schematics to the right hand side of the diagram demonstrate tectonic stress fields applicable to each step (1-3) and the relative position of a 400 °C thermal gradient: at position 3, the stress field σ_1 becomes the principle constraint during exhumation, initiating the process of fluid and volatile release. Diagram and model by Gaboury (2019).

Recent research in the Southern Alps of New Zealand (Cave et al., 2017; Pitcairn et al., 2014; Pitcairn et al., 2010; Pitcairn et al., 2006; Upton and Craw, 2014; Wannamaker et al., 2002) provides insight into metamorphic processes, rheology and deformation during an active collision. It is hypothesised that this setting is an example of a gold-producing 'conveyor belt' (Figure 3.4) which invokes metamorphic conditions and variable rates of uplift to explain gold mobility and distribution. Their evidence suggests that Au, As, Sb and Hg are

mobilised by metamorphic processes in large volumes: an estimated 11,27 t of Au, 10.1 Mt As, 47,000 t Hg, 560,000 t Sb and 14,000 Mt H₂O / 1 Myr (Pitcairn et al., 2014). Research of active orogens provides an indication of processes that may have been present in the Palaeozoic Caledonian(-Appalachian) Orogen of interest to this study, particularly concerning gold mobility and distribution.

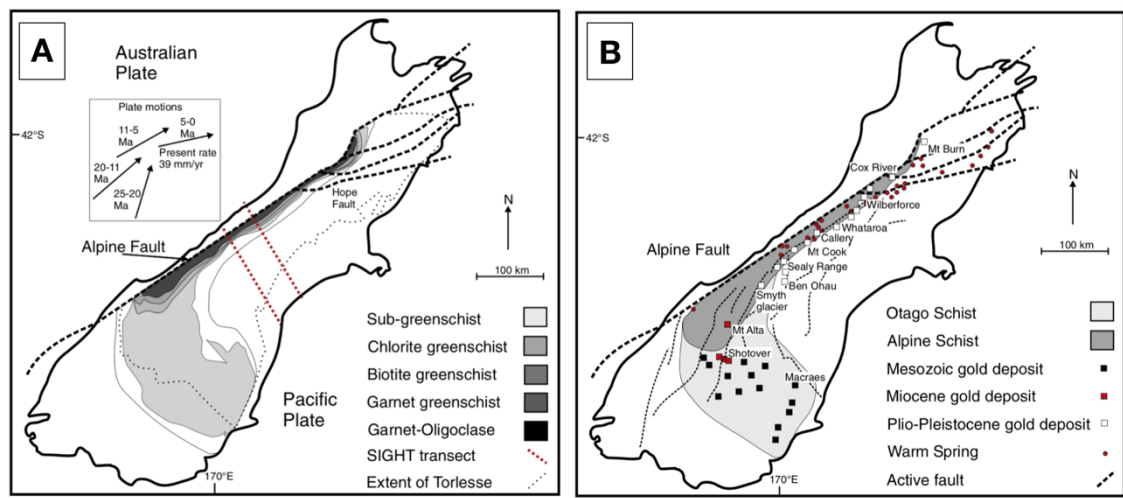


Figure 3.4. (A) A map showing metamorphic facies distribution within the Alpine and Otago Schists of New Zealand's South Island, the position of the major crustal structures (principally the SW-NE trending Alpine Fault) and vectors of the Australian plate from 25 Ma to the present (the red dashed lines indicate geophysical transects which supported generation of the model); (B) the locations of Au deposits; older deposits have an affinity with Otago Schist (principally characterised by lower greenschist metamorphism), while more recent deposits in the Miocene and Plio-Pleistocene (c. 5 Ma to 12 ka) are hosted by the Alpine Schist (generally upper greenschist facies) proximal to the Alpine Fault (Craw et al., 2002; Pitcairn et al., 2014; Wannamaker et al., 2002).

3.2.iii. Pyrite, pyrrhotite and orogenic gold

Early diagenetic pyrite in carbonaceous shales is hypothesised as a primary source of orogenic gold (Large et al., 2012; Large et al., 2011; Large et al., 2009). The process by which gold and associated trace elements are incorporated into the structure of pyrite is a matter of some conjecture (e.g. Pokrovski et al., 2019; Tauson et al., 1998), however a shale-horizon

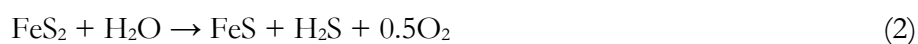
source model is widely accepted in a variety of settings (e.g. Meffre et al., 2008; Palenova et al., 2015; Sack et al., 2018; Selvaraja et al., 2017) and has been proposed for deposits hosted by the Dalradian Supergroup in Ireland and Scotland of interest to this study (Parnell et al., 2017).

Trace elements, dissolved in oceanic settings either within the water column itself or the pore waters of sediments, are adsorbed onto the surface of pyrite which grows under euxinic deep-water conditions, incorporating those elements into the sulphide structure (Gregory et al., 2015). Pyrite growth itself is controlled by depletion of oxygen, this is understood to be linked to biogenic activity within upper-most sediments, along with sulphate-reducing bacterial activity (Scholtz and Neumann, 2007; Schieber, 2002; Folk, 2005 cited in Large et al. 2009). Large et al. (2009) demonstrate a sequence of trace element incorporation into diagenetic and hydrothermal pyrite in samples of orogenic (Bendigo, Australia; Sukhoi Log, Russia; Spanish Mountain, Canada) and Carlin-type systems: within the earliest diagenetic forms tested, trace elements (Cu, Pb, Zn, Co, Ni, Mn, V, Mo, As, Bi, Au, Ag, Se, Te) are transferred into grains as nano-scale particles, into the structure of pyrite itself, or into organic matter present within pyrite as intergrowths. Pyrite grains of this class, which may form rapidly under low-temperature (<150 °C) conditions and tend to have a fine-grained framboidal appearance (Butler and Richard, 2000 cited in Large et al, 2009), are shown to have high Ag/Au, V/Al and Ni/Co ratios. Trace element concentrations within such early pyrite has been shown to mirror coeval oceanic-atmospheric conditions throughout geological time, for example Ni and Co distribution in sedimentary pyrite is considered to be related to Large Igneous Province (LIP) events, while Se and Mo have a relationship with ocean oxygenation (Large et al., 2014). Recrystallisation occurs during late diagenesis and early metamorphism; resulting in the transfer of metals from the earliest phase (Cu, Pb, Zn, Mn, V, Ni, Mo, Au, Ag and Te) into inclusions within the outer zones of secondary pyrite overgrowths as discrete phases, e.g. chalcopyrite, galena, free gold,

sphalerite and tellurides. Additional recrystallisation may occur as a result of hydrothermal fluid interactions, leading to cyclical growth of As, Co and Ni. The mechanisms by which Au may be adsorbed to sulphide surfaces and controls on concentrations which may be incorporated are described in detail by Reich et al. (2005) and Deditius et al. (2014).

Scale can present a particular challenge in studies of such deposits; for example, Sukhoi Log, an orogenic deposit in Russia is considered of ‘giant’-size (Large et al., 2009); Palenova et al. (2015), hypothesised that multiple polychronous and polygenic ore-forming processes may be attributable to such large deposits, and sought to test this model using samples from the smaller Proterozoic deposits of Kopylovsky and Kavkas, constituents of the Artemovskiy cluster in the Bodaybo district of Russia. Results were found to be supportive, showing a decrease in contents of Au, Ag, Co, Pb, Sb, Bi, Te, Ba, Mo and Tl in pyrite attributed to metamorphic processes, compared with diagenetic framboidal forms, and an increase observed for Ni, Cu, As and Se.

Conversion of pyrite to pyrrhotite during metamorphism is considered a key reaction for the liberation of Au, As and S (Large et al., 2009; Pitcairn et al., 2006; Thomas et al., 2011):



This reaction occurs at the upper greenschist to lower amphibolite facies boundary, as metamorphic waters are released due to the dehydration of chlorite at temperatures between 450 and 600 °C. Thomas et al. (2011) found that a modified version of this reaction may occur within carbonaceous shales at lower temperatures (250 to 300 °C):



Conversion is therefore not strictly controlled by temperature, as reaction with carbon as an active reductant, derived from graphite within highly organic units, may also initiate this process; Fe-rich sediments are additionally viewed as a favourable prerequisite and major control for conversion of pyrite to pyrrhotite within this system.

3.2.iv. Transport and emplacement mechanisms

Current theories of orogenic gold systems favour emplacement proximal to major tectonic boundaries characterised by crustal-scale fault structures (Bierlein and Crowe, 2000) and focused fluid flow during active phases of deformation and metamorphism (Hagemann and Cassidy, 2000). Physico-chemical controls on the transport of gold by hydrothermal fluids include pressure and temperature, sulphur and oxygen fugacity, salinity, pH and redox conditions, while the key processes which govern the redistribution and deposition of gold include cooling, decompression, phase separation (incl. boiling), interactions with rocks and mixing with external waters (Pokrovski et al., 2014). Grade distribution is understood to be governed specifically by fluid decompression and boiling (Garafalo et al, 2014). The timing of metamorphic fluid mobility may be heterogeneous, released and emplaced at different times during the evolution of an orogen, at depths lower than the paleodepth of ore bodies; fluids transit shear-zone fracture networks to the locations of deposition, interacting during their ascent with rocks hosting those fractures, modifying major and trace element signatures of carrier fluids. Controls specifically relating to the transport of gold-bearing hydrothermal fluids transiting deformation networks during collisions include rheological differences, rock inhomogeneity and the permeability of units (Upton and Craw, 2014). Thompson and Connolly (1992) provide detailed information on the physics of metamorphic fluid flux; they note that permeability (K_ϕ)-porosity (Φ) contrast within the crust controls the location of metamorphic ‘aquifers’, and suggest that it may be possible to detect such conduits using

geophysical methods, e.g., using detection of high electrical conductivity and low-velocity seismic reflectors. The rheology of rocks is an important factor focusing fluids between zones of relative weakness and strength, for example at the regional scale between crustal blocks bearing different structural histories. Upton and Craw (2014) note that such boundaries, where inhomogeneity between juxtaposed units is most considerable, are of key importance in tectonically-driven hydrothermal systems. Rheology and rock inhomogeneity may be inherited, or change during deformation.

3.3. Vein-hosted gold in Ireland and Scotland

3.3.i. Tectonics, metamorphism and deformation

Orogeny-associated gold occurrences have a spatial association with the Fair Head-Clew Bay Line (FH-CBL) on the island of Ireland, and its continuation, the Highland Boundary Fault (HBF) in Scotland (Earls et al., 1996) (see Figure 3.5). This major structure and tectono-stratigraphic boundary marks the southern extent of the Grampian terrane, a geological unit comprised primarily of the metasedimentary rocks of the Dalradian Supergroup: a late Proterozoic to early Cambrian (800-515 Ma) basin, deformed and uplifted by the cumulative events of the Palaeozoic Caledonian-Appalachian Orogeny (475-405 Ma) (Chew and Strachan, 2014) (see Figure 3.6 and Figure 3.7). Immediately adjacent to the FH-CBL to the south-east in County Tyrone, Northern Ireland lies the Tyrone Igneous Complex (TIC), an inlier of exposed ophiolite, arc-related rocks and intrusives.

In Ireland and Britain, the sequence of events which comprise the Caledonian Orogeny can be subdivided into three discrete phases: the Ordovician Grampian Phase (475-460 Ma), the Silurian Scandian Phase (~440 Ma) and the Devonian Acadian Phase (405 Ma). During the Grampian Phase (often referred to as the ‘Grampian Orogeny’), the Laurentian

continental margin north-west of the FH-CBL - HBF suture collided with an oceanic arc terrane to the south-west (see Figure 3.7, Figure 3.6). Remnants of this arc are identified within the Tyrone Igneous Complex (TIC) to the south of the FH-CBL in Northern Ireland, along with formations at Lough Nafooe in County Mayo, western Ireland, where rhyolites, basalts and meta-basites are found (Figure 3.5).

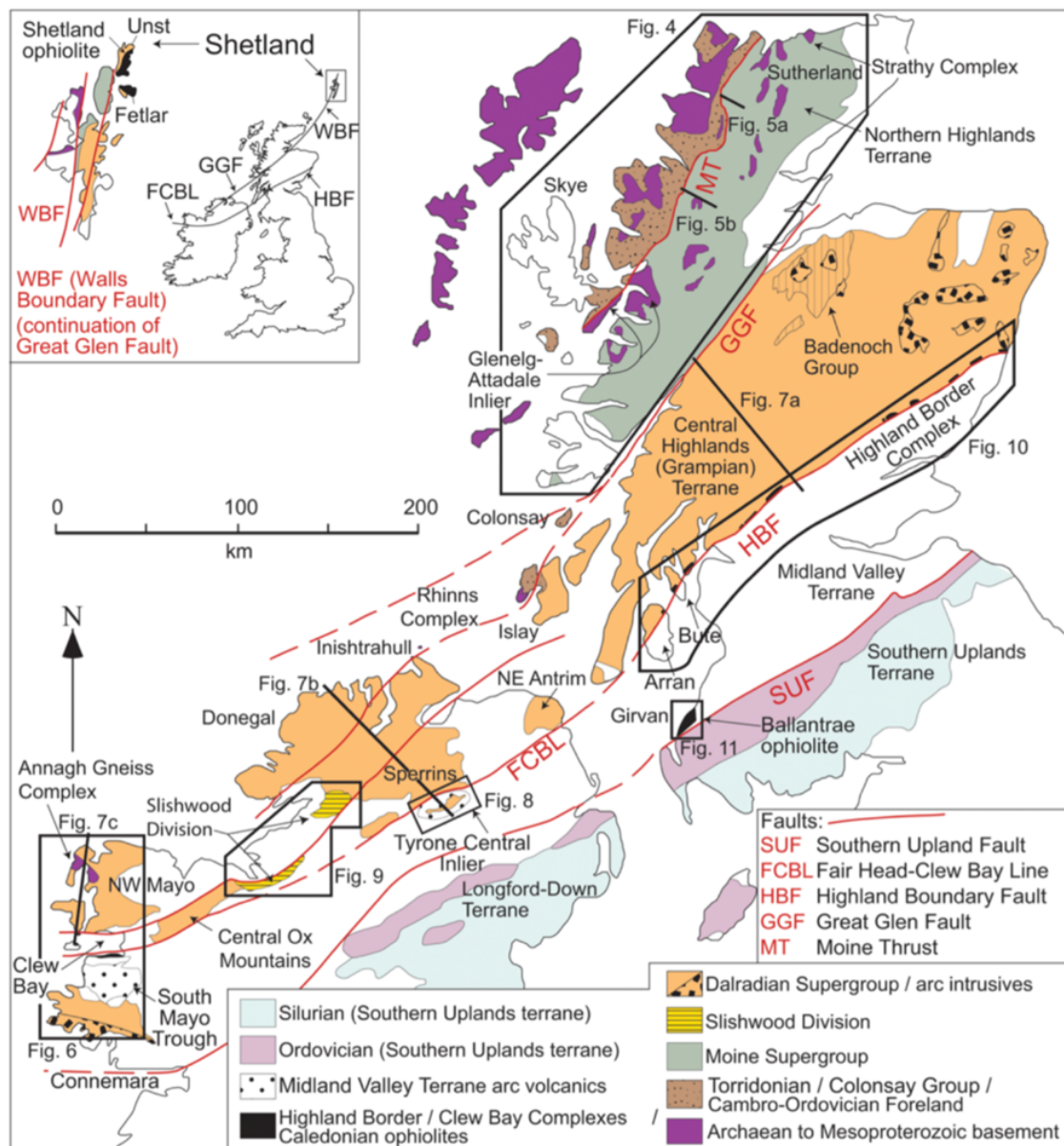


Figure 3.5. Tectono-stratigraphic position of the Grampian Terrane (in orange), comprising Dalradian Supergroup meta-sediments deformed during the Caledonian Orogeny (Chew and Strachan, 2014)

The Scandian Phase (~440 Ma) records the continent-continent collision of Laurentia and Baltica. This phase is not recorded in Ireland, though is preserved in the Northwest Highland Terrane of Scotland (and in Eastern Greenland). This event resulted in metamorphism and deformation on a regional scale during the Silurian, particularly of the Moine Supergroup. The Acadian Phase (405 Ma) is the name given to the continent-continent collision of Laurentia and Avalonia, which is considered the final stage of the closure of Iapetus (Chew et al., 2014).

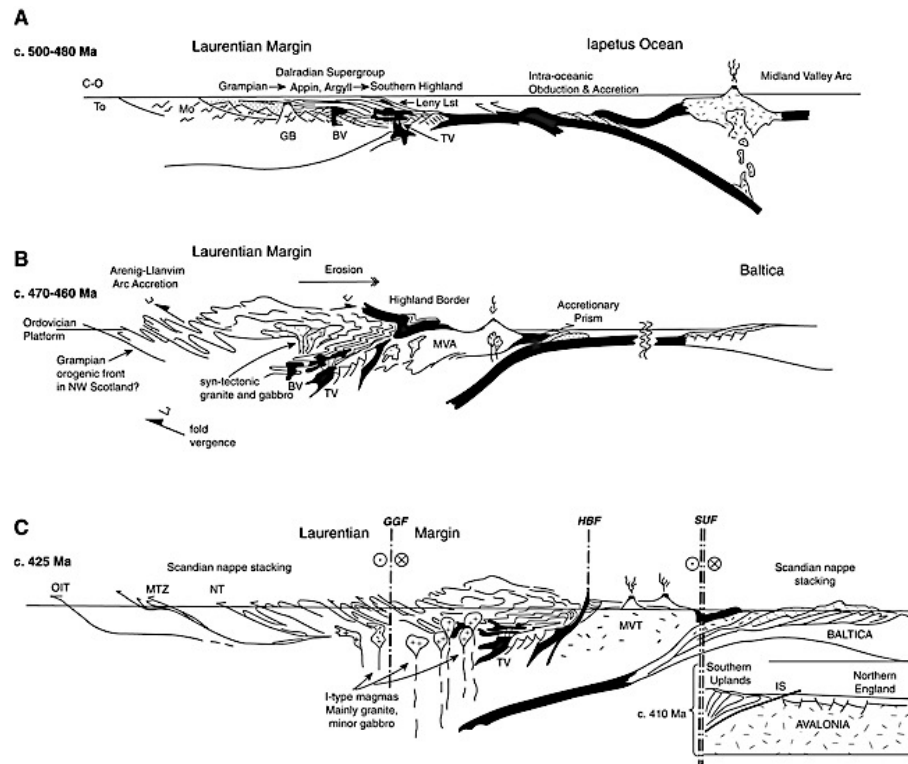


Figure 3.6. Tectonic framework of Caledonian Orogeny phases in cross-section (NW-SE). A: pre-Grampian Phase, B: post-Grampian Phase, C: pre-Acadian Phase (Leslie et al., 2008).

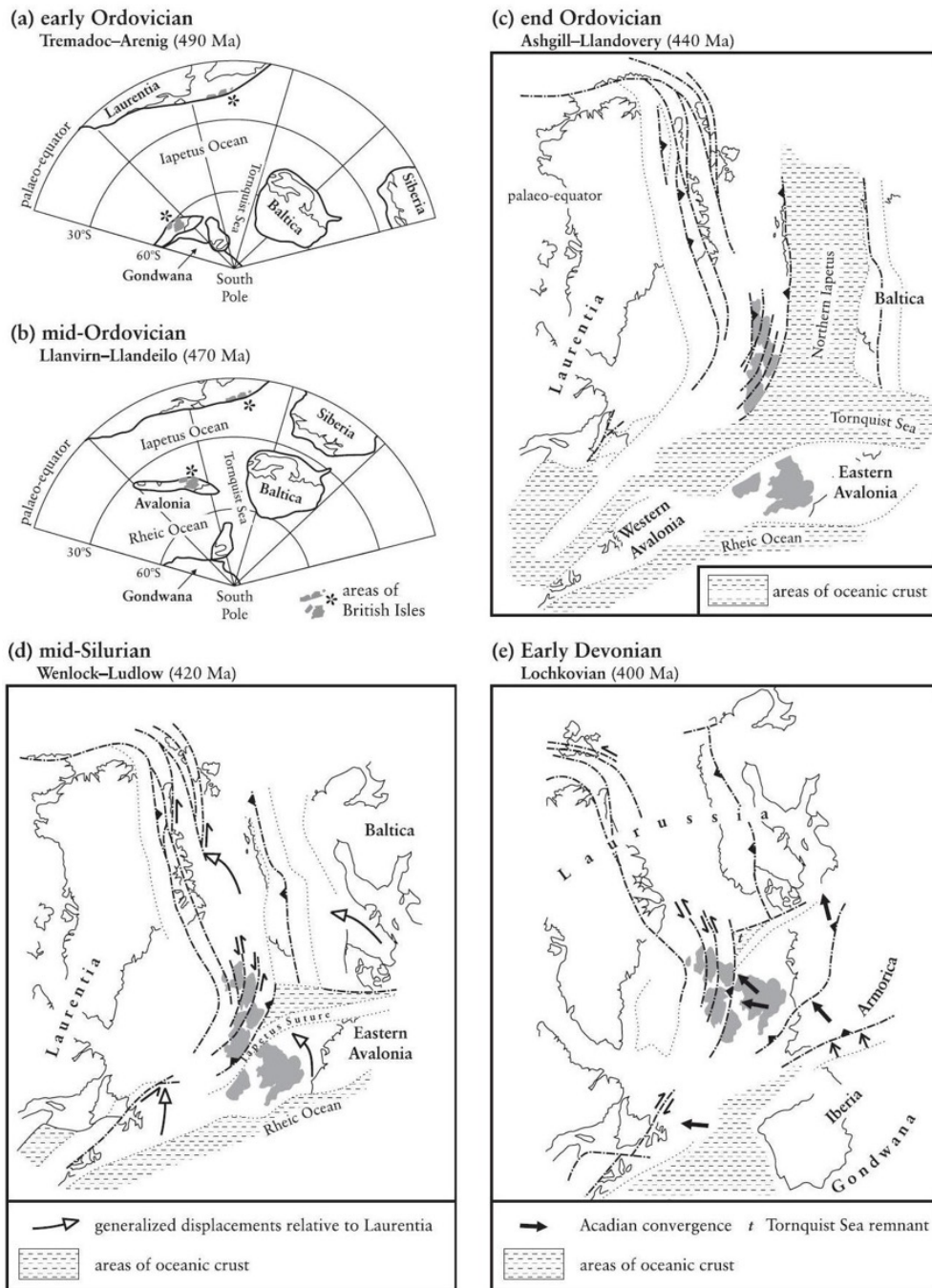


Figure 3.7. Tectonic convergence between the Ordovician and Devonian: (a) early Ordovician continental configuration; (b) mid-Ordovician convergence; (c) the end-Ordovician configuration showing the relative positions of northern and southern Ireland and Britain separated by the Iapetus Ocean; (d) the mid-Silurian configuration and displacements; (e) the final Iapetan-closure stage of the Caledonian Orogeny during the Early Devonian (Stephenson and Thomas, 1999).

This phase is attributed to impingement of Iberia and Armorica, and fragmentation of the Gondwanan supercontinent, closing the Rheic Ocean to the south and causing significant deformation (Woodcock and Strachan, 2012).

3.3.ii. Irish and Scottish deposits

The largest estimated Irish-Scottish vein-hosted gold resources are found in the Sperrin Mountains of Northern Ireland at Curraghinalt (33,000oz at 26.04 g/t for 0.04 Mt measured, 3.033 Moz at 14.95 g/t for 6.31 Mt indicated and 3.038 Mt at 12.24 g/t for 7.72 Mt inferred using a cut-off grade of 5 g/t (Dalradian Resources Inc., 2018) and Cavanacaw (32,202 oz at 7.24 g/t for 138,241 T measured, 147,784 oz at 6.78 g/t for 679,992 T indicated, 341,123 oz at 7.71 g/t for 1,373,879 T inferred using a 2 g/t cut-off (Galántas Gold Corporation, 2014) along with regional prospects. They lie geologically within the Grampian tectono-stratigraphic terrane, proximal to the WNW-ESE trending Fair Head – Clew Bay Line (Parnell et al., 2000), the suture of the Grampian phase (orogenic peak c. 468 Ma) of the Caledonian Orogenic Cycle (c. 475-405 Ma) (Chew et al., 2009a) (see previous section). Their stratigraphic position is controversial; there is a consensus that occurrences of interest to this study in Ireland are hosted within the Argyll Group (Dalradian Supergroup; Table 3.2).

The timing of emplacement for the largest of the two deposits, Curraghinalt, has been constrained by Rice et al. (2016) to a maximum interval of 462.7-452.8 Ma, within the Ordovician (using $^{40}\text{Ar}/^{39}\text{Ar}$ dating of sericite and Re-Os molybdenite within micro-shears which cross-cut the principal gold-bearing veins), post-dating the Grampian orogenic peak (c. 468 Ma). Deposits in Scotland may be later: precious metal mineralisation in the Tyndrum area has been dated by Treagus et al. (1999) to the Silurian-Devonian boundary, c. 410 Ma (indicated using $^{40}\text{Ar}/^{39}\text{Ar}$ dating of K-feldspars in hydrothermal veins, accepting a limitation in potential loss of argon during subsequent fracturing and hydrothermal events).

Quartz-sulphide vein arrays hosting mineralisation in Tyrone are accommodated by basin formations of the Dalradian Supergroup, which exhibits several phases of deformation, and coeval metamorphic conditions ranging between greenschist and amphibolite facies (Alsop et al., 2001; Chew et al., 2009a; Fettes, 1979).

Interpretations proposed for the source and emplacement of Au in the Sperrin Mountains vary. Attention is drawn by Rice et al. (2016) to the host architecture: (i) that veins are found in a collisional zone, within which the margin of a continent was obducted over an inbound island arc (remnants of which form the Tyrone Igneous Complex to the south-east of the Omagh Thrust); (ii) that subsequent to a phase of expedient orogenic uplift, a thick sequence of meta-sediments was overlying the arc which retained heat and was fertile and (iii) that collapse and extension would have resulted in increased permeability of the crust. These factors would likely control the localised distribution of Au, and are considered by Rice et al. (2016) to present environmental conditions conducive to long-lived hydrothermal fluid mobility. They consider that multiple sources were available for the provision of heat, energy, fluids and metals within the arc itself and a permeable overlying crust within which fluids were circulating, and present fluid mixing as a plausible control on mineralisation. Analyses of metal contents suggest multiple sources: S and Pb isotope signatures are presented by Parnell et al. (2000) and Standish et al. (2014), the results of which suggest a link to the island arc, and that arc sources feed volcanogenic massive sulphide (VMS) -style mineralisation and other metalliferous occurrences within the Tyrone Igneous Complex (TIC) (see Hollis et al., 2014). Standish et al. (2014) suggest that Pb may be additionally sourced from the Dalradian meta-sediments themselves. Local Mo, Bi and Te enrichments at the Curraghinalt deposits are hypothesised by Rice et al. (2016) to be derived from intrusive sources, however they also point out that the closest dyke to that deposit is more than 10 km away.

Southern Sperrins, Northern Ireland

<i>Locality</i>	<i>Group (Subgroup) within Dalradian Supergroup</i>	<i>Reference</i>	<i>Citing, if applicable</i>
Curraghinalt	Argyll	Rice et al. (2016)	Alsop and Hutton (1993)
Cavanacaw	Southern Highland	McFarlane et al. (2009)	Geological Survey of Northern Ireland (1995)
	Argyll (Easdale)	McFarlane et al. (2009)	Alsop and Hutton (1993) Long (1997)
			<i>new evidence; geophysical</i>
		Tanner (2014)	McFarlane et al. (2009)
Curraghinalt & Cavanacaw	Southern Highland	Lusty et al. (2009)	Geological Survey of Northern Ireland (1997)
		Earls et al. (2003)	Arthurs (1976) Smith and Johnston (1994)
	Argyll (Easdale)	Long (1997)	<i>new evidence</i>
	Argyll	Earls et al. (2003)	Alsop and Hutton (1993) Arthurs et al. (1994)
		Tanner (2014)	<i>citing previous studies</i>

Ox Mountains, Ireland

Cloonacool	Argyll	Playfair Mining (2016)	<i>new evidence; mapping</i>
		Long and Max (1977)	Taylor (1968b)

Perthshire, Scotland

Cononish	Argyll (Easdale)	Lyell (2019)	Tanner and Thomas (2009)
		Hill et al. (2015)	<i>new evidence; S-isotopes</i>

Grampian Terrane (Scotland and Ireland)

Pyritiferous shale	Argyll (Easdale)	Parnell et al. (2017)	Moles et al. (2015)
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Table 3.2. The stratigraphic level of gold occurrences and localities of interest to this study are a subject of much debate (those of the Sperrins gold deposits are particularly controversial): this table presents recent designations according to a selection of recent studies in the literature.

This information and evidence of fluid mixing presented in inclusion work by Wilkinson et al. (1999) and Parnell et al. (2000) presents a broad consensus that multiple sources are feasible for metalliferous deposits in the Sperrin Mountains.

Dalradian Supergroup strata within the Appin and Argyll Groups, exposed across the north-west of Ireland, contain shale horizons which are considered to be a likely source of gold for deposits. A recent study by Parnell et al. (2017) presents geochemical data which indicate that Au and Te mobility is observed within organic pyritic sediments of the Easdale Subgroup (Argyll Group) in both Ireland and Scotland, suggesting fertility for auriferous mineralisation. They observed Au and Te (+/- Pb) enrichment within the rims of pyrite grains, suggesting mobility synchronous with metamorphism. Pyrite data are consistent with findings a variety of settings from the Archean to the Cenozoic by previous workers which demonstrate that carbonaceous shales may act as a sink for trace elements, including Au (Gregory et al., 2015; Large et al., 2012; Large et al., 2009; Steadman et al., 2015). A synopsis by Gregory et al. (2015) showed that trace elements contained in sedimentary pyrite are recorded in an approximate order of abundance: $As \geq Ni > Pb \geq Cu \geq Co \geq Mn > Sb \geq Zn \geq Se \geq Mo > Ag \geq Bi > Te \geq Cd > Au$. Parnell et al (2017) also report an absence of trace elements including Au and Te within examined samples of pyrrhotite in Irish-Scottish shale samples, advocating pyrite to pyrrhotite conversion reactions as a key process mobilising Au during the Grampian orogenic event, consistent with the model of Phillips and Powell (2010).

3.4. Mineral exploration and mining background

3.4.i. The Pb-Zn extractive industry

Ireland has been highly successful in the discovery and exploitation of Pb-Zn resources in the Midlands region, an area which has come to be known as ‘The Irish Orefield’; the region

includes such deposits as Tara (Navan), Lisheen and Galmoy (Wilkinson et al., 2015), the development of which led to the country acceding to its current position as Europe's largest zinc producer (Minerals Ireland, 2020). These deposits lie on an approximately SW-NE trend to the south of the Iapetus Suture, and significant work is going into exploration of its Carboniferous stratigraphy, supported by research by iCRAG (Irish Centre for Research in Applied Geosciences, 2020b). The largest Irish Pb-Zn mine, Tara, operated by Swedish mid-tier Boliden, directly employed approximately 580 people, and had an annual turnover of €276.1 million in 2017 (Boliden Group, 2020; The Irish Times, 2020). Lead and zinc concentrates produced from the c. 2.6 million tonnes of ore mined each year are transported by rail to Dublin port for export. The mine has provided a significant economic impact for the Navan area and production is expected to continue beyond 2023 following the discovery of 'Tara Deep', an orebody at depths of between 1.2 and 1.9 km (Boliden Group, 2017). This discovery was made using successful deployment of seismic and electromagnetic geophysical methods in tandem with geological interpretation, highlighting the importance of using novel exploration and modelling methods in securing future resources in the Irish Orefield. iCRAG is assisting explorers in the search for economic zinc finds along the trend, with projects in structural, fluid and stratigraphic modelling, isotope and trace element geochemistry, along with optimisation of geophysical techniques (Irish Centre for Research in Applied Geosciences, 2020b). Zinc is principally used to galvanise iron and steel due to its chemical properties as an anti-corrosion agent (Royal Society of Chemistry, 2020b). It is also used in medicine, agriculture, and research has suggested that Zn-based batteries may be a viable alternative to lithium-ion batteries for electric vehicles, enabling rechargeability and lowering costs (Li and Dai, 2014).

3.4.ii. Diversifying Ireland's minerals sector

While Ireland is a significant Zn-Pb producer, it also has a history of producing other metals, specifically copper, for example in geological terranes in the south; deposits at Allihes on the Beara Peninsula in County Cork, and Bunmahon in County Waterford are considered an important part of Ireland's mining heritage (Cowman, 1983). Modern exploration in copper is underway in West Cork; a joint-venture partnership between Altius and First Quantum Minerals is investing in exploration of targets which may see a revival of Ireland's copper industry (Altius Minerals Corporation, 2020).

While interest in strata which were a significant source of copper production in previous centuries is seeing a revival, there is recognised potential for further diversification of Ireland's minerals sector (Lusty, 2016). While energy critical elements (ECEs) offer a tantalising exploration target in the 21st century economy, gold in the emergent camp in the north of Ireland has shown the most promise as a new frontier for the industry and development of indigenous resources (e.g. Dalradian Resources Inc., 2018).

Gerard Boate, a Dutch physician (Molhuysen and Blok, 1918), in 'Ireland's Naturall History' (1652) (Figure 3.8) reported the following account of a discovery in the Moyola River of County Tyrone in the mid-17th Century:

“a credible person hath given me to understand, that one of his acquaintances had severall times assured him, that out of a certain rivelet in the County of nether-Tirone, called Miola (the which rising in the Mountains Slew-galen, and passing by the village Maharry, falleth into the North-west corner of Lough Neaugh, close by the place where the River Band commeth out of it) hee had gathered about one dram of pure gold; concluding thereby, that in aforesaid Mountains rich Gold-mines doe lye hidden”

The described location lies approximately 30 km to the north-east of a series of gold discoveries in the Sperrin Mountains in rocks of the Dalradian Supergroup (McArdle et al., 1987). Within these strata, gold occurrences of economic interest were discovered during a particularly active period of exploration during the 1980s (Earls, 2009); a systematic search was undertaken across the island at this time for potential resources (McArdle et al., 1987). In 2009, more than 50% of Northern Ireland was under a mineral prospecting licence or application, including the Sperrin Mountains (Lusty et al., 2009), indicative of continued interest in the discovery of new deposits.

Curraghinalt (Figure 3.9) is currently the largest estimated gold resource on the island of Ireland and is considered by its commercial operators as one of the highest grade undeveloped gold resources in the world (Dalradian Resources, 2016). Discovered in 1983 by Ennex (Colman, 2000), this project is in development; an Ni 43-101 compliant feasibility study was recently published for the resource (MacDonald et al., 2017). Cavanacaw, also in Co. Tyrone, is an active mine; the deposit was discovered by RioFinEx in 1987. It comprises the Kearney vein swarm (N-trending) and a series of gold occurrences across the full extent (20km x 5 km) of an uplifted block of Dalradian Supergroup strata bound by faults known as the Lack Inlier (McFarlane et al., 2009; Phelps and Mawson, 2013).

In the Ox Mountains of County Sligo, gold-associated sulphides identified include pyrite and minor galena hosted by quartz veins in float, returning grades of up to 9.80 g/t at Cloonacool and 3.43 g/t at Cabragh. The ‘Furze’ vein-envelope identified in outcrop (including zones of silicified, chloritised and graphitic alteration) at Cloonacool was drilled in 2016, with assay results suggesting that a ‘large gold-bearing system’ may have been discovered with values >1g/t encountered in all 9 diamond holes drilled (Playfair Mining Ltd., 2016). Another recent discovery has been made on the Inishowen Peninsula in County Donegal, where gold in float has been identified at grades of up to 104 g/t. Gold is found at the locality within pyrite- and sphalerite- bearing quartz veins with grades of up to 10.3 g/t

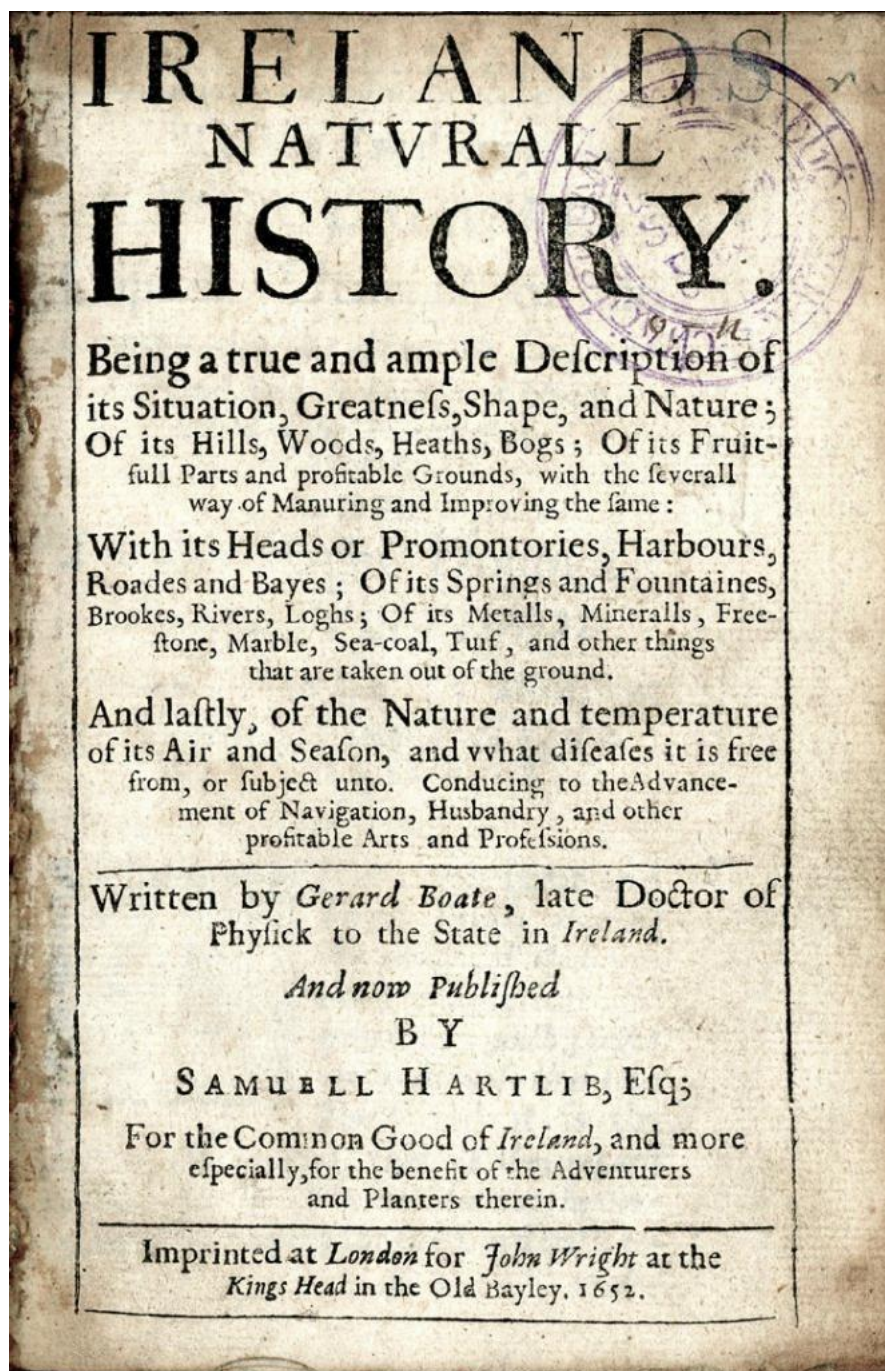


Figure 3.8. Cover of Ireland's Natural History (1652), an important early work reporting on matters of interest to mineral prospectors, containing the first published account of gold in County Tyrone. The manuscript was published as stated 'for the Common Good of Ireland, and more especially, for the benefit of the Adventurers and Planters therein'. Boate passed away in 1650 after serving as 'Doctor of Physic to the State of Ireland' in 1649, and began writing this work four years before arriving in Ireland (Dublin City Council, 2020).



Figure 3.9. Drilling in the Sperrin Mountains at Curraghinalt, January 2016 (photograph by author).

over a metre (drill hole 16-MR-03) (Connemara Mining, 2016). Alluvial gold is also recognised across the north of Ireland, for example in the Mourne Mountains of County Down (Smith et al., 1996) (Figure 3.10).

Along-trend to the north-east in Scotland, gold exploration has also borne success, for example at Cononish, 4 km SSW of Tyndrum in the Stirling District where a deposit is being developed by Scotgold Resources Limited who report resource estimates of 169,200 oz Au at grades of between 12.7 and 14.1 g/t (along with 631,300 oz Ag) (Scotgold Resources Limited, 2017). The deposit was discovered by Ennex in 1984, and is hosted by quartz-carbonate veins which strike NE-SW over a total length of over 1km, cross-cutting Appin and Grampian Group stratigraphy. The main sulphide mineral is pyrite, with minor sphalerite, galena and chalcopyrite (Colman, 2000; Snowden Mining Industry Consultants Limited, 2008). The Tyndrum locality also hosts base metals and is a significant historical

producer of lead, which following its discovery in 1741 was producing for over a century (Scotgold Resources Limited, 2017).

Gold in quartz veins was discovered in Dalradian meta-sediments by Colby Gold p.l.c. in 1988 at Calliacher Burn and Urlar Burn, 3-4 km south of Aberfeldy in Perthshire; grades of 8.81 g/t were recorded in veins striking over 87.5m (Colman, 2000). In Aberdeenshire, close to Towie, Ennex encountered gold in the early 1980s from pan concentrate and regional prospecting. While under licence by Navan Resources during the early 1990s, drilling in this area intercepted up to 22.5 g/t over a metre. Greenore Gold p.l.c. who are conducting initial exploration fieldwork and diamond drilling at the prospect have reported grades of 4 m at 0.57 g/t and 1.2 m at 3.16 g/t in core, 6.26 g/t Au in outcrop, and up to 53.7 g/t in gold-bearing float. Ag, Cu, Pb and Zn of potential economic significance has been recorded by the company in rock and soil samples (GreenOre Gold p.l.c., 2017a). Bedrock samples of up to 57 g/t have also been encountered by the same prospectors in Ayrshire (GreenOre Gold p.l.c., 2017b).



Figure 3.10. Gold-panning in a stream near Hilltown, County Down (Northern Ireland) with the Irish Association of Economic Geologists, June 2009 (photograph by author).

Chapter Four: Analytical methods and proof of concept

4.1. Methodology

Analytical techniques used during this study are described in detail within individual chapters as appropriate to each phase of work. Methods were selected based on which would be the optimal tool to answer a research question, with approaches targeted rather than systematic and adapted as required in each case. The four techniques that proved most valuable in this research were optical microscopy, Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS/EDX) (all conducted at iCRAG Lab@TCD) and Laser Ablation Inductively Coupled Plasma Mass Spectroscopy (LA ICP-MS) (pursued at the Trinity College Dublin Geochemistry Laboratories).

4.1.i. Optical microscopy, SEM and EDS/EDX: iCRAG Lab@TCD

The initial focus in all cases was on identifying key mineralogical and petrographic information; specifically, sulphide mineralogy, the identification of inclusions and metalliferous phases (e.g. visible gold, galena, sphalerite), and the relationship of sulphide minerals to both host veins (e.g. quartz-carbonate) and host rock deformation fabrics. This work was conducted using Olympus BX60 and Nikon Eclipse LV100 optical microscopes

equipped with high-resolution cameras, with images acquired and processed using Nikon NiS-Elements AR (Advanced Research) software. As sulphide minerals and metals appear opaque in transmitted light, reflected light was the principal capability used for optical work and imaging. The merits of this approach are demonstrated in all chapters; an example of which is presented in *Chapter Five* wherein pyrite generations are discriminated at the Curraghinalt deposit using this technique: two syn-deformational phases (Py₁ and Py₂) are identified within veins which formed synchronous with host fabrics, while ore-stage Py₃ is observed within veins cross-cutting host penetrative fabrics. Transmitted light microscopy was useful in this study in examination of gangue minerals within host fabrics, for example in *Section 7.5* where chlorite is observed replacing garnet porphyroblasts within Slieve League Formation samples from Glencolumbkille in County Donegal, confirming retrograde metamorphic conditions were pervasive. Thin section preparation was optimised with a view to maximising the width available for subsequent destructive analytical methods, particularly LA ICP-MS which involves the removal of material from the thin section for analysis. This restricted the ability to use some traditional techniques of optical microscopy, for example the use of birefringence, however the selected section width (60 µm) was found to be largely sufficient for the acquisition of data using reflected and transmitted light. Image-J, an open-source java-based software package (Laboratory for Optical and Computational Instrumentation, University of Wisconsin), was found to be a convenient tool in post-processing of images and for taking measurements.

High-resolution raster scanning and the acquisition of major element data was conducted using the in-tandem methodologies of SEM and EDS/EDX (see Figure 4.1 and Figure 4.2). These methods were found to be particularly useful in resolving the relationship of metalliferous phases, for example at Curraghinalt, where a sequence is determined in *Section 5.9* for the emplacement of gold and tellurides within late fracture networks. Element mapping using this combined approach enabled the discrimination of phases,

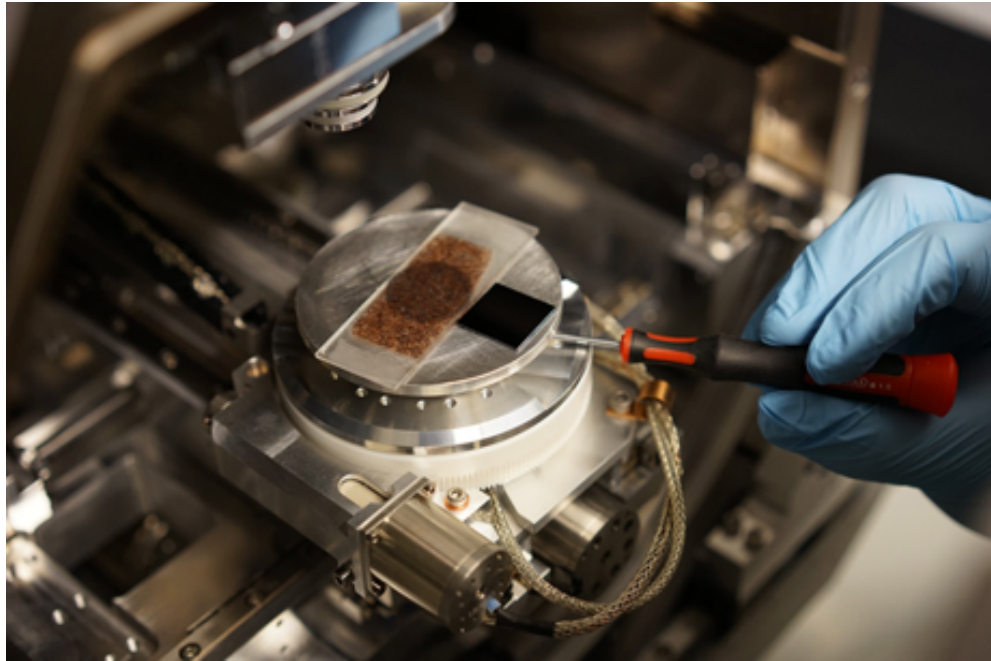


Figure 4.1. Interior of TIGER Field Emission Scanning Electron Microscope (FE-SEM) with a sample thin section (Trinity College Dublin, 2019).

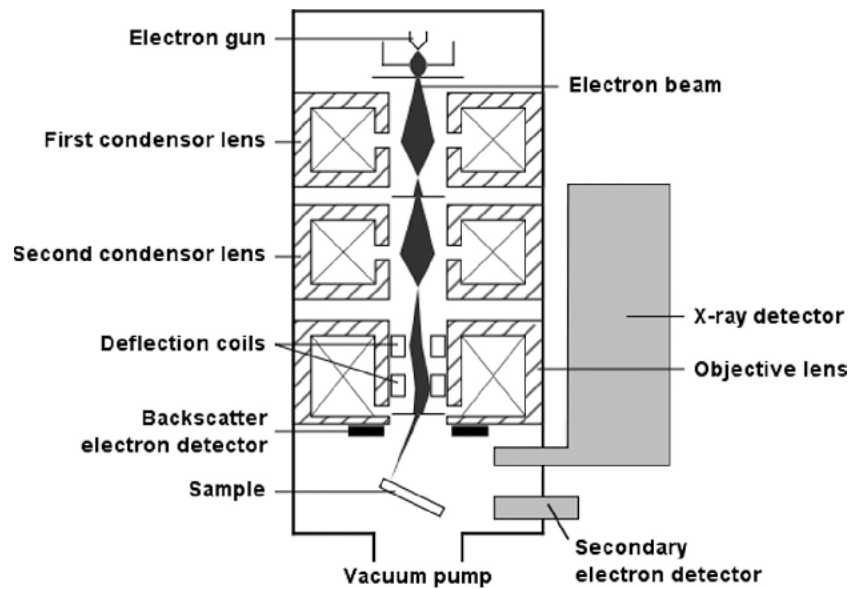


Figure 4.2. Model of Scanning Electron Microscope gun mount (Hamilton and Quail, 2011)

for example at the Cloonacool prospect in *Section 6.5.ii.* where a relationship is determined between early pyrite (Py₁) and Ti-oxides. Two systematic tasks were undertaken using EDS/EDX: (i) the acquisition of Au and Ag abundance data for auriferous particles, and (ii) acquiring an Fe standardisation dataset for use in LA ICP-MS data processing. The following instruments were used for SEM and EDS/EDX analyses: a Tescan (Czech Republic) MIRA 4-XMU Field Emission Scanning Electron Microscope (FE-SEM) equipped with Backscatter Electron (BE) and Cathodoluminescence (CL) detectors, with an Oxford Instruments X-Max 150mm² detector for EDS/EDX; and the TIGER (Tescan Integrated Geo Elemental Raman), a custom instrument involving Tescan, Oxford Instruments (UK) and WITec (Germany) which has an additional Oxford Instruments X-Max 150mm² detector and a WITec RISE (Raman Imaging and Scanning Electron) system. For raster scan processing and interface with SEM systems, the Tescan Essence software platform was used, while EDS/EDX analysis was conducted using interaction with AZtec microanalysis software by Oxford Instruments.

4.1.ii. LA ICP-MS: Geochemistry Laboratories, TCD

In order to determine the abundance and distribution of trace elements within individual targeted sulphide grains of interest, specifically of pyrite and pyrrhotite, a Teledyne CETAC (Nebraska, USA) G2 193nm UV laser equipped with a HelEx II 2-volume cell, coupled to a Thermo (Massachusetts, USA) Elemental iCapQs mass spectrometer. Specific parameters for experiments and the use of ancillary devices is described within individual subsequent chapters. User interface was provided by Chromium (for Laser Ablation) and Qtegra (for ICP-MS) software platforms, with time-resolved data processed using Iolite 3.0, a tool developed at the University of Melbourne, Australia.

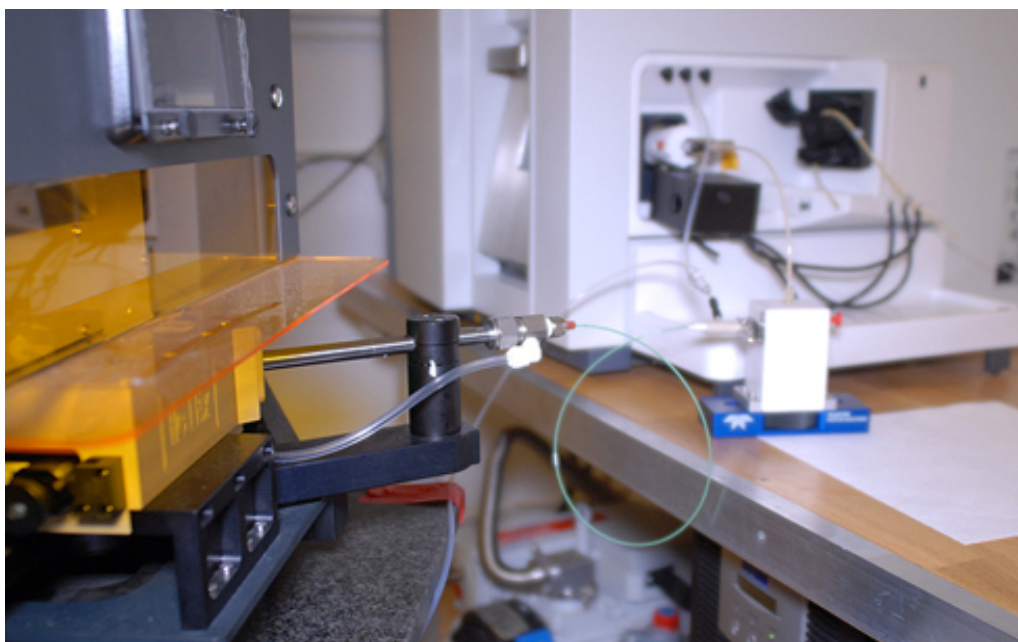


Figure 4.3. Photograph of Laser Ablation chamber (left) and ICP-MS (right). (Trinity College Dublin, 2019).

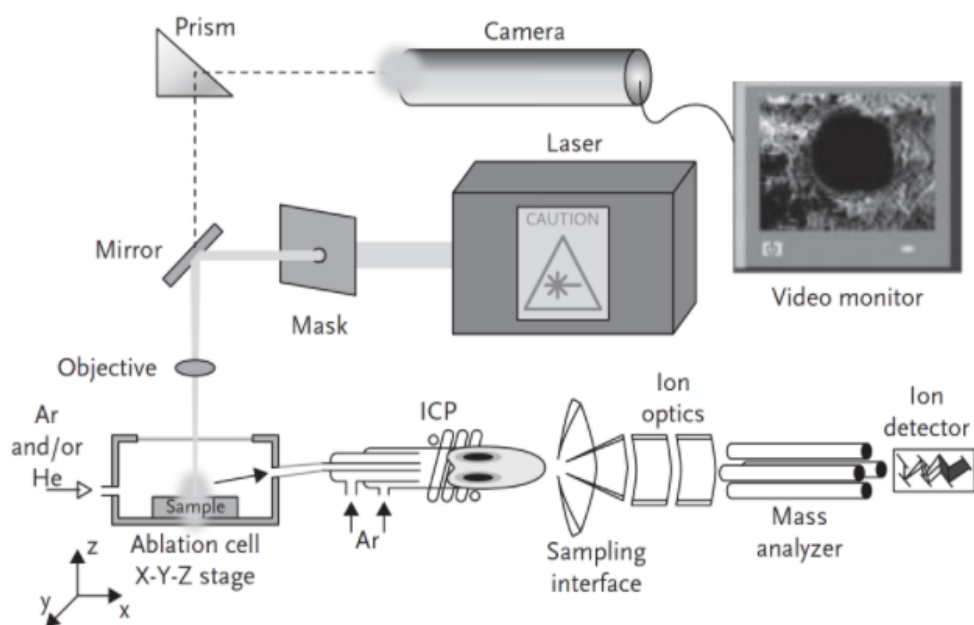


Figure 4.4. Schematic diagram of a Laser Ablation ICP-MS system (Ghent University Department of Chemistry, 2020).

Two in-situ methods were used in this study: (i) spot analyses, wherein a small amount of sample material is ablated by the laser from a defined location with a specific shape and size (e.g. a 20 μm circle) and analysed by the ICP-MS, and (ii) raster element mapping, conducted using the ablation of a suite of user-defined parallel continuous lines (10 μm in width), usually defining a rectangle or a square (e.g. 500 μm x 500 μm). Datasets acquired during this study included spot analyses on samples of pyrite and pyrrhotite from Appin and Argyll Group formations of County Donegal in *Chapter Seven* which allowed for key trace element abundances and ratios to be determined, and raster element mapping of Curraghinalt ‘ore-stage’ pyrite described in *Section 5.11.iii.* which reveals the extent of Au-bearing cataclastic micro-fracture networks. The results for spot analyses were processed quantitatively using a Fe standard data acquired using EDS/EDX analyses, while maps were processed semi-quantitatively, accounting for the presence of adjacent non-sulphide material with different physical and chemical properties. The interpretation of results from LA ICP-MS spot analyses was aided by the use of IoGAS (Reflex, Australia), a software package which allows for the computation and export of statistical information and plots.

4.1.iii. Advantages and limitations of EDS/EDX and LA ICP-MS techniques

Technique selection was motivated and necessitated by the requirements of specific questions and tasks at hand, in light of the advantages and limitations of those techniques.

EDS/EDX proved a vital petrographic tool for both targeted and systematic tasks in addition to early reconnaissance exploratory work. For mineral phases such as pyrite, chalcopyrite and galena and for those occupying the rock matrix (e.g. chlorite, monazite), the abundances of major elements within those phases was determinable using this method. Individual micro-fractures of pyrite could be targeted using the SEM, allowing for the identification of minerals (e.g. tellurides) and the sequence of their emplacement (see *Chapter*

Five). EDS/EDX mapping of minerals phases (e.g. pyrite) was undertaken to examine the distribution of major elements and inclusions (e.g. galena). EDS/EDX analyses are suitable for such tasks due to the precision with which such analyses can be targeted using the SEM. However, this method cannot be used to examine trace element concentrations, such as those recorded within the lattice of pyrite, due to its relatively high detection limits.

Detection limits

EDS/EDX has the capability of detecting element concentrations in bulk materials above 0.1 wt% (1,000 ppm); trace element concentrations defined as those below 0.01 wt% are therefore below the limits of detection (Nasrazadani and Hassani, 2016). For the task of determining concentrations within pyrite, LA ICP-MS was more appropriate as detection limits, depending on a number of factors, may be one to four orders of magnitude lower than those achievable using EDS/EDX. For LA ICP-MS, detection limits vary depending on the volume of ablated material, analyte mass, ionisation energy of the analyte, its isotopic abundance and ion transmission efficiency for each individual analysis; aerosol size distribution and transport efficiency while in transit to the ICP-MS are also factors (Rodushkin and Axelsson, 2003 in Limbeck et al., 2015).

Two methods are used to calculate the limit of detection in LA ICP-MS: proposed by Longerich et al. (1996) and described in Petrus et al. (2017), the first is as follows:

$$\text{LOD} = \frac{3\sigma_b}{S} \sqrt{\frac{1}{N_a} + \frac{1}{N_b}}$$

(LOD = limit of detection, σ_b = standard background deviation, S = sensitivity, N_a = numbers of analyses (pixels), N_b = number of background samples derived from a blank map).

The second method proposed by Pettke et al. (2012) (described in Petrus et al., 2017) is as follows :

$$\text{LOD} = \frac{3.29 \left[R_b \times DT \times N_a \left(1 + \frac{N_a}{N_b} \right) \right]^{1/2} + 2.71}{N_a \times DT \times S}$$

(LOD = limit of detection, R_b = background count rate, DT = analyte dwell time, N_a , N_b and S are as previous, while 3.29 and 2.71 are from a choice of a 95% confidence level and Poisson distribution).

As stated by Petrus et al. (2017), both equations depend on a series of factors which vary from analysis to analysis, therefore limits of detection are unique to each individual measurement.

Considerations regarding limits of detection present LA ICP-MS as advantageous over EDS/EDX analyses for the specific tasks of detecting trace concentrations within the lattice of host minerals (e.g. pyrite) and mapping their distributions.

Raster element mapping

Both EDS/EDX and LA ICP-MS methods were used for raster element mapping, to visualise (most commonly semi-quantitatively) the distributions of analytes and mineral phases. The resolution of rendered images for both methods is largely a function of time and resources (e.g. carrier gasses); the higher the resolution required, the longer the running time of the experiment and the greater the resources required to complete it.

Using EDS/EDX in tandem with the SEM, high quality raster element maps can be rendered at the scale of grains (e.g. of Fe and S in pyrite at Cloonacool, see *Section 6.5.ii*) and at the scale of minerals situated within individual micro-fractures (e.g. of Bi, Ag and Te in pyrite micro-fractures at Curraghinalt, see *Section 5.9*). LA ICP-MS raster element mapping

was used to analyse distributions of trace elements, taking advantage of lower detection limits offered by this technique, as aforementioned. LA ICP-MS maps may appear pixelated where a large spot size is selected for a region of interest, and at a higher resolution where a smaller spot size is used, or a larger region of interest selected.

Spectral interferences

Interferences, whereby a spectral overlap occurs between isobaric and polyatomic species, present a limitation in both EDS/EDX and LA ICP-MS methods, however strategies are available to alleviate these and overcome this issue which have been used in this study. For ICP-MS this is of particular concern. Spectral interference is considered to be largely matrix-dependent and specific to individual analysis. They are caused by atomic or molecular ions with the same mass-to-charge as analytes of interest (May and Wiedmeyer, 1998); an example of this would be an interference between the ^{78}Se isotope and argon, a gas used during experiments (^{40}Ar , $^{38}\text{Ar}^+$). The formation of interfering species, loss or contamination of target analytes is to be avoided in the design of experiments; non-instrumental approaches, alternate methods of introducing samples, modification of instruments and high-resolution ICP-MS are among recommendations to reduce spectral interference (Lum and Leung, 2016). A signal-smoothing device developed in-house is used optionally in this study to eliminate interferences: this enhances the sensitivity of the signal and reduces oxide formation through the introduction of a flow (e.g. 7 ml/min) of N_2 to the sample-gas mixture.

For EDS/EDX, one strategy to alleviate interferences concerns coatings in sample preparation: a coating is applied to thin sections in order to make them conductive. X-rays are produced from the coating material; while a carbon, Au, Pt or other conductive coating may be applied, a carbon coating is deemed most appropriate as it minimises spectral interference (e.g. Microscopy Australia, 2016).

Reducing sampling time

The use of the Aerosol Rapid Introduction System (ARIS) in certain experiments conducted in this thesis, connecting the HelEx II laser ablation cell to the ICP-MS instrument, enables minimal transfer volume to be delivered directly to the torch without using internal valves. This provides a fast washout, reducing the dead volume inside the cell. This is advantageous to the user in lowering the sampling time (Teledyne Cetac Technologies, 2020) with implications for additional spot analyses within sessions and higher resolution raster element mapping.

4.1.iv. Additional methods

A limited set of supporting Electron Micro-Probe Analyses (EMPA) were conducted as part of this study at the University of New Brunswick in Fredericton, Canada to examine Fe content of pyrite, methods are described within *Chapter Five*.

The Leapfrog 3D modelling package (Seequent, New Zealand) was used in *Chapter Six* specifically for the visualisation of drill-hole data and the location of samples as demonstrated in *Section 6.4.i.* of this thesis, however macro-scale geological modelling (e.g. of lithology, structure) was not undertaken as this was deemed to be beyond the parameters of this micro-analytical study.

4.1.v. Rationale for not using certain methods

Certain analytical techniques which have contributed immensely to the science of ore deposit research are not undertaken in this study.

Alternative (or additional) techniques not selected as part of this work include fluid inclusion analysis of quartz within veins (e.g. Wilkinson, 2001), structural field-work (e.g. Deng et al., 2015), in-situ geochronology (e.g. Rice et al., 2016), S-isotope geochemistry (e.g. LaFlamme et al., 2018) and palaeo-continental reconstruction (e.g. Xiao et al., 2015). Some of these techniques have been used extensively in the past, providing a foundation of knowledge on chronologies of mineral emplacement events, discrimination of potential sources and useful insights into ore-forming processes. It could be considered that omission of certain methods places limitations on interpretations and models presented; however it is the view of the author that while these techniques were not deemed to be necessary to address questions in this thesis, they may serve to *test* and *augment* proposed models in future studies.

Characterisation of fluid inclusions (e.g. Wilkinson et al., 1999) is considered beyond the scope of this study. Such an approach is recommended for future work, e.g., to characterise precursor fluids associated with precursor pyrite generations at Curraghinalt (see *Chapter Five*). Examination of fluids from different stratigraphic levels within the Dalradian Supergroup (e.g. the Appin and Argyll Groups) would also be a worthwhile next step in testing and augmenting proposed models.

Studies of the structural deformation history pursued historically in the north-west of Ireland and in Scotland (e.g. Chew and Strachan, 2014) provide a key reference point to this work. It is considered that characterisation of the relationship of veins to episodes of the Grampian Orogeny would benefit from systematic examination of vein/fabric relationships from the scale of an individual gold occurrence to that of an inlier. The

examination of regional-scale structures (e.g. of nappes and thrusts north-west of the Sperrins Inlier) and associated quartz veining is recommended by this study.

The timing of pyrite generations is presented in this study in *relative* terms (e.g. at Curraghinalt, see *Chapter Five*). Mobility of trace elements recorded within those phases at a prospect or deposit can be related to phases in the regional deformation history through the petrographic examination of their relationship to host rock fabrics. Geochronological studies of minerals encapsulated by encountered pyrite generations, e.g. the dating of muscovite in Curraghinalt Py₂ using ⁴⁰Ar/³⁹Ar (e.g. Cao et al., 2018), may provide a temporal constraint on early trace element mobility in absolute terms, in addition to a relative constraint linked to deformation.

Advancing methodology in the use of S-isotopes is demonstrably valuable in discriminating sources of metals for a variety of deposit types (e.g. LaFlamme et al., 2018). Sulphur data has been acquired in previous research (e.g. Earls et al., 1996) which provides evidence of multiple sources of gold in the Sperrins Inlier.

Data available in the literature for the relative positioning of palaeo-continents during the Caledonian Orogenic Cycle have been used as a reference, however engaging in reconstructions as part of this study was not pertinent to answering research questions. Future students may find online materials available at www.deeptimemaps.com (by Colorado Plateau Geosystems, Inc., USA) a useful resource.

Innovative and powerful new techniques in the realm of ‘big data’ are being developed. Such methods may be applied to large datasets available from the inter-governmental Tellus survey (Lusty et al., 2009). The use of artificial intelligence to form predictions based on large datasets of particular intrigue in the contemporary debate of how to secure vital resources (KoBold Metals, 2020). However, engagement with those methods lies beyond the scope of this project and is conceptually different to the targeted approach taken by this study.

4.2. Proof of concept

It was hypothesised during the development of the project that chemical zonation of pyrite, such as that observed within significant orogenic gold deposits encountered in the literature (e.g. Large et al., 2009; Velásquez et al., 2014) is observable in the Irish-Scottish Caledonides, and should preserve the history of metal and trace element mobility during orogenesis. An experiment was designed to both test this hypothesis and provide quantitative information as a ‘control’ by chemically mapping a regional sample of pyrite, distal to any known Au mineralisation. One such sample analysed by Laser Ablation ICP-MS was a grain designated ‘AR03a_1’, an euhedral pyrite porphyroblast hosted by metasedimentary rocks of the Dalradian Supergroup on the Isle of Arran, Scotland (see Figure 4.5), approximately 10km SW of Lochranza at the north-western corner of the island and proximal (within 1km) to the Highland Boundary Fault (suture of the Grampian orogen).



Figure 4.5. (A) The location of the sample area in the context of the Western Isles of Scotland, (B) location of the area in map 'A' in relation to Britain and Ireland (base maps from scribblemaps.com).

Element raster mapping was conducted using the Laser Ablation ICP-MS system described in *Section 4.1.ii.* with the ablation cell retrofitted with a Teledyne Cetac Aerosol

Rapid Introduction System (ARIS), connecting the ablation cell to the ICP-MS torch. Analyses were performed by ablating lines using a 10 μm beam, proceeding as a continuous profile at 60 $\mu\text{m}/\text{sec}$ with a repetition rate of 50 Hz and a fluence of 1.5 J/cm^2 , all other parameters being kept constant. Analytes selected were ^{51}V , ^{55}Mn , ^{59}Co , ^{60}Ni , ^{63}Cu , ^{75}Ag , ^{77}Se , ^{95}Mo , ^{107}As , ^{121}Sb , ^{125}Te , ^{197}Au , ^{202}Hg , ^{208}Pb and ^{209}Bi , with dwell times across the mass range constant (0.02 s). Data were calibrated with line analyses of NIST 612, BCR-2G glass standards and the MASS-1 sulphide standard. Data reduction was performed using Iolite ('trace element' data reduction scheme), and element maps produced using Cellspace.

Five distinct growth zones were identified (see Figure 4.6) with respect to Ag, As, Bi, Co, Cu, Mo, Ni and Se. The core (Py_1) of the grain is relatively depleted in Ag, Bi, Co, Cu, and Se, with a rim enriched in Cu and Co (yellow band). A distinct banding (possible S_0 banding or early S_1 fabric) is observed with respect to the Ni distribution in the core, and correlates with the distribution patterns of As and Co. A second pyrite growth zone (Py_2) is clearly evident with elevated As, Bi, Co and Se contents. The third zone (Py_3) is demarcated by sharply elevated Ni contents, and forms the approximate inner boundary limit of elevated Se contents in the grain; outer growths are relatively depleted. A fourth zone of pyrite (Py_4) has slightly elevated Ni contents, and marks the limit of elevated contents for the grain. The outermost zone of pyrite (Py_5) is depleted in Bi, Co and Mo, but elevated concentrations (Cu, Mo, and Ag) do occur on the outer rims of the pyrite grain. A possible sixth boundary within Py_5 is also observed, characterised by elevated As near the top of the grain featured here. Au was below the instrumental detection limit, which was predicted given the location, distal to any known Au mineralisation.

Chemical mapping of this sample by Laser Ablation ICP-MS revealed a strong zonation, which preserves distinct trace-element signatures consistent with evolving metamorphic fluids. This proof of concept experiment demonstrates the potential of

chemical analyses of pyrite to elucidate information on metalliferous mobility as metamorphic-hydrothermal fluids interacted with the Grampian terrane during orogenesis.

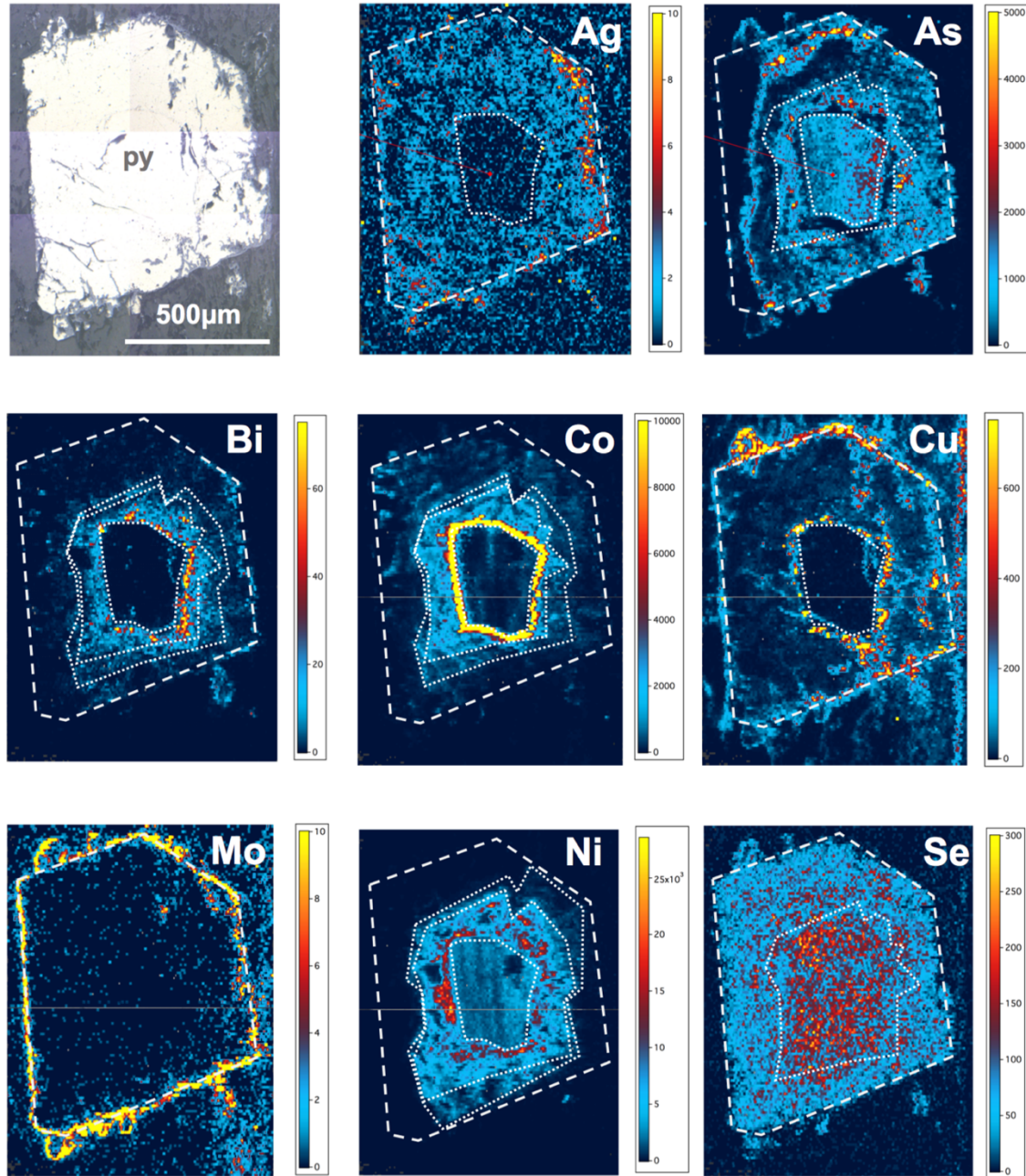


Figure 4.6. Sample AR03a_1 Laser Ablation ICP-MS raster element maps showing the distribution of selected analytes (Ag, As, Bi, Co, Cu, Mo, Ni and Se) in parts per million (ppm). Long dashed line annotation indicates the boundary of the grain, while short dashed annotation indicates the zone boundaries within it, as suggested by the relative enrichment and depletion of recorded element concentrations. A reflected light image of the grain is shown for reference at the top-left.

Chapter Five: Polymetallic emplacement associated with deformation during the Grampian Orogeny: geochemical evidence from the Curraghinalt gold deposit, Northern Ireland

5.1. Abstract

Curraghinalt, located 17km NE of Omagh in the Sperrin Mountains of Northern Ireland, is an orogeny-associated gold deposit contained within a WNW-ENE trending swarm of steeply dipping (55-70° toward NE) quartz-carbonate veins, hosted by metamorphic rocks of the Neoproterozoic-Cambrian Dalradian Supergroup. These rocks were uplifted and deformed during the Grampian arc-continent collisional phase (475-460 Ma) of the Caledonian-Appalachian Orogenic Cycle (475-405 Ma). Visible gold has a recognised association with pyrite, the dominant sulphide mineral encountered. Analyses of pyrite using in-situ Energy Dispersive X-Ray Spectroscopy (EDS/EDX), Electron Micro-Probe Analysis (EMPA) and Laser Ablation Inductively Coupled Plasma - Mass Spectroscopy (LA ICP-MS) reveal evidence for three distinct generations (Py₁₋₃) which constrain the relative timing of emplacement to episodes in the regional deformation history. Py₁ within early veins is

broadly aligned with regional S₂/S₃ Grampian fabrics and records an early Zn-Ni signature (median Zn 5,030 ppm, n=35; Ni 2,410 ppm, n=35), while Py₂ overgrowths have an entrained schistosity indicating growth during prograde development of these fabrics; Au is elevated in Py₂ with a median of 3.69 ppm (IQR 2.02-10.1 ppm; n=34) and is coincident with elevated Co, Ni and As. Py₃, occurring within the vein swarm cutting the host penetrative fabric, exhibits elevated Ni (median 126 ppm, IQR 16.3-337 ppm; n=128). Gold particles are encountered within micro-fractures of Py₃ which this study proposes have been exploited by a late fluid, precipitating with Bi- and Ag- tellurides, along with chalcopyrite. Observations suggest that visible Au may be restricted to this late fluid, a departure from previous paragenetic interpretations. The presence of relatively elevated Au within early Py₂ may be an indicator of prolonged mobility in system fluids, while the identification of auriferous pyrite generations in early veins may be diagnostic of world-class orogenic Au systems.

5.2. Introduction

Gold deposits within the orogenic class account for approximately 40% of global gold endowment and are therefore economically significant (Goldfarb, 2017). While our understanding of these deposits has developed appreciably in recent decades in terms of tectonics and metamorphism (Goldfarb et al., 2001; Goldfarb et al., 1998; Groves et al., 2003; Pitcairn et al., 2014; Wyman et al., 2016), metal mobility and transport mechanisms (Garofalo et al., 2014; Kerrich and Fyfe, 1981; Klein, 2014; Phillips and Powell, 2010; Pitcairn et al., 2014; Pitcairn et al., 2006), host minerals (Large et al., 2012; Large et al., 2009; Li et al., 2014) and distinguishing characteristics from other types of systems (Hart and Goldfarb, 2005), questions remain, particularly with respect to the relationship of gold emplacement to deformation, transport processes and sources of metals. This is particularly

pertinent to systems where there may be additional complexities, for example due to the presence of proximal volcanic arc terranes, or periodically reactivated structures. Supported by petrographic constraints, advancing techniques in retrieving trace element geochemical records preserved within sulphide minerals offer a suitable method of constraining metal enrichment to specific events in the evolution of an orogeny.

Pyrite, commonly associated with gold in this deposit class, has the capacity to retain diagenetic and hydrothermal chemical signatures within growth zones attributable to specific events (Large et al., 2009; Li et al., 2019; Li et al., 2014; Velásquez et al., 2014). Advancing microanalytical approaches toward extracting this information, including LA ICP-MS techniques, present an opportunity to significantly augment our understanding of metal mobility and emplacement of vein-hosted orogeny-associated gold deposits, along with a potential tool for prediction. The central objective of this contribution is to devise an augmented paragenetic sequence of metal emplacement at the Curraghinalt gold deposit in Northern Ireland, through the use of such techniques.

This study presents results obtained using in-situ EDS/EDX, EMPA and LA ICP-MS analyses of pyrite grains within resource-hosting veins which cross-cut regional S_2/S_3 Grampian fabrics, alongside grains contained within earlier syn-deformational, fabric-parallel veins previously considered to be an unlikely carrier of gold (e.g. Parnell et al., 2000). A revised paragenetic model considers the relationship between gold mobility, metamorphism and deformation at Curraghinalt, accounting for distinct metalliferous emplacement events. The relationship between Au, Ag and tellurides is examined, and a new interpretation of prolonged gold mobility across the system proposed.

5.3. Geological background

Gold deposits are identified in north-west Ireland and Central Scotland, adjacent to the approximately SW-NE trending Fair Head – Clew Bay Line (FH-CBL) and the contiguous Highland Boundary Fault (HBF) (Wilkinson et al., 1999), a lineament interpreted as a major fault zone active at various times throughout the Palaeozoic and considered a major control on deformation, magmatism, mineralisation and sedimentation (McCaffrey, 1997). This zone is understood to represent the suture of the Laurentian continental passive margin and an intra-oceanic arc, which collided during the Ordovician Grampian event (475-460 Ma) (Dewey and Shackleton, 1984) recognised as the initial phase of the Caledonian Orogenic Cycle (475-405 Ma) which culminated in the closure of the Iapetus Ocean (Chew et al., 2009b). Deposits hosted within quartz-carbonate vein networks are constrained to formations of the Dalradian Supergroup, a Neoproterozoic-Cambrian sedimentary basin (c. 800-515 Ma) which was uplifted and deformed during the Grampian event (Daly et al., 2009). Discrete deformation events are recognised within the Dalradian (D₁-D₄), of which D₃ (in the Sperrin Mountains Inlier of interest to this study) is associated with the Grampian metamorphic peak at greenschist to amphibolite facies conditions c. 468 Ma (Chew et al., 2009b; Fettes, 1979; Fettes et al., 1985).

Curraghinalt in County Tyrone, Northern Ireland (Figure 5.1) is the largest vein-hosted Au(-Ag) deposit thus far discovered and is the focus of this contribution; resources of 6.35 Mt at 15.02 g/t for 3.07 Moz contained Au in the indicated category, and 7.72 Mt at 12.24 g/t for 3.04 Moz contained Au in the inferred category have been estimated to date (SRK Consulting (Canada) Inc., 2018). While Curraghinalt is at an advanced stage of development, active mining is taking place at Cavanacaw, an adjacent Au-Ag-Pb deposit located approximately 30 km to the south-west (Parnell et al., 2000). Additional stratigraphically contiguous Au occurrences in Ireland are recognised along the trend in

Ireland, for example at Cloonacool within the Ox Mountains of Co. Sligo (Playfair Mining Ltd., 2016). An important Scottish example hosted by the Dalradian Supergroup is the Cononish Au-Ag deposit, near the village of Tyndrum approximately 70km NNW of Glasgow (Tanner, 2012).

5.4. Structural controls on gold distribution

Au distribution in the Sperrin Mountains Inlier is believed to be influenced by the presence of three principle regional structures (see Figure 5.1): the SSW-NNE trending Omagh Lineament, the SW-NE trending Omagh Thrust and the Sperrin Nappe (or ‘Sperrin Fold’), an F₂ recumbent antiform which has an ESE-WNW to SE-NW axial trace (Earls et al., 1996). Locally to Curraghinalt, E-W trending dextral strike-slip structures control the distribution of auriferous quartz veins (Tanner, 2014).

The first of the major structures, the Omagh Lineament (Figure 5.1c), is one of a suite of N-S to NNW-SSW trending ($\sim 12^\circ$ E) deep-crustal structures first conceptualised following mapping observation of lineaments at this orientation in County Donegal by Hutton and Alsop (1996), supported by patterns observed in Dalradian sedimentation and regional strike-swings from NE-SW to NNE-SSW (Earls et al., 2003). It is hypothesised by Earls et al (1996) that N-S structures acted as a control on sedimentation during the Neoproterozoic now exposed in the Sperrin Mountains region, and as reactivated conduits for gold mineralisation. Regional N-S trending mineralised veins are observed, for example at Cavanacaw (McFarlane et al., 2009). The predicted lineament has been substantiated by geophysical work conducted through the all-Ireland, multi-disciplinary ‘Tellus’ geological survey, with a linear magnetic anomaly identified at the predicted location and N-S to NNE-SSW orientation, theorised to reflect a dyke intruding along a pre-existing structure (Earls and Stewart, 2016).

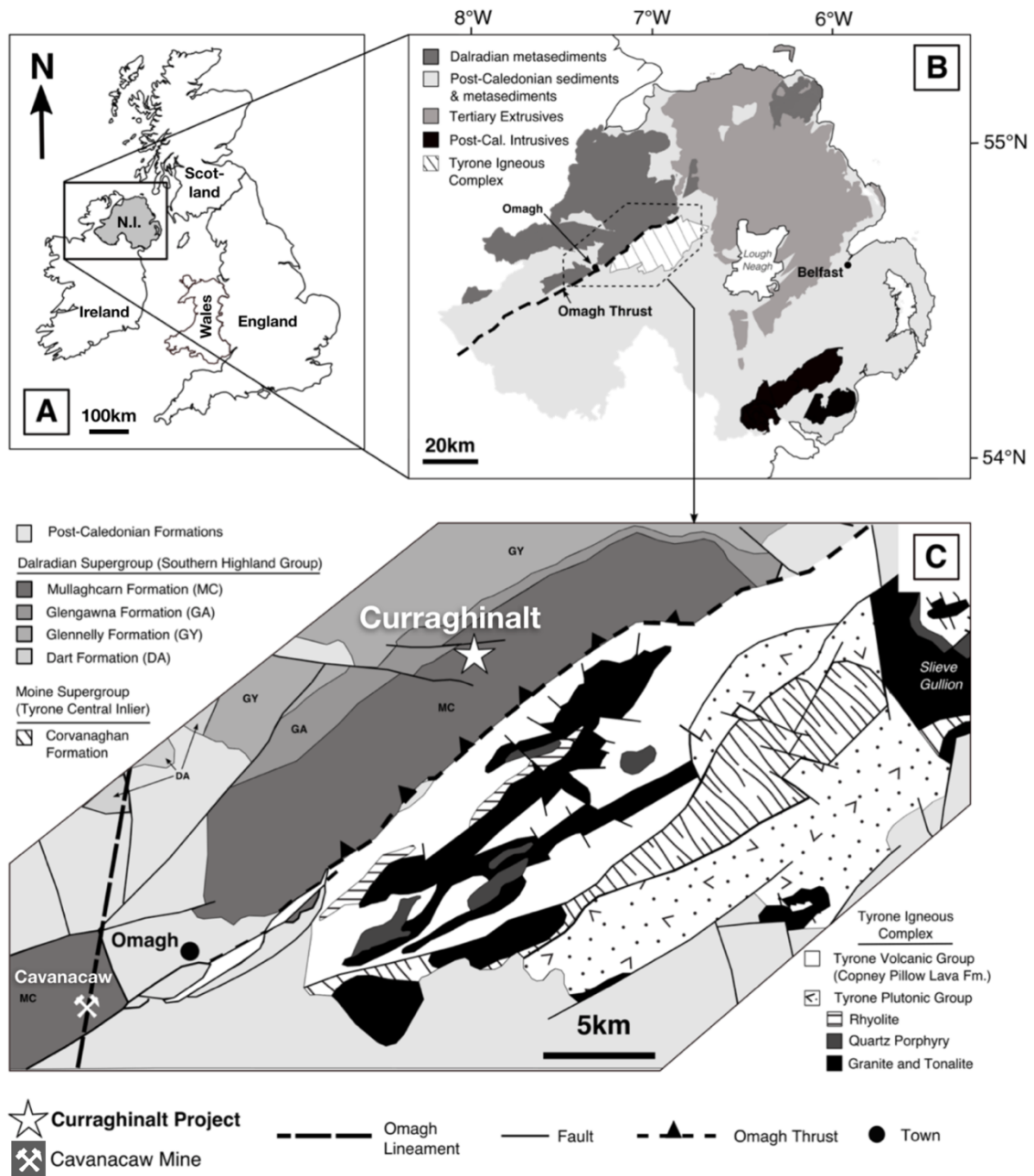


Figure 5.1. (A) Schematic map of the islands of Ireland and Britain, with Northern Ireland shaded; (B) generalised geology of Northern Ireland with relevant co-ordinates: Dalradian Supergroup formations to the north-west of the Omagh Thrust, of interest to this study, are marked in a dark grey. The Tyrone Igneous Complex is hatched, units of which are remnant of the island arc (SE) which collided with Laurentia (NW) during the Grampian episode (peak at 468 Ma) of the Caledonian Orogenic Cycle (475-405 Ma). The broad geographic area of interest in the Sperrin Mountains area is marked and expanded in map (C) (adapted from Mitchell, 2004); (C) The position of Curraghinalt and Cavanacaw deposits are designated in the context of local formations, with the generalised geology of the Tyrone Igneous Complex (TIC) to the south-east of the Omagh Thrust presented in additional detail (adapted from Rice et al., 2016 and Mitchell, 2004).

The Omagh Thrust (Figure 5.1b and Figure 5.1c) marks the suture where the island arc was subducted beneath the Laurentian margin during the Grampian episode. The Sperrin Mountains Inlier of Dalradian Supergroup (Laurentian) formations lie to the north-west, while the Tyrone Igneous Complex (TIC) to the south-east comprises arc-related rocks and supra-subduction zone ophiolitic components (Hollis et al., 2011). According to Earls et al. (1996), the thrust dips gently to the NW, with observed lineations within mylonites plunging consistently toward WNW, indicating oblique dextral-thrust motion.

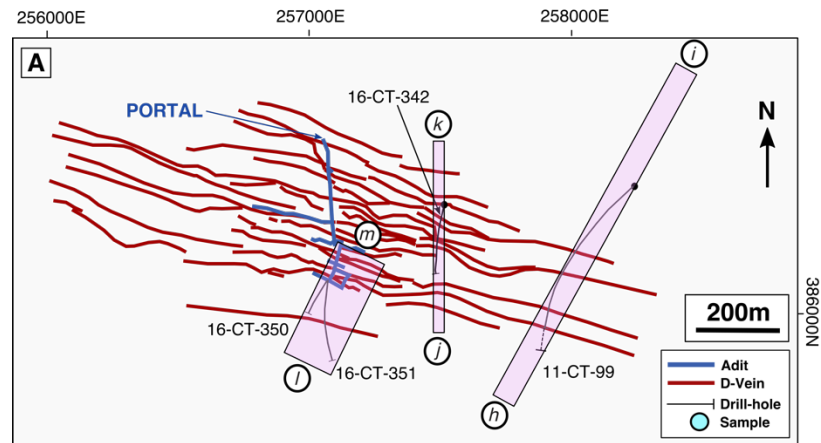
An overturned, tight to isoclinal F_2 fold known as the ‘Sperrin Nappe’ to the north-west controls the geometry of Southern Highland and Argyll Groups proximal to the Omagh Thrust. Curraghinalt veins are located on the SE limb of this fold, at the boundary of the Mullaghcarn and Glengawna Formations (see Figure 5.1c). Hutton and Alsop (1996) suggest that the collapse of the Sperrin Nappe during the later stages of the Grampian arc-continent collision may have led to fluid being released during downdip extension of the Omagh Thrust hanging wall.

Integration of data from field mapping, prospecting, fluid inclusion work, geochemical and geophysical surveys has led to a robust understanding of the significance of these structures in both metal emplacement and controls on the Dalradian Supergroup across the Sperrins (Earls and Stewart, 2016).

5.5. Vein architecture and host stratigraphy

The estimated resource at Curraghinalt is confined to a stacked swarm of quartz-carbonate-sulphide ‘shear-veins’ (referred to by commercial operators as ‘D-veins’, part of a naming system applicable to resource modelling which includes specific identifiers for contiguous vein envelopes e.g. ‘Crow’, ‘Bend’) which dip at between 55° and 75° to the north-east and cross-cut regional S_2/S_3 composite Grampian fabrics (Figure 5.2). These are

PLAN VIEW :



CROSS SECTIONS :

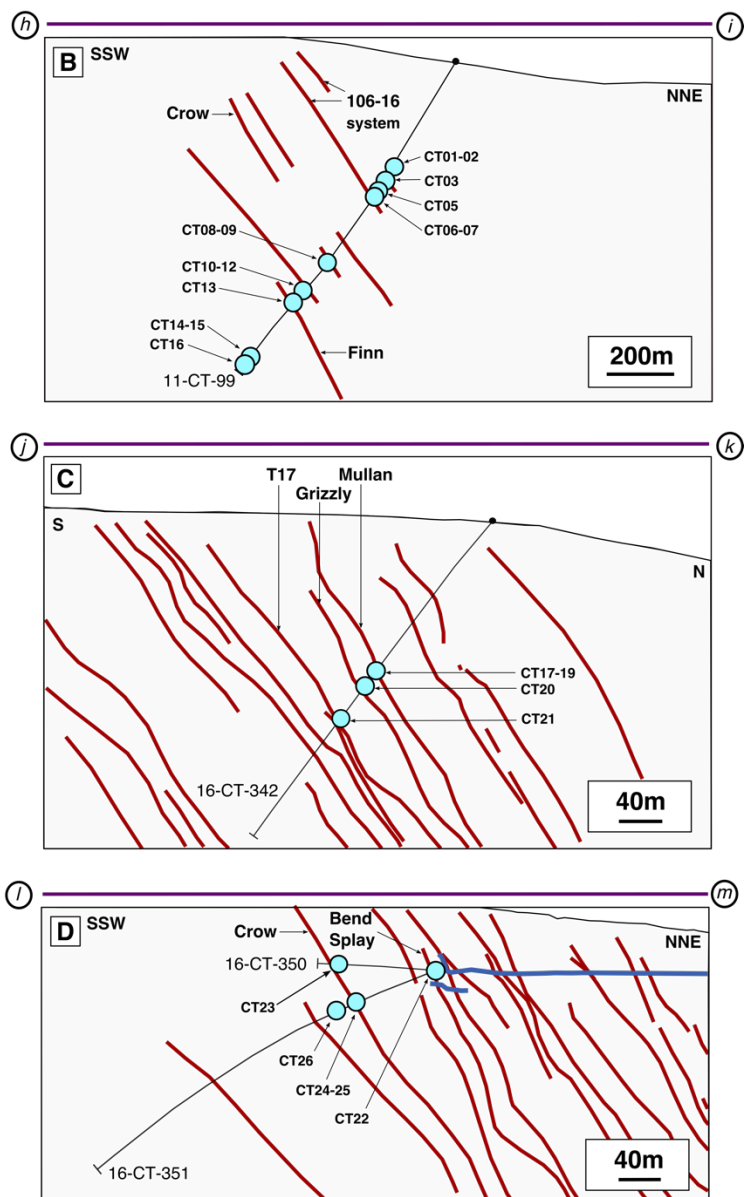


Figure caption overleaf

Figure 5.2. (A) Sampled drill-holes, geometry of the principle WNW-ESE trending Curraghinalt vein swarm (resource-associated shear-vein zones). The approximately N-S trending adit is shown in dark blue; (B) SSW- NNE cross-section of drill-hole 11-CT-99 (looking WNW), with locations of samples CT01-CT16 retrieved from ‘106-16 system’, ‘Finn’ and ‘Crow’ indicated; (C) S-N cross-section of drill-hole 16-CT-342 (looking W) with locations of samples CT17-21 of the ‘Mullan’, ‘Grizzly’ and ‘T17’ veins; (D) SSW-NNE cross-section of drill-holes 16-CT-350 and 16-CT-351 (samples CT22-CT26), which included material from ‘Bend Splay’ and ‘Crow’. Peak metamorphism is associated with final Grampian compressional phase and D₃ deformation, the timing of which, inferred from studies in western Ireland, is constrained to c. 468 Ma (Chew, 2009). Adapted and attributed from maps and cross-sections provided by Dalradian Resources Ltd.

associated with arrays of narrow extensional veinlets (‘C-veins’). Shear-veins vary in width from the centimetre-scale to over 3 metres and have been traced along strike over 1,900m and to depths downdip of approximately 1,000 m (SRK Consulting (Canada) Inc., 2018). An earlier set of ‘metamorphic’ quartz veins occurring sub-parallel to fabrics have also been recognised (Parnell et al, 2000).

The Curraghinalt shear-vein swarm is located approximately 4 km north of the Omagh Thrust, hosted by semi-pelites of the Mullaghcarn Formation, close to the boundaries of graphitic pelites of the underlying Glengawna Formation (see Figure 5.1c) (Earls et al., 2003). The parent unit of the Mullaghcarn and the Glengawna formations is listed presently by the British Geological Survey (2020) lexicon as the Southern Highland Group, referencing the work of Arthurs (1976) and Hartley (1937). This view is supported by Smith and Johnston (1994). However, the exact stratigraphic positioning of these formations is the subject of debate: they are placed by Alsop and Hutton (1993) within the Argyll Group, also proposing that they be grouped within a wider ‘Sperrin Formation’. Long (1997) support the view that they reside within the Argyll Group and more specifically suggest that strata in the southern Sperrins area lie within the Easdale Subgroup.

Locally, two E-W shears are observed intersecting the swarm: the Kiln Shear and to the south, the Crow Shear. These are considered to be consistent with a lateral ramp in the

footwall of the Omagh Thrust, with dextral movement on those shears generating extensional structures, providing favourable pathways for fluid mobility (Parnell et al., 2000).

Mineral assemblages recognised across the Sperrin Mountains Inlier of the Dalradian Supergroup include albite, muscovite, biotite, epidote, chlorite and actinolite, suggesting widespread upper greenschist-facies metamorphic conditions (Hartley, 1937), however the presence of garnet porphyroblasts within the southern Sperrins suggest a localised relatively higher grade of metamorphism. It is suggested that chloritic rims of these porphyroblasts may indicate a retrogressive stage linked to activity of the Omagh Thrust during the late Caledonian (Cooper and Johnston, 2004 in Mitchell, 2004).

The host Mullaghcarn Formation is described petrographically in a study by Arthurs (1976) as a 4 km wide zone of muscovite quartz-schists with a shallow overall dip to the north, which have been thrust to the south over the Tyrone Igneous Complex by the Omagh Thrust (Figure 5.1c). These rocks are described in the study as pale grey in colour, containing metamorphic minerals including muscovite, biotite and chlorite, with rare garnet predominantly at its most southerly extent. Where chlorite is observed within specific horizons, these are referred to as 'green beds'.

The Glengawna Formation, underlying the Mullaghcarn, occupies a zone 500-1500 m in width and is also dominated by quartz-schists. Diagnostic of the Glengawna however are galena-bearing pale epidote quartz-schists and garnet bearing forms of graphitic schist. Evidence has been presented by Alsop and Hutton (1993) of graded bedding suggesting that the Mullaghcarn Formation is inverted, a finding supported by Arthurs (1976). It has been suggested that the contact between the two formations may lie to the north-west of the Curraghinalt adit, however more recent observation of graphitic pelites within the adit itself suggests it may lie to the south-east (Earls et al, 1996). In either case, it is likely that the contact lies proximal to Curraghinalt shear-veins hosting the deposit.

5.6. Mineralisation and fluids

Gold associated with the resource at Curraghinalt has been identified by previous workers principally as inclusions within pyrite grains and fractures: as discrete visible phases, alloyed with silver as fine-grained ‘electrum’ (Earls et al., 1996); the timing of emplacement has been constrained to a 10 Myr interval within the mid- to late- Ordovician (using methods including Re-Os dating of molybdenite within micro-shears cross-cutting host veins and sulphides; 462.7-452.8 Ma; Rice et al., 2016) and therefore late-orogenic with respect to the Grampian collisional event.

Previous work in ascribing mineralisation to a paragenetic sequence and determining potential system processes is largely supported by investigations of fluid inclusions within host quartz phases. Studies by Earls et al. (1996), Wilkinson et al. (1999) and Parnell et al. (2000) have revealed four such fluid events (Q_{1-4}) within host shear-veins; as veins cross-cut the S_2/S_3 Grampian fabrics, they are interpreted as post-dating the metamorphic peak. Q_2 (containing two-phase or three-phase $H_2O-CO_2-NaCl-KCl$ fluid inclusions; interpreted by the authors as possibly being compositionally magmatic) is reported by Wilkinson et al (1999) to be the most abundant phase carrying ‘primary Au’, while Q_3-Q_4 (containing liquid-vapour and monophasic-liquid $H_2O-NaCl-CaCl_2$ fluid inclusions), which has been observed to cross-cut pyrite grains, is interpreted to be a basinal brine associated with late remobilisation. Pyrite, arsenopyrite, chalcopyrite, tennantite-tetrahedrite and tellurides of Bi, Au-Ag, Hg and Pb along with auriferous electrum (e_1 , 930 – 980 ‰ fineness Au) have been attributed to Q_2 , while more Ag-rich electrum (e_2 , 800 – 890 ‰ fineness Au) occurring with tennantite-tetrahedrite, chalcopyrite, sphalerite, galena, ferroan carbonates and barite is associated with later Q_4 (Wilkinson et al., 1999). Earlier schistosity-parallel quartz veins have also been identified, however these were not attributed as a likely origin for Au mineralisation, based on low-pressure estimates of specific mineral inclusions (<1 kbar). A

biotite-bearing greenschist-facies assemblage was identified in association with those veins, suggesting contemporary pressure conditions of 4.5-5.5 kbar and temperatures of 450-500 °C (Parnell et al., 2000).

A black shale source for Au mineralisation along the Caledonian trend in both Ireland and Scotland has been suggested based on trace element geochemical studies of regional pyrite and sulphur isotopes (Parnell et al., 2017). This proposal is consistent with studies of orogenic systems in other parts of the world, for example, Au is recognised within growth zones in shale-hosted syn-sedimentary pyrite found in the Eastern Goldfields of Western Australia (Steadman et al., 2015).

While a magmatic origin for ‘primary gold’ has been evoked in previous studies based on fluid inclusion studies of quartz, the deposit architecture overall as described by previous workers nevertheless fulfils criteria for classification within the ‘orogenic’ class of Au deposits hosted by metamorphic rocks, which include (i) synchronicity with the late stages of compressional orogens, (ii) emplacement within zones of structural complexity adjacent to deep crustal faults, (iii) ore formation within veins (precipitated by fluids mobilised by major seismic events due to pressure fluctuations), and (iv) an association with greenschist facies conditions and retrograde pressure-temperature paths (Goldfarb et al, 2005).

5.7. Sampling and analytical methodology

5.7.i. Overview

26 samples of NQ-diameter (47.6mm) drill-core measuring between 5 and 21cm in length were obtained at the Curraghinalt deposit (see Figure 5.2). Sampling was designed to be representative, with material collected from sulphide-bearing vein and wall-rock material (Figure 5.3), including samples where vein/wall-rock boundaries were clearly visible (e.g. CT20). The locations of retrieved core included the most easterly extent of the known vein swarm from surface-collared drill-hole 11-CT-99 (including intercepts with the ‘106-16’ and ‘Finn’ veins (16 samples, CT01-16), the centre of the swarm from surface-collared drill-hole 16-CT-342 (including ‘Mullan’, ‘Grizzly’ and ‘T17’ veins; 5 samples, CT17-21) and the lower swarm to the south from two drill-holes collared underground within the adit, 16-CT-350 and 16-CT-351 (‘Bend Splay’ and ‘Crow’ veins; 5 samples, CT22-26). Cut slabs were prepared in the Geology Department, Trinity College Dublin (TCD) using a manual saw, which were then prepared as a set of 37 thin sections, 60 μm in width, by Thin Section Lab (Toul, France).

From these sections, petrographic and microanalytical work has been undertaken at iCRAG Lab@TCD and the Geochemistry Laboratories, TCD which included work using reflected light microscopy (occasionally denoted as ‘RL’ in this chapter), Scanning Electron Microscopy (SEM) methods and Laser Ablation Inductively Coupled Plasma - Mass Spectroscopy (LA ICP-MS) (spot analyses and raster element mapping). A supporting phase of work was conducted on samples using Electron Micro-Probe Analysis (EMPA) to record major element compositions, completed at the Microscopy and Microanalysis Facility, University of New Brunswick (UNB), Canada.

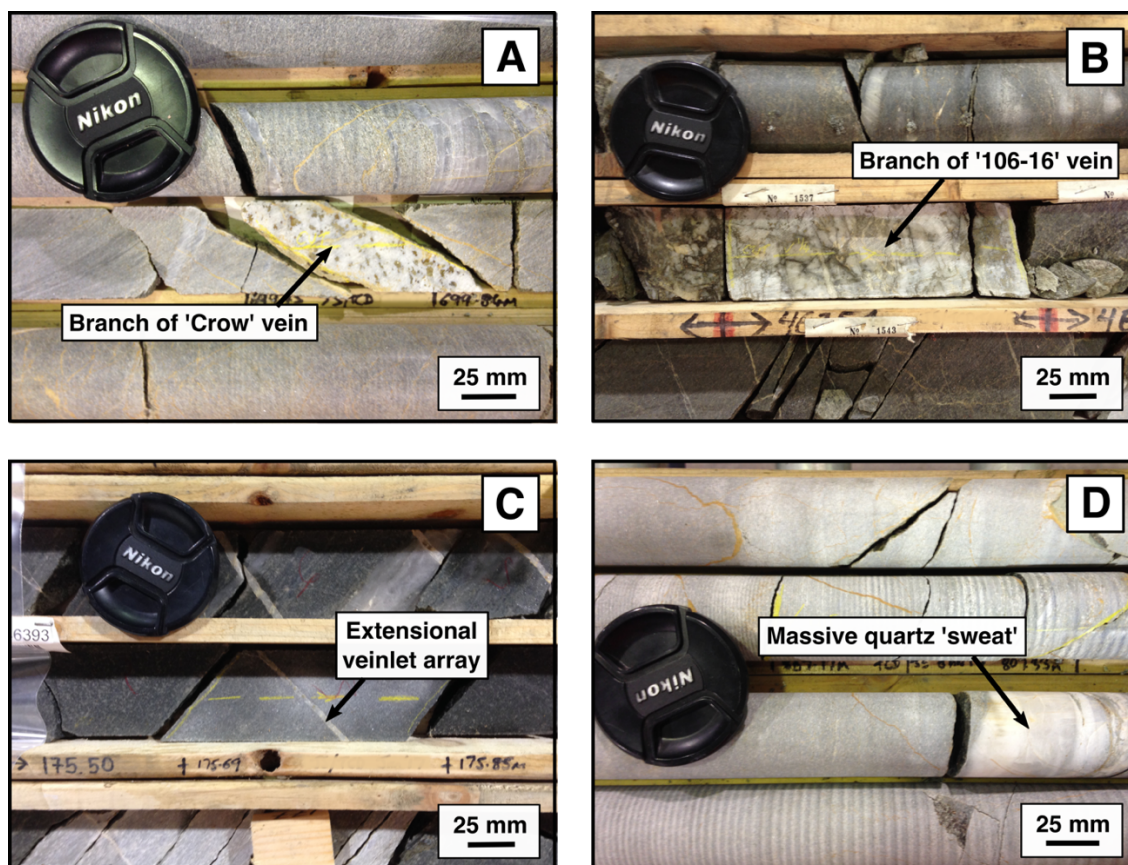


Figure 5.3. Examples of vein types observed at Curraghinalt in drill-core samples: (A) shear-vein, branch of ‘Crow’ (southerly part of the WNW-ESE trending vein swarm) hosted by psammite sub-perpendicular to host fabrics, containing disseminated pyrite (sample CT09, drill-hole 11-CT-99, 699.75-699.84m); (B) shear-vein, branch of ‘106-16’ vein system (central vein swarm) hosted by semi-pelite containing disseminated and stringer-type pyrite, multiple quartz phases are observed (sample CT06, drill-hole 11-CT-99, 467.51-467.71m); (C) part of an extensional array cross-cutting the semi-pelite host rock fabric (sample CT18, drill-hole 16-CT-342, 175.69-175.85m); (D) massive quartz ‘sweat’ hosted by psammite (sample CT11, drill-hole 11-CT-99, 807.17-807.33m).

5.7.ii. Reflected light microscopy

Petrographic examination of polished thin sections (60 μm) was conducted at iCrag Lab@TCD, using Olympus BX60 and Nikon Eclipse LV100 optical microscopes, both equipped with reflected light capability and a high-resolution camera system. Microscopic examination allowed for the determination of mineralogical compositions and the discerning of textural variations between

various growths of pyrite and associated sulphide minerals. The distribution of visible Au and other observable phases in samples was noted, while identification of textural differences, overgrowths and deformation allowed for an interpretation of the relative timing of mineralisation. The observation of relic grain boundaries noted by the presence of inclusion trails in pyrite grains was also recorded. Petrographic work using reflected light microscopy in conjunction with Scanning Electron Microscopy (SEM) aided the targeting of compositionally zoned grains for LA ICP-MS analysis.

5.7.iii. Scanning Electron Microscopy (SEM)

Mira 4 XMU and Mira 3 TIGER Variable Pressure Field Emission Scanning Electron Microscopes (SEM) (TESCAN, Czech Republic) at iCRAG Lab@TCD were used in this study, enabling high resolution examination of polished sections at high magnifications and the confirmation of mineral compositions in micro-scale grains associated with sulphides using Energy Dispersive X-ray Spectroscopy (EDS/EDX). For imaging and EDS/EDX analyses, the SEM was run at a voltage of 15-20 kV and a working distance of 15-18.5 mm; for cathodoluminescence (CL), 20mm was deemed appropriate. Images characterising sulphide textures and grain-gangue relationships were acquired using Everhart-Thornley (E-T), Backscattered Electron (BSE) and CL detectors (a TESCAN Panchromatic CL detector was used on the Mira 4, while a TESCAN Rainbow CL detector was used in Mira 3 TIGER analyses). A current of 300 pA was used for most analyses with the exception of CL studies which required high currents of up to 2.8 nA. Essence (TESCAN) and AZtec X-ray microanalysis software (Oxford Instruments, United Kingdom) were utilised for SEM operation, image acquisition and processing of EDS/EDX analyses. Two standard blocks were used: a custom block (#217) by Micro-Analysis Consultants (MAC) Ltd. (U.K.), and block MINM25-23 by Astimex Standards Ltd. (Canada). Instrument stability was monitored during analytical sessions through measurements of a cobalt puck within the MAC #217 standard block. All analyses were conducted at iCRAG Lab@TCD, Trinity College Dublin.

5.7.iv. Electron Microprobe Analysis (EMPA)

Analyses were conducted immediately adjacent to spot analyses of ore-stage Py₃ (n=154) (for S, Mn, Fe, Zn and In). Wavelength-Dispersive X-ray (WDX) spectrometric analyses provide a robust internal ⁵⁷Fe standard for the processing of data from individual Laser Ablation ICP-MS in situ analyses, to enable fully quantitative results with optimal precision and record major element compositions. EMPA was carried out using a JEOL 733 Electron Microprobe at the Microscopy and Microanalysis Facility, University of New Brunswick (Fredericton, Canada). Sphalerite, marcasite and troilite were used as calibration standards.

5.7.v. Laser Ablation ICP-MS spot analyses

In-situ analyses were completed on pyrite from 3 selected Curraghinalt samples: CT12, representing the earliest recognised veins in the system sub-parallel to the regional Grampian S₂/S₃ schistosity, CT20, from the ‘Grizzly’ shear-vein envelope sub-perpendicular to this fabric at the centre of the swarm, and CT24, retrieved from ‘Crow’, one of a series of shear-veins at the base (southern extent) of the system. Data is presented in this study for ⁵⁵Mn, ⁵⁹Co, ⁶⁰Ni, ⁶³Cu, ⁶⁶Zn, ⁷¹Ga, ⁷⁵As, ⁹⁵Mo, ¹⁰⁷Ag, ¹²¹Sb, ¹²⁵Te, ¹⁸²W, ¹⁹⁷Au, ²⁰²Hg, ²⁰⁵Tl, ²⁰⁸Pb and ²⁰⁹Bi. ⁵¹V, ⁷⁸Se and ¹¹³In were also analysed, however due to uncertainty relating to potential polyatomic interferences for ⁵¹V (with argon and nitrogen, gasses used in LA ICP-MS) and of ¹¹³In with ¹¹³Cd evidenced in cross-checks with internal standards, these results were rejected. Deleterious elements As, Sb and Hg are considered separately in presentation of results and discussions.

The median wt.% value of ⁵⁷Fe for tested Py₃ using Electron Microprobe Analysis (EMPA) was used for internal standardisation in all phases (47.1 wt.%). This was deemed appropriate as tested pyrite was found to be approaching a stoichiometric composition. Median values for selected analytes are presented for the three principle generations of pyrite

recognised (Py₁₋₃), along with median key diagnostic ratios (e.g. Au/Ag, Au/Te and Co/Ni) and enrichments >100ppm. Presented data do not preclude the possibility of micro-inclusions resulting in an elevated signature, e.g. of sphalerite and galena.

Analyses were performed using a G2 193 nm Excimer ArF laser (Teledyne Cetac, USA) with a HelEx II 2-volume cell coupled to an Elemental iCapQs mass spectrometer (ThermoFisher Scientific, USA) at the Geochemistry Laboratories, TCD. The ablation cell was retrofitted with a variable volume device developed in-house linking the cell to the ICP-MS torch. This device enables smoothing of the signal between the laser and the mass spectrometer, enhanced sensitivity of the signal and reduced oxide formation through the introduction of a flow of 7 ml/min of N₂ to the sample-gas mixture (Zhou et al., 2017). A spot size of 25µm x 25µm was used, with a repetition rate of 10 Hz and a fluence of 1.1 J/cm². Data were calibrated with analyses of NIST-610 and NIST-612 (National Institute of Standards and Technology, USA), BCR-2G (United States Geological Survey, USA) and MUL-ZnS (Montanuniversität Leoben, Austria) standards and a MASS-1 sulphide standard (United States Geological Survey, USA) using identical parameters. Sample pre-ablation and ablation was conducted in a He gas flow; while in transit to the ICP-MS, the ablated aerosol was mixed with Ar. Data were processed using Iolite 3.0 (Wavemetrics, USA) with consideration of the individual spot profiles; it was considered crucial that the full depth of ablation was accounted for and spikes which would indicate the ablation of an inclusion were recorded. Individual ⁵⁷Fe values specific to each spot were used as an internal standard, as recorded using Electron Microprobe Analysis (EMPA) where available. The IoGAS software package (Reflex, Australia) was used to interpret results.

5.7.vi. Laser Ablation ICP-MS trace element raster mapping

Line (raster) analyses were conducted from which semi-quantitative maps were produced; data are presented for mapping of 3 pyrite grains (2 of Py₁₋₂ grains, 1 of a Py₃ grain) on 2

polished thin sections (CT12 and CT20). Mapping was conducted to examine the relative difference in concentrations between generations, to reveal the internal crystallographic structure and fracturing of grains and to examine the positioning of auriferous particles with respect to this structure. Experiments were designed for a 1mm x 1mm area at a spot size of 10 μm x 10 μm , in order to maximise resolution, particularly in revealing the internal structure of grains and to minimize the influence of c.10 μm inclusions on output with adjacent pixels.

The ablation cell was retrofitted with an Aerosol Rapid Introduction System (ARIS; Teledyne Cetac, USA), which ensures fast washout by carrying the sample to the ICP-MS torch directly without using internal valves (Petrus et al., 2017; Zhou et al., 2017). Analyses were performed by ablating lines using a 10 μm beam, proceeding as a continuous profile at 60 $\mu\text{m}/\text{sec}$ with a repetition rate of 50 Hz and a fluence of 1.5 J/cm², all other parameters being kept constant. Analytes included ⁵⁵Mn, ⁵⁹Co, ⁶⁰Ni, ⁶³Cu, ⁶⁶Zn, ⁷¹Ga, ⁷⁵As, ⁹⁵Mo, ¹⁰⁷Ag, ¹²¹Sn, ¹²¹Sb, ¹²⁵Te, ¹⁸²W, ¹⁹⁷Au, ²⁰⁵Tl, ²⁰⁸Pb and ²⁰⁹Bi. Dwell times across the mass range were kept constant (25 ms). Data were calibrated with line analyses of NIST 612, BCR-2G glass standards and MASS-1 sulphide standard using a 10 μm beam. Sample pre-ablation and ablation was conducted in a He gas flow while in transit to the ICP-MS the ablated aerosol was mixed with Ar. Time-resolved mass spectrometric data were processed and Cellspace maps produced using Iolite 3.0 (University of Melbourne, Australia), in tandem with Igor Pro 6 (Wavemetrics, USA). The 'Trace_Elements' data reduction scheme was selected in Iolite using semi-quantitative mode. This mode was chosen as both grain and host matrix material were analysed in single maps. The MASS-1 sulphide standard was used as the reference material and a 5000 cps threshold used to mask low signals, reduced to zero where appropriate.

5.8. Pyrite petrography

Pyrite is the most abundant sulphide mineral within the Curraghinalt system: it is observed within all vein types and as discrete porphyroblasts in altered wall-rock. A variety of pyrite morphologies ranging from 10 μm to over 1 mm in size have been recognised, these include euhedral to anhedral forms in various deformation states along with their respective overgrowths. Three generations of pyrite can be discriminated using petrographic and mineral-chemical criteria, herein designated as Py_1 - Py_3 ; Py_3 is host to ore-stage mineralisation and associated with discrete phases of visible gold. A summary of petrographic observations for Py_{1-3} is presented in Table 5.1.

The earliest recognised phases of pyrite are Py_1 and overgrowths of Py_2 , observed within ankerite-quartz-sulphide veins which are transposed by an enveloping schistosity corresponding to the penetrative S_2/S_3 Grampian fabric (Figure 5.4A), and likely correspond to schistosity-parallel ‘metamorphic veins’ observed by Parnell et al (2000). Grains are highly angular and brittlely deformed, with Py_1 representing the internal phase and the earliest generation. Py_1 is characterised by coarse, subhedral and angular grain cores, largely recrystallised and optically homogenous. Grains are xenomorphic, evidence that growth was largely inhibited by gangue mineralogy within the vein, however imaging by cathodoluminescence (CL) demonstrates that Py_1 - Py_2 composite grains overgrow phases of quartz within host veins, annealing of pyrite suggesting minor re-equilibration under prograde conditions (Figure 5.5). This phase exhibits a broad alignment with the enveloping fabric, and contains micro-inclusions ($<10\ \mu\text{m}$) of galena and sphalerite occurring as clusters or aligned trails. These may be explained by exsolution from the pyrite matrix (e.g. Deditius et al., 2011), a hypothesis tested in this contribution using in-situ Laser Ablation ICP-MS methods.

Pyrite Phase	Py ₁	Py ₂	Py ₃
Stage	Pre-ore stage	Pre-ore stage	Ore stage
Visual characteristics	>1mm irregular xenomorphs, mostly homogenous.	External zone <1mm, irregular. Pitted, inclusions & silicates present.	Cataclastic masses >1mm, subhedral grains <100µm. Late Cp, Au-Ag and telluride infill of fractures.
Grain zonation	Internal geochemically distinct phase of simple-zoned grains	External geochemically distinct phase of simple-zoned grains	Simple or oscillatory zoned
Host vein type	S ₂ /S ₃ -parallel ankerite-quartz-sulphide veinlets	S ₂ /S ₃ -parallel ankerite-quartz-sulphide veinlets	Resource-associated quartz-ankerite-sulphide shear-veins oblique to S ₂ /S ₃ fabrics
Diagnostic inclusions	Fine galena + sphalerite	Al-silicates	Bi-telluride
Auriferous particles	Restricted to micro-fractures.	Restricted to micro-fractures.	Dominantly within micro-fractures and along grain boundaries

Table 5.1. A summary of petrographic observations for recognised generations of pyrite (Py₁, Py₂ and Py₃).

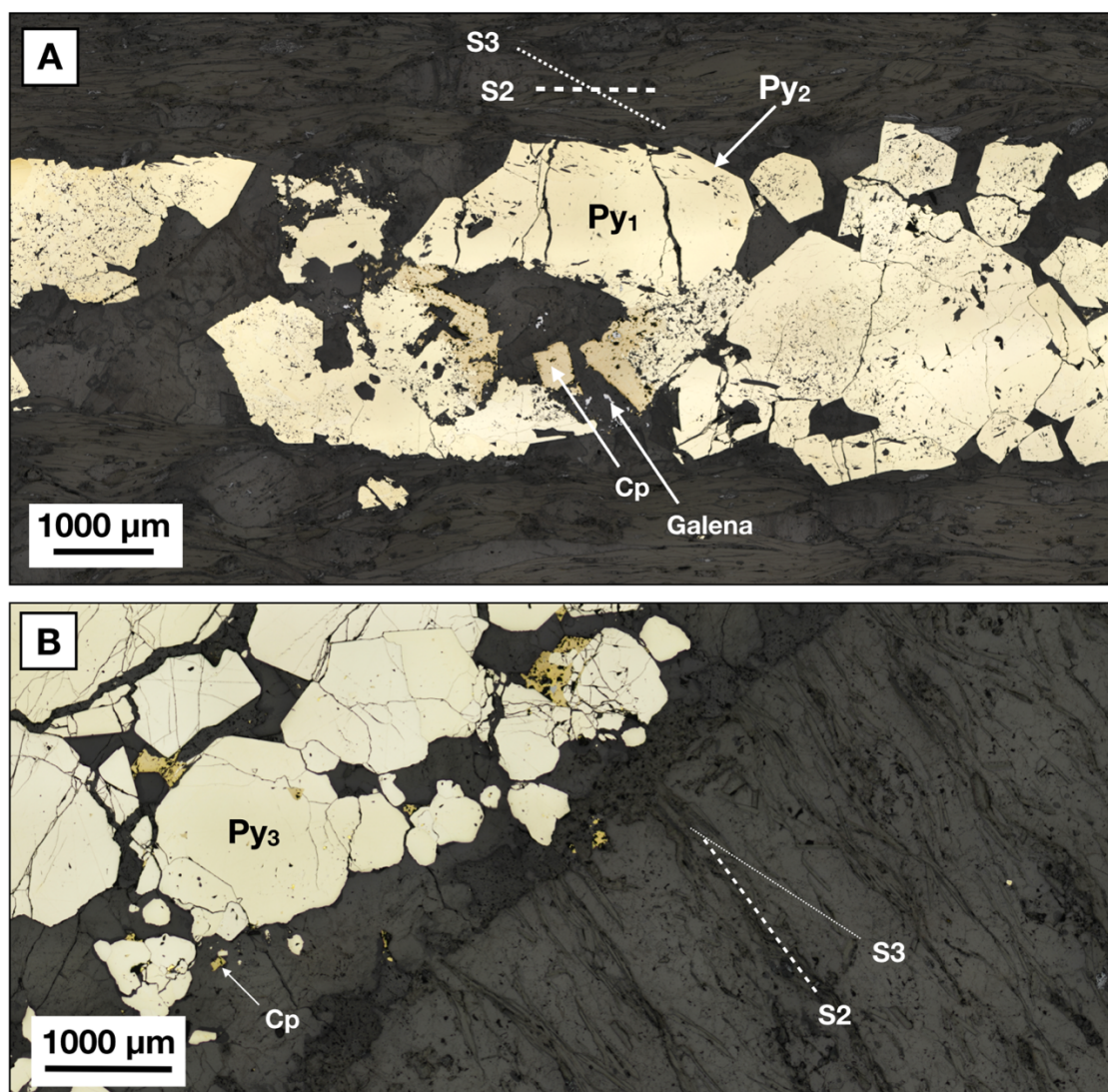


Figure 5.4. (A) Reflected light image of Py₁ and Py₂ overgrowth phase in S₂/S₃ fabric-parallel vein comprised of ankerite and quartz (sample CT12, drill-hole 11-CT-99, 819.04-819.24m); (B) oblique spatial relationship of quartzose vein hosting ore-phase Py₃ with the S₂/S₃ fabric of the host rock in sample CT20 (drill-hole 16-CT- 342, ‘Grizzly’ vein zone, 199.83-199.93m).

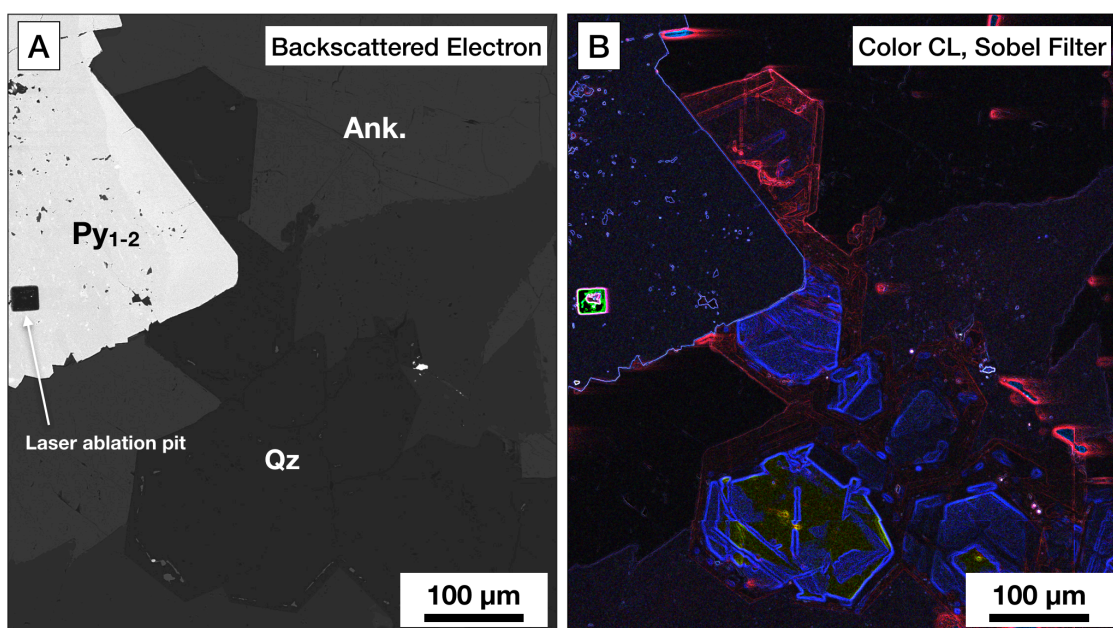


Figure 5.5. (A) Region of interest within S_2/S_3 fabric-parallel vein (sample CT12, drill-hole 11-CT-99, 819.04-819.24m) showing the relationship of a Py_{1-2} grain to the gangue minerals (quartz and ankerite); (B) colour cathodoluminescence (CL) image, with a Sobel filter applied to emphasise boundaries; pyrite is observed to overgrow quartz crystals which have formed an adjoining mass to the right of the image. A high voltage of 20 kV was used with an absorption current of 2.8 nA. The working distance was 19.85 mm with a scan speed setting of 9 (1.0 ms/pxl).

A second, sub-millimetric generation (Py_2) occurs as distinct growth zone surrounding Py_1 marked by inclusions of muscovite which exhibit aligned growth with S_3 fabrics in the enveloping schistosity. This concomitant growth strongly indicates that Py_2 is a late overgrowth of Py_1 . Such overgrowths may form as a response to increasing metamorphic grade (e.g. Craig et al., 1998) and may therefore be considered supporting evidence of prograde metamorphic conditions during growth of Py_2 . Both of these phases are cross-cut by fine sulphide-veinlets containing pyrite, chalcopyrite and auriferous particles, commonly associated with major fractures cross-cutting the host quartz-ankerite vein and sulphides. Chalcopyrite is observed replacing Py_2 within this vein type, whilst galena occurs independently within the micro-

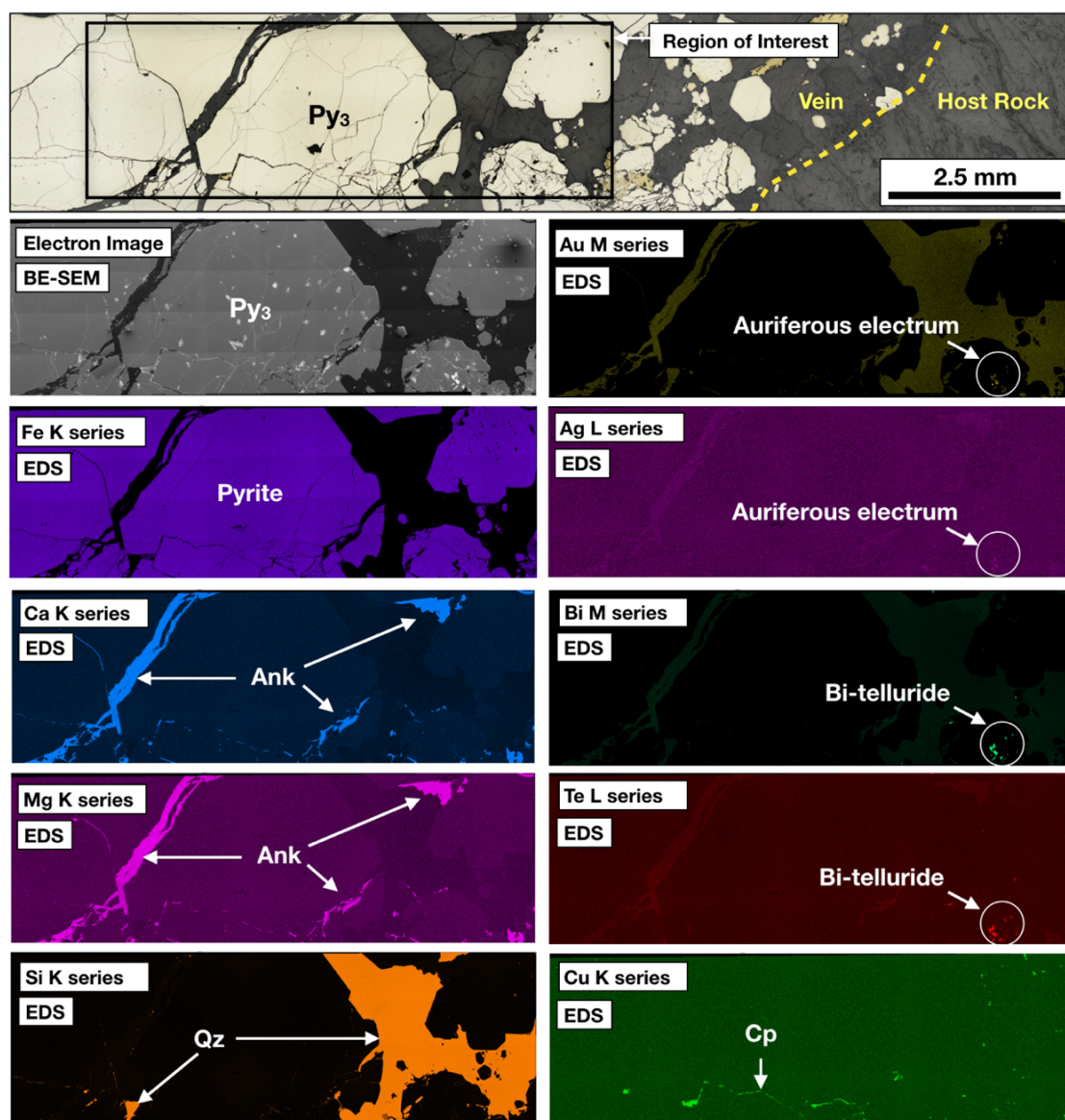


Figure 5.6. Locations of mineral phases within a region of interest for ore-stage veins containing Py_3 (sample CT20; drill-hole 16-CT- 342, ‘Grizzly’ vein zone, 199.83-199.93m). The top image in reflected light shows the region of interest in thin section within the boundary of the vein, while the spatial distribution of elements of interest are determined using Energy Dispersive X-ray Spectroscopy (EDS/EDX). Quartz is the dominant gangue mineral, while ankerite is also observed. The technique confirms fracture-hosted Cu, with Bi-telluride and auriferous electrum occurring within a cluster to the bottom-right of respective images.

veinlets.

The most voluminous phase of pyrite (Py₃) at Curraghinalt occurs exclusively within the principal late quartz-ankerite-sulphide shear-veins (Figure 5.4B) which cross-cut the penetrative S₂/S₃ fabric of the host Dalradian pelitic to psammitic sequence, confirming late-orogenic emplacement and precipitation under post-peak metamorphic conditions. Grains exhibit a variety of morphologies: they are medium to coarse, may be euhedral, subhedral or anhedral, and can have angular or rounded edges. In many of the examined veins, Py₃ exhibits cataclastic textures indicative of brittle deformation. Chalcopyrite and tetrahedrite are also observed in association with Py₃ infilling late fractures, flooding interstices and replacing grains. In some veins (e.g. 'Grizzly'), they exhibit a plain, homogenous appearance, while in others (e.g. 'Crow') they show optical evidence of concentric zonation. Mapping using Energy Dispersive X-Ray Spectroscopy (EDS/EDX) reveals the distribution of ankerite and quartz with respect to Py₃ grains within host veins (Figure 5.6), while also identifying Au, Bi, Te and Cu discrete phases within tested grains and micro-fractures: for example, chalcopyrite is observed to infill these structures.

Disseminated porphyroblasts (<50 µm) are also observed within the wallrock proximal to sulphide-bearing veins; grain-fabric relationships indicate growth early during prograde metamorphism, contemporary with Py₁ and Py₂.

5.9. Discrete gold and telluride phases

Visible Au particles are identifiable using reflected-light microscopy. These are dominantly associated with 'ore-stage' Py₃ (within retrograde shear-veins that cross cut penetrative S₂/S₃ Grampian fabrics) and exhibit a textural association with Bi- tellurides. They are additionally

observed at the junctions of micro-fractures which cross-cut Py_1 and Py_2 within earlier schistosity-parallel veins.

Auriferous particles tend to be rounded due to their softness (2.5-3 on Moh's hardness scale), exhibiting pitted surface textures indicative of abrasion. Four distinct and characteristically ductile morphologies are observed: (i) $< 30\ \mu\text{m}$ particles which appear encapsulated within pyrite, chiefly recognised within the outer 10-20% of the grain area, (ii) dendritic infill of fine cross-cutting micro-fractures, (iii) elongate blebs which follow the edges of grains, and (iv) as 'free gold' particles within host gangue minerals spatially disassociated from cataclastically deformed pyrite grains. In reflected light, particles exhibit a yellow hue, while Backscattered Electron (BSE) response to Au and Ag using Scanning Electron Microscopy (SEM) is higher than that of host grains and gangue mineralogy due to their atomic nuclei, (resulting in a relative bright appearance in imaging).

Particles contained internally within grains positioned in micro-fractures and dendritic infill reveal key element associations and a sequence of emplacement. They tend to favour junctions or 'bottle-necks' within micro-fracture networks: these may be argentiferous (e.g. Figure 5.7B), containing $< 20\ \text{wt.}\%$ Ag. Bi- and Ag- tellurides occur coincidentally with the precipitation of the Au amalgam. Examples are presented from within Py_3 micro-fractures where Bi-telluride (Figure 5.7A) and Ag-telluride (Figure 5.8C) have subsequently filled available space. Au-Ag telluride zones (likely to be petzite, Ag_3AuTe_2) may be observed proximal to auriferous particles engulfed by Ag-telluride (hessite, Ag_2Te). Chalcopyrite is observed to heal micro-fractures both preceding (Figure 5.7B) and following Au-Ag-Bi-Te emplacement suggesting fluctuation of conditions and episodic opening and closing of the system. Panchromatic imaging by cathodoluminescence (CL) reveals the infiltration of micro-fractures by a quartz fluid, proposed as a likely carrier of Au, Ag, Bi, Te and Cu (Figure 5.8D).

Analyses (n=34) of gold particles associated with ore-stage Py_3 in samples from the central and lower veins of Curraghinalt by EDS/EDX analysis reveal mean concentrations of 82.66 wt.% Au and 11.63 wt.% Ag, with Au fineness ranging from 780 to 968 ‰ (average,

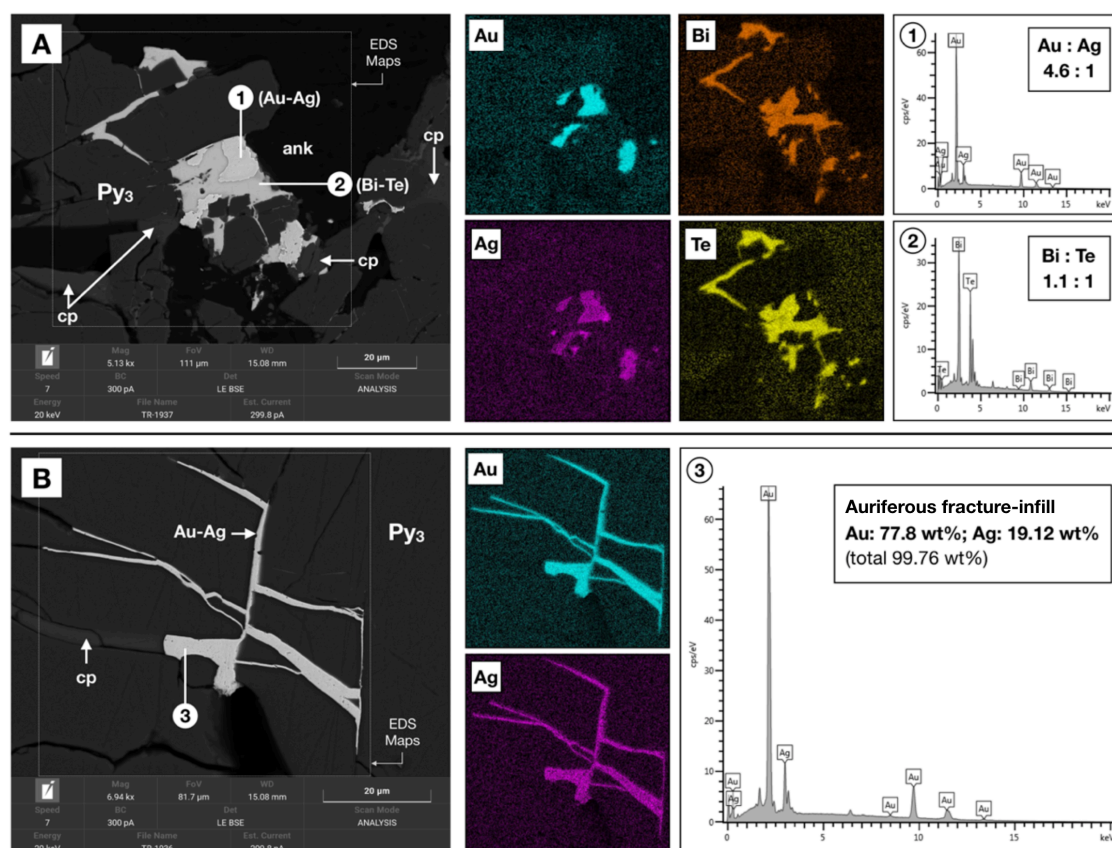


Figure 5.7. Two regions of interest associated with Py_3 (sample CT20; drill-hole 16-CT- 342, ‘Grizzly’ vein zone, 199.83-199.93m), analysed using a Scanning Electron Microscope in Backscattered mode (BSE), with accompanying maps acquired using Energy Dispersive X-ray Spectroscopy (EDS/EDX, TruMap mode) and spectra for spot analyses at specific numbered locations (see annotation in A and B). Analyses were conducted using a current of 300 pA and a voltage of 20 keV. Due to the analytical field of view being $<10\ \mu\text{m}$ for location 1 and 2, only the ratios of Au:Ag and Bi:Te are presented, while quantitative data is presented for location 3. (A) Intergrowth at a Py_3 boundary associated with a fracture, containing regions of auriferous infill and a larger encompassing region of Bi- telluride. Pyrite is surrounded by ankerite, while fractures additionally contain chalcopyrite. (B) Au(-Ag) infill of narrow micro-fractures at a Py_3 boundary. Results demonstrate a petrographic association between Au-, Ag-, Bi- and Te-bearing minerals (+ Cu), and a spatial association of these minerals with micro-fractures suggesting syn- to post- cataclastic emplacement.

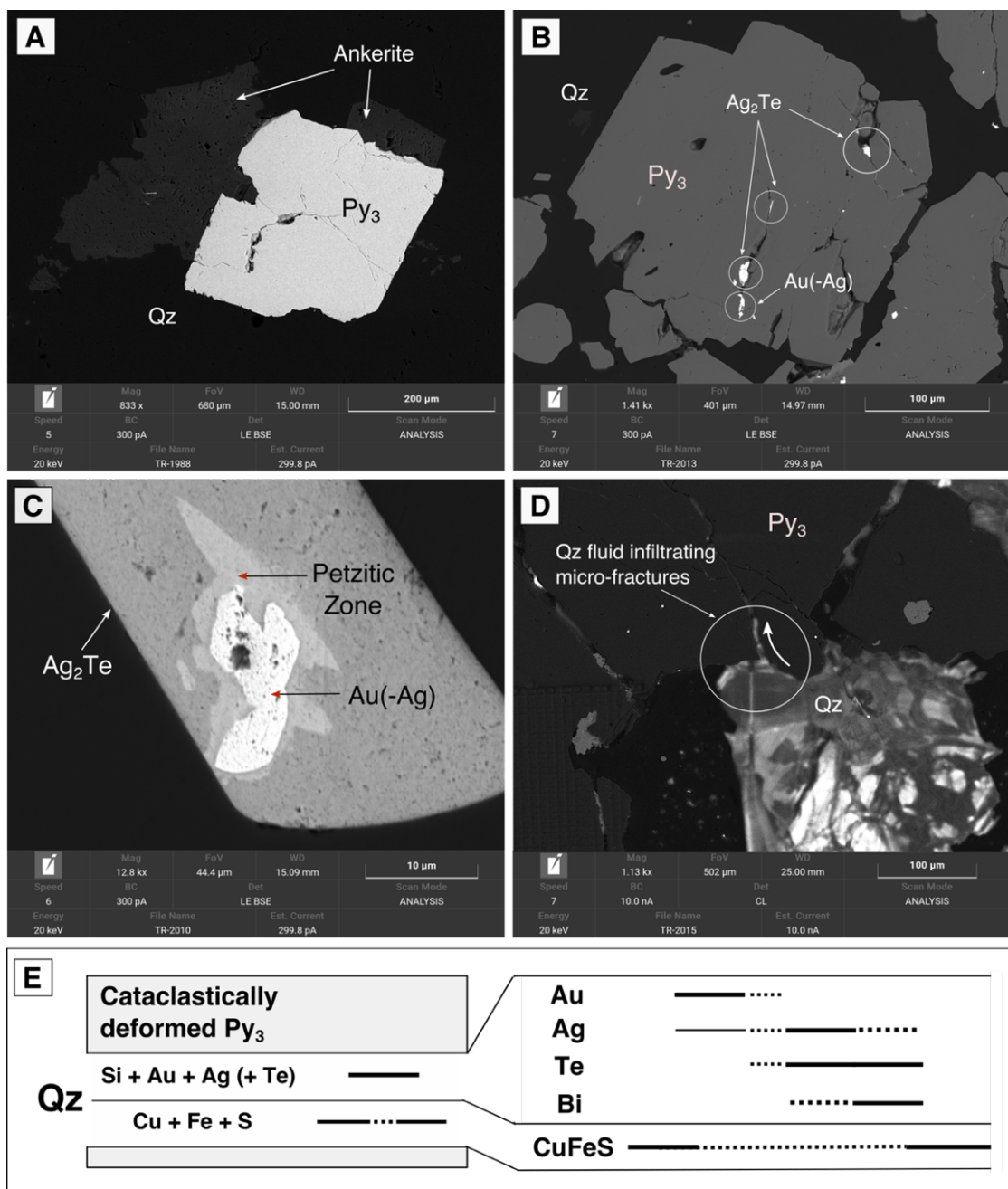


Figure 5.8. (A) Backscattered Electron (BSE) image of fractured Py_3 with associated gangue minerals (quartz and ankerite) (sample CT25; ‘Crow’ shear-vein zone, drill-hole 16-CT-351, 86.45-86.52m); (B) Au(-Ag) and Ag_2Te identified within Py_3 micro-fractures (BSE image) (sample CT25; ‘Crow’ shear-vein zone, drill-hole 16-CT-351, 86.45-86.52m); (C) a transitional petzitic (Au-Ag -telluride) zone may be encountered between Au(-Ag) and hessite phases (BSE image) (sample CT20; drill-hole 16-CT-342, ‘Grizzly’ vein zone, 199.83-199.93m); (D) panchromatic CL reveals a late quartzose fluid exploiting the micro-fracture network (sample CT20; drill-hole 16-CT-342, ‘Grizzly’ vein zone, 199.83-199.93m); (E) petrographically constrained chemical paragenesis within auriferous fractures: initial precipitation of Au, followed by hessite (Ag_2Te) and Bi-tellurides, with evidence of infilling chalcopyrite both prior and subsequent to Au-Ag-Bi-Te phases.

877 ‰). Fineness values >960 ‰ are observed for 7 samples, confirming that a subset of the tested population does not exhibit amalgamation resulting from a significant argentiferous component to the emplacing fluid. [Due to the proportion of Ag for all tested samples falling below the 30-70 wt.% range criterion for electrum (Spiridonov and Yanakieva, 2009), this study preferentially refers to such amalgams as ‘gold particles’ or ‘auriferous particles’; Ag contents at recorded concentrations <30 wt.% are considered to be an impurity (Craw et al., 2017)]. Observed particles provide evidence of chemical equilibrium between Au, Ag, Bi and Te for visible phases, suggesting a common fluid source and supporting an overall Au-Ag-Bi-Te signature for the Curraghinalt deposit. Within micro-

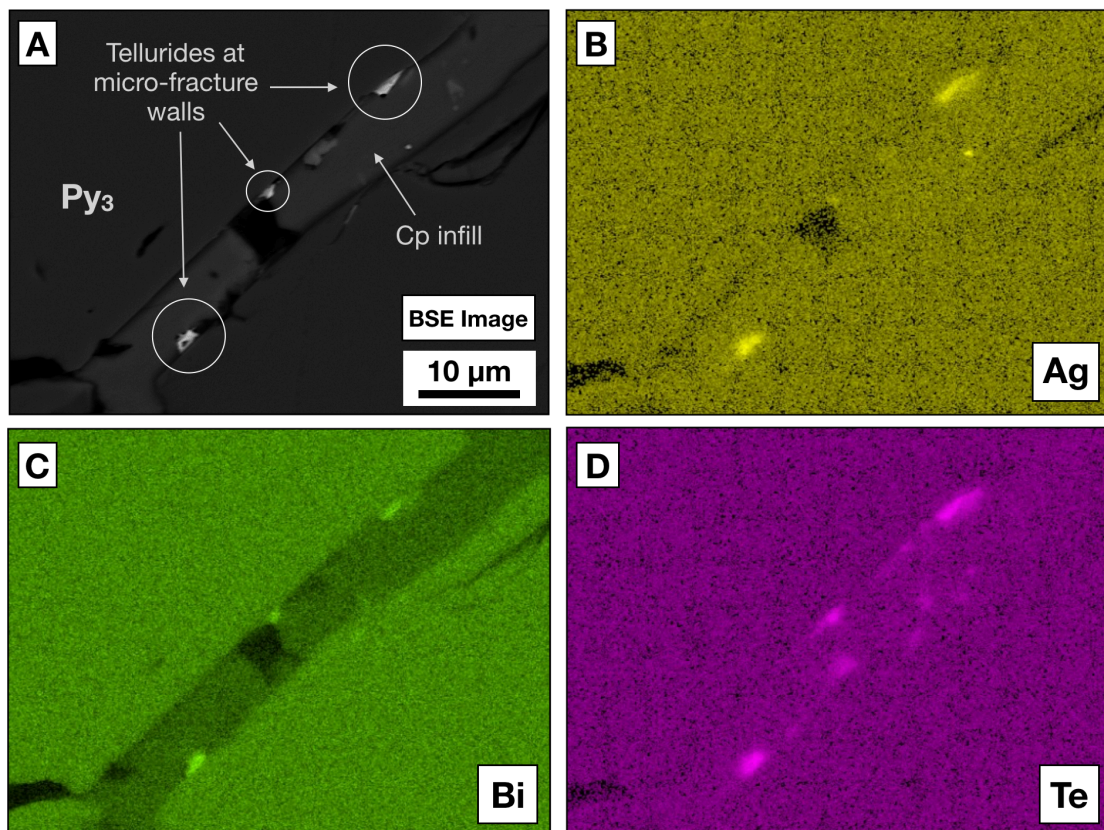


Figure 5.9. Nucleation of tellurides along micro-fracture walls acting as a reactive surface within cataclastically deformed Py_3 (sample CT20; drill-hole 16-CT- 342, ‘Grizzly’ vein zone, 199.83-199.93m), evidenced in EDS/EDX mapping of Ag, Bi and Te.

Type	Location	Fe (wt.%)	Ag (wt.%)	Te (wt.%)	Au (wt.%)	Bi (wt.%)	Total (wt.%) (incl. all elements)
Gold	Grizzly *	0.37	3.22		80.72		88.62
Gold	Grizzly	2.31	2.70		81.62		92.49
Gold	Grizzly *	0.50	2.76		83.38		97.00
Gold	Crow	1.14	21.80		77.88		103.31
Gold	Crow	2.69	20.79		78.76		104.92
Gold	Grizzly	0.50	16.15		81.72		105.46
Gold	Grizzly	0.41	11.49		71.78		87.73
Gold	Grizzly	0.26	9.37		74.60		87.43
Gold	Grizzly	1.24	15.86		69.95		95.89
Gold	Grizzly	2.59	15.31	1.33	64.51		87.60
Gold	Grizzly	0.64	13.14		71.56		89.57
Gold	Grizzly	2.71	18.51		66.51		89.81
Bi-Te	Grizzly	0.98		30.02		49.33	86.84
Bi-Te	Grizzly	0.46		47.05		51.30	100.18
Bi-Te	Grizzly	0.49		47.07		51.15	100.63
Bi-Te	Grizzly	1.84		47.27		50.12	101.13
Bi-Te	Grizzly	1.71		39.74		42.34	85.08
Bi-Te	Grizzly	0.49		29.04		47.98	85.58
Bi-Te	Grizzly	0.99		39.74		43.01	84.88
Volynskite	Grizzly	0.53	17.15	37.53		30.08	85.75
Hessite	Crow	1.38	62.56	36.18			106.24
Hessite	Grizzly	2.37	62.33	36.18			105.79
Hessite	Crow	2.20	63.13	36.36			108.46
Hessite	Grizzly	0.28	53.69	30.95			91.30
Hessite	Grizzly	0.50	54.04	30.96			91.53
Hessite	Grizzly	3.90	47.87	26.44			87.58
Hessite	Grizzly	1.93	54.22	31.89			91.36
Petzite	Grizzly	0.44	37.44	27.72	22.33		90.98

Table caption overleaf

Table 5.2. Representative quantitative analyses of auriferous particles and Bi- Ag- telluride discrete phases associated with Py_3 from samples within the Grizzly (sample CT20; drill-hole 16-CT-342, 199.83-199.93m) and Crow shear-vein zones (sample CT25; drill-hole 16-CT-351, 86.45-86.52m). Asterisks for two analyses indicate that these results have been retrieved from particles at grain boundaries, all other analyses lie within micro-fractures. The reason that analytical totals do not equal 100 wt.% is that they are the result of an imperfect iterative procedure, in which the mass fraction for each element in the unknown is calculated (Goldstein et al., 2017). Totals below unity (100 wt.%) may be due to a missing element (e.g. from an oxidised region of the examined thin section), reduced excitation volume, sample geometry (e.g. films or inclusions; the quality of polishing), or deviations of measurement conditions between the known (for information on standards; see *Section 5.7*) and unknown (sample). Where totals exceed unity (100 wt.%), this is likely due to deviations from measurement conditions or the geometry of the sample; certain results <90 wt.%, based on experimental observations, are likely to be resultant of fields of view <20 μm for certain analyses necessitated by the size of available particle surface areas.

fractures, rounded visible auriferous particles are observed, particularly within fracture junctions, adhering to the boundaries of those fractures which have been subsequently infilled by Bi-telluride (Figure 5.8A). Evidence indicates that the walls of these fractures provided a reactive surface for the nucleation of these particles. This study also observes examples of micro-fracture walls acting as a substrate for the precipitation of Bi- and Ag-tellurides (Figure 5.9). Fracture-wall nucleation is interpreted as an important mechanism for metalliferous emplacement; grain boundaries may also have provided a reactive surface. A sequence of observable emplacement of Au, Ag, Bi and Te phases and subsequent chalcopyrite, observed as a late phase sealing micro-fractures, is presented in Figure 5.8. Cook and Ciobanu (2005) note that Bi-Te phases associated with gold emplacement are commonly observed within orogenic systems, along with other types of deposits including volcanogenic massive sulphide (VMS), epithermal-porphyry and intrusion-related deposits.

Inspection of grains using Scanning Electron Microscopy (SEM) methods has provided robust evidence of Au emplacement within micro-fractures, a viable mechanism

for nucleation and a preferential sequence of precipitation. This study proposes that the late fluid event at Curraghinalt was likely to be the carrier of resource-associated Au, rather than earlier quartz phases, a hypothesis tested in LA ICP-MS work in *Section 5.11.iv.* of this study.

5.10. Major element composition of pyrite

Electron Microprobe Analyses (EMPA; n=154) were carried out for S, Mn, Fe, Zn and In on 3 samples (CT07, ‘106-16’ vein, n=30; CT20, ‘Grizzly’ vein, n=40; CT24, ‘Crow’ vein, n=84) of ore-stage Py_3 to determine major element composition of pyrite. For a total of 154 analyses (Table 5.3), the median Fe content reports as 47.1 wt.% (IQR = 46.9 - 47.3 wt.%), while median S is 53.0 wt.% (IQR = 52.1 - 53.1 wt.%). Fe abundances for pyrite between veins are comparable: for sample CT07 (‘106-16’) the median value is 47.1 wt.%, for CT20 (‘Grizzly’) this value is slightly lower at 46.8 wt.%, while for CT24, Fe contents are more similar to ‘106-16’ at 47.2 wt.%. For S, contents are marginally lower in pyrite from the central ‘Grizzly’ vein (51.8 wt.%) relative to ‘106-16’ (53.04 wt.%) and ‘Crow’ (52.95 wt.%). Median values and limited interquartile ranges of 0.41 wt.% for Fe and 1.02 wt.% for S demonstrate that Py_3 exhibits a near-stoichiometric composition; the median recorded concentration of Fe for the full dataset was selected for internal standardisation in Laser Ablation ICP-MS analyses. Indium is not recorded in Py_3 , while Zn reports an overall median concentration of zero (IQR = 0-0.01 wt.%); the median Mn content for this phase is 0.0007 wt.% (IQR = 0 – 0.007 wt.%). Totals for EMPA analyses averaged 99.8%, ranging between 98.0 and 101%.

Analytes	Fe (wt.%)	S (wt.%)	Zn (wt.%)	Mn (wt.%)
All samples, n=154				
Median	47.1	52.9	0.00	0.00
Interquartile Range	0.41	1.02	0.01	0.01
25th percentile	46.9	52.1	0.00	0.00
75th percentile	47.3	53.1	0.01	0.01
106-16 vein (CT07), n=30				
Median	47.1	53.0	0.00	0.00
Interquartile Range	0.33	0.66	0.01	0.01
25th percentile	46.9	52.6	0.00	0.00
75th percentile	47.3	53.2	0.01	0.01
Grizzly vein (CT20), n=30				
Median	46.9	51.8	0.00	0.00
Interquartile Range	0.21	0.29	0.01	0.01
25th percentile	46.7	51.7	0.00	0.00
75th percentile	46.9	52.0	0.01	0.01
Crow vein (CT24), n=84				
Median	47.3	53.0	0.00	0.00
Interquartile Range	0.22	0.41	0.01	0.01
25th percentile	47.1	52.8	0.00	0.00
75th percentile	47.3	53.2	0.01	0.01

Table 5.3. Summary of Electron Microprobe Analysis (EMPA) results for ore-stage Py_3 for the full dataset (n=154) and specifically for tested veins '106-16' (sample CT07), 'Grizzly' (CT20) and 'Crow' (CT24). Indium is excluded from the table as all results were below instrument detection.

5.11. Trace element abundance and compositional zonation

5.11.i. Composition and development of early Py_1

Laser Ablation ICP-MS spot analyses ($n=35$) for Py_1 reveal that median trace element concentrations for recorded elements are <100 ppm, with the exception of Zn (median = 5,030 ppm, IQR = 4,000-7,400 ppm; $n=35$) and Ni (median 2,410 ppm, IQR = 1,850-3,420 ppm; $n=35$). Au is detected in all analyses, recording a median concentration of 0.19 ppm (IQR = 0.14 – 0.22 ppm; $n=35$). Zn correlates positively (Spearman rank) with Mn ($\rho = 0.78$), Ga (0.58), Ag (0.55), Sn (0.49); for Ni, a positive correlation is observed with Au (0.49). The median concentration of Pb in this phase is 17.9 ppm (IQR = 11.9-29.4 ppm; $n=35$), correlating with Au ($\rho = 0.62$). Seven outliers (further than $1.5 \times (\text{Q3}-\text{Q1})$ from the median) are recorded for Zn (up to a maximum concentration of 21,700 ppm), while two outliers for Pb (max. 150 ppm) are recorded which are ascribed to inclusions mentioned below. The results of spot analyses for Py_1 (Figure 11) form confined clusters when projecting element ratios; most values lie within an order of magnitude on their respective axis. An Au/Ag ratio of 0.05 reflects the relative enrichment of Ag (median 5.12 ppm, IQR = 2.31 – 7.03 ppm; $n=35$) in comparison to Au (median 0.19 ppm, IQR = 0.14 – 0.22 ppm; $n=35$). Average Co/Ni for this phase is 0.05; Co is relatively depleted overall (median 92.2 ppm, IQR = 63.0 – 122 ppm; $n=35$) in relation to Ni.

Laser Ablation ICP-MS element raster mapping (Figure 5.13 and Figure 5.14) of selected regions demonstrate broad homogeneity in Zn concentrations within this phase ($>1,000$ ppm Zn); Ni distribution (also habitually $>1,000$ ppm) shows more heterogeneity suggesting an internal distortion of the lattice and possible syn-deformation emplacement conditions. A diagnostic feature of Py_1 identified during petrographic work is the presence of micro-inclusions of sphalerite ((Zn,Fe) S) and galena (PbS), a trait not observed within other phases; results of spectroscopic analyses suggest inclusions and elemental

concentrations within the host lattice are co-genetic. Co enrichment (>1,000 ppm) is observed at phase boundaries.

5.11.ii. Py₂ development and early Au mobility

The second recorded generation of pyrite, Py₂, is characterised petrographically as overgrowths of Py₁ within early ankerite-quartz veins sub-parallel to the S₂/S₃ fabric (Figure 5.4). Py₂ is distinctive from Py₁ in its internal architecture and chemical record of retained abundances. Enrichment is recorded in spot analyses (n=35) for both Co (median 105 ppm, IQR = 26.2-498 ppm; n=32) and Ni (median 191 ppm, IQR = 4.95-1,005 ppm; n=32). The Co/Ni ratio for this phase is two orders of magnitude higher than for Py₁ at 5.66. Positive correlations are observed for Co with Ni ($\rho = 0.67$; Spearman rank) and Zn (0.54), while Ni also correlates positively with Mo (0.49) and Zn (0.43); Pb and Bi also have a demonstrable relationship ($\rho = 0.67$) (Figure 5.11). Analyses confirm a median Au value of 3.69 ppm (IQR = 2.02 – 10.1 ppm; n=34). A spatial distribution of Au values > 1ppm are revealed in LA ICP-MS element raster mapping (Figure 5.13 and Figure 5.14): distribution in both mapped areas is heterogeneous, with areas containing values in the 10-100 ppm range, while values in other regions lie between 1-10 ppm. The relative enrichment of Au within this phase is considered to be the first stage of regional Au mobility evidenced at Curraghinalt (Stage I).

Regions with more elevated values appear to be coincident with micro-fractures containing elevated Bi and Te, suggesting that they are coincident with a predicted phase of late enrichment. Interquartile ranges in spot analyses spanning 2-3 orders of magnitude for Co and Ni are reflected in LA ICP-MS element raster maps (Figure 5.13 and Figure 5.14) which demonstrate a distinctive oscillatory zonation. Zn, Ag, Co and Cu show a relative depletion in Py₂, suggesting those elements were not a significant component of fluids pervasive in the system during the growth of this phase.

Phase	Py ₁				Py ₂				Py ₃			
n	n=35				n=35				n=137			
An.	n > LOD	Med.	IQR		n > LOD	Median	IQR		n > LOD	Median	IQR	
			25th perc.	75th perc.			25th perc.	75th perc.			25th perc.	75th perc.
⁵⁵ Mn	35	6.60	4.80	9.50	26	8.25	4.95	1,005	17	3.80	2.80	99.0
⁵⁹ Co	35	92.2	63.0	122	32	105	26.2	498	129	72.3	17.0	216
⁶⁰ Ni	35	2,410	1850	3,420	32	191	22.9	778	128	126	16.3	337
⁶³ Cu	35	50.0	33.6	111	32	4.93	0.98	9.30	66	1.91	0.91	3.63
⁶⁶ Zn	35	5,030	4,000	7,400	7	39.0	12.6	290	10	6.55	2.03	94.5
⁷¹ Ga	35	0.91	0.69	1.22	12	0.13	0.08	0.18	30	0.04	0.03	0.05
⁷⁵ As	15	15.6	3.80	29.5	35	14,680	8,250	20,800	126	3.77	2.44	6.15
⁷⁸ Se	2	45.5	45.0	46.0	1	58.0	58.0	58.0	7	23.7	17.0	47.0
⁹⁵ Mo	3	0.08	0.04	0.13	6	0.10	0.08	0.16	26	0.18	0.06	1.51
¹⁰⁷ Ag	35	5.12	2.31	7.03	26	0.37	0.14	0.87	64	0.48	0.13	2.10
¹¹⁸ Sn	32	3.92	1.02	15.8	0	<LOD	<LOD	<LOD	2	0.45	0.28	0.62
¹²¹ Sb	30	1.04	0.48	2.30	11	0.72	0.48	1.31	29	0.49	0.32	0.86
¹²⁵ Te	15	0.41	0.32	0.53	15	0.78	0.46	1.19	124	5.21	2.15	10.6
¹⁸² W	1	0.04	0.04	0.04	7	0.19	0.08	0.29	7	0.05	0.01	0.29
¹⁹⁷ Au	35	0.19	0.14	0.22	34	3.69	2.02	10.1	69	0.31	0.08	0.66
²⁰² Hg	35	1.73	1.37	2.22	35	0.89	0.57	1.50	128	0.57	0.38	0.85
²⁰⁵ Tl	2	0.02	0.02	0.02	4	0.03	0.03	0.04	16	0.02	0.01	0.03
²⁰⁸ Pb	35	17.9	11.9	29.4	34	4.85	0.94	19.8	85	1.10	0.13	5.06
²⁰⁹ Bi	16	0.04	0.03	0.07	22	1.22	0.18	5.40	94	0.86	0.09	3.57
Au/Ag	0.05				23.7				0.94			
Au/Te	0.39				9.90				0.07			
Co/Ni	0.05				5.66				2.59			
> 100 ppm	Ni, Zn				Co, Ni, As				Ni			

Table 5.4. Median values and interquartile ranges for tested analytes, using ablated spots on pyrite phases Py₁₋₃ (n=207). Key average ratios (Au/Ag, Au/Te, Co/Ni) and enrichments (>100 ppm) are reported. Median detection limits were as follows: ⁵⁵Mn, 4 ppm; ⁵⁹Co, 0.32 ppm; ⁶⁰Ni, 1.6 ppm; ⁶³Cu 0.38 ppm; ⁶⁶Zn, 2.2 ppm; ⁷¹Ga, 0.04 ppm; ⁷⁵As, 0.78 ppm; ⁷⁸Se, 13 ppm; ⁹⁵Mo, 0.05 ppm; ¹⁰⁷Ag, 0.07 ppm; ¹¹⁸Sn, 0.14 ppm; ¹²¹Sb, 0.07 ppm; ¹²⁵Te, 0.24 ppm; ¹⁸²W, 0.05 ppm; ¹⁹⁷Au, 0.02 ppm; ²⁰²Hg, 0.45 ppm; ²⁰⁵Tl, 0.01 ppm; ²⁰⁸Pb, 0.04 ppm; ²⁰⁹Bi, 0.01 ppm.

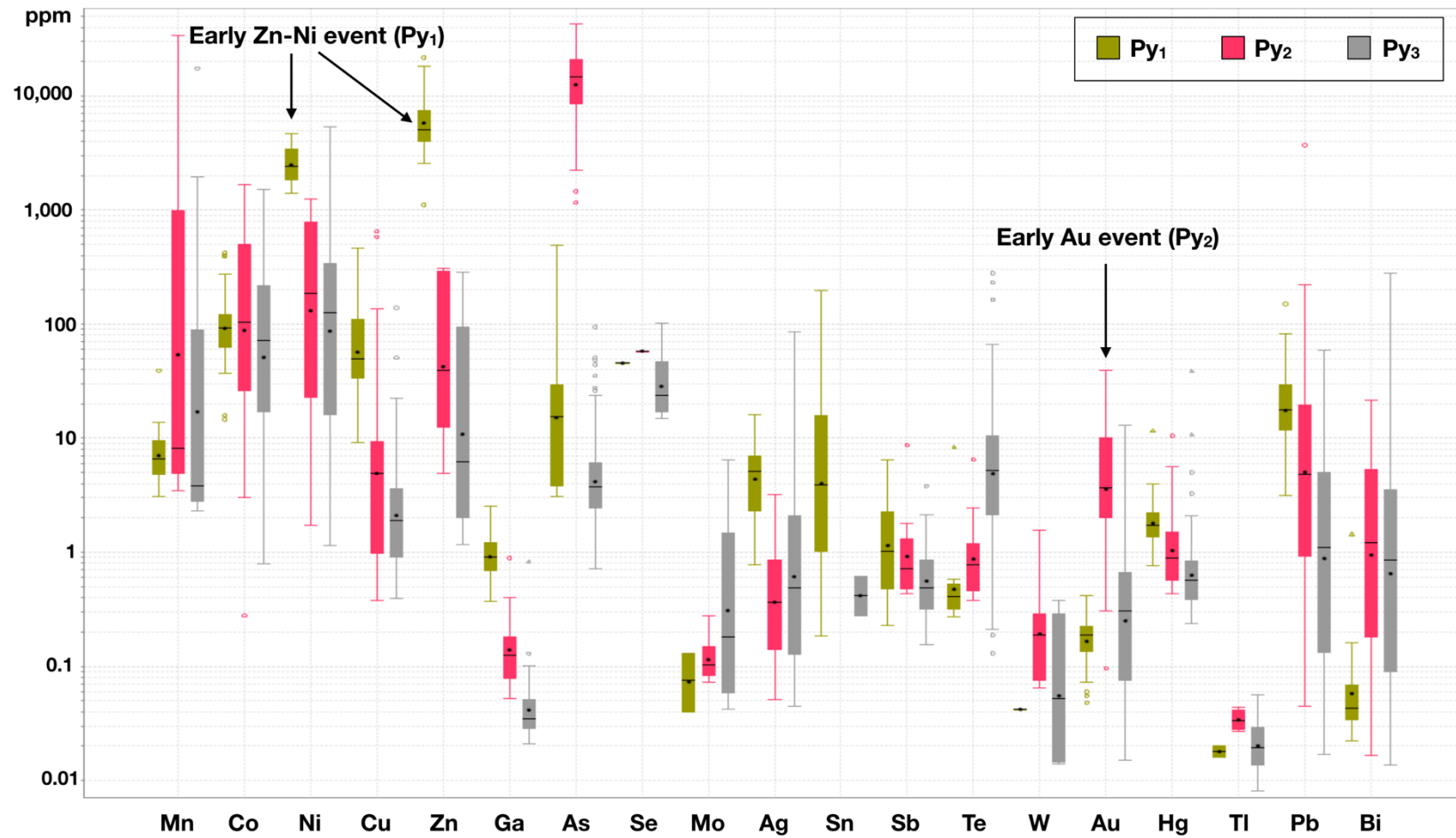


Figure 5.10. Box and whisker plots of trace elements concentrations acquired using Laser Ablation ICP-MS for 237 spot analyses within phases Py₁, Py₂ and Py₃. The box is the interquartile range (upper Q1 to upper Q3); black dots are means, lines are medians; a circle is an outlier 1.5 x the IQR, while a triangle is an outlier 3 x the IQR. Whiskers represent extreme values which are not outliers.

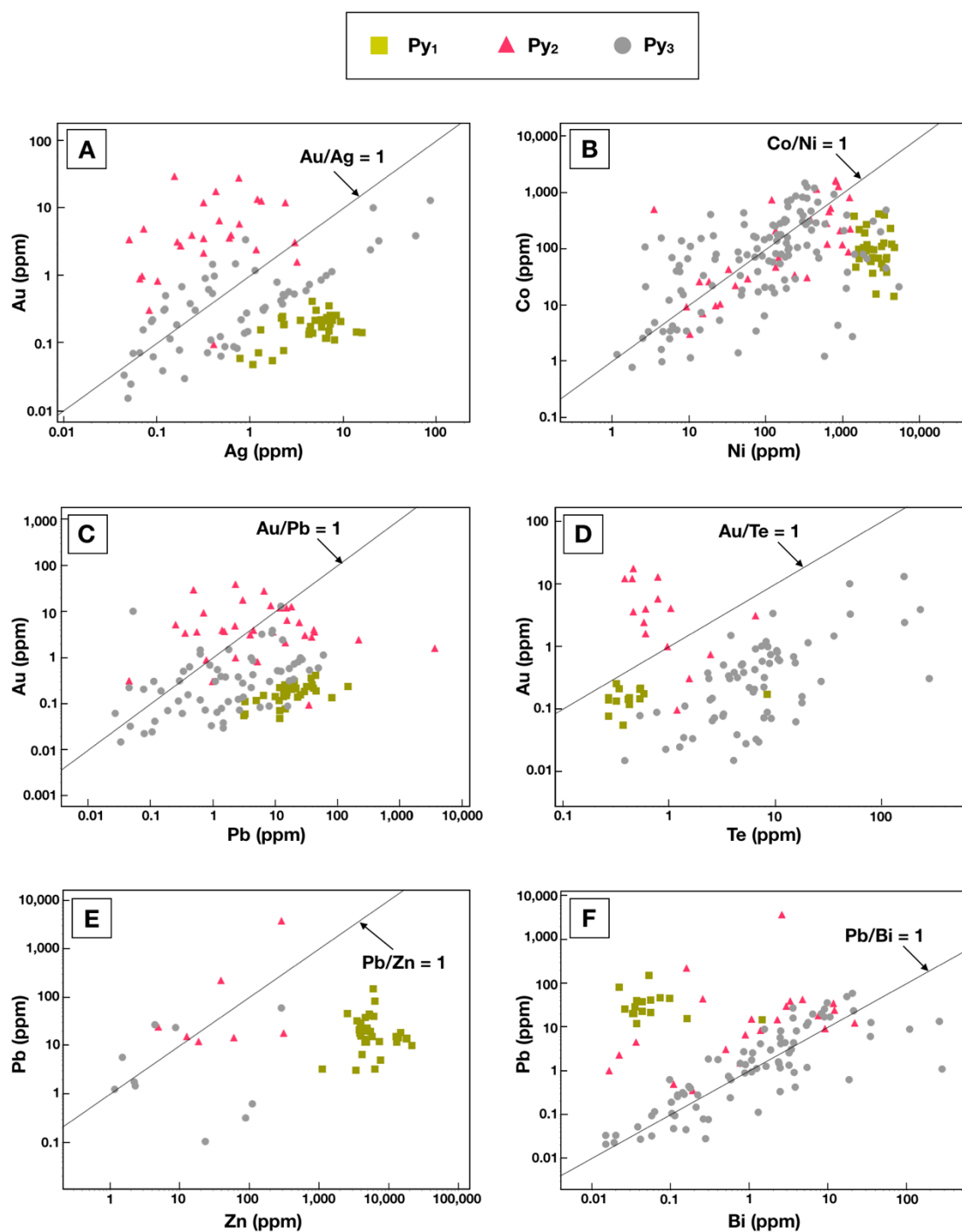


Figure 5.11. Ratios of Au/Ag (A), Co/Ni (B), Au/Pb (C), Au/Te (D), Pb/Zn (E) and Pb/Bi (F) concentrations for phases Py_{1-3} determined using Laser Ablation ICP-MS spot analyses ($n=237$).

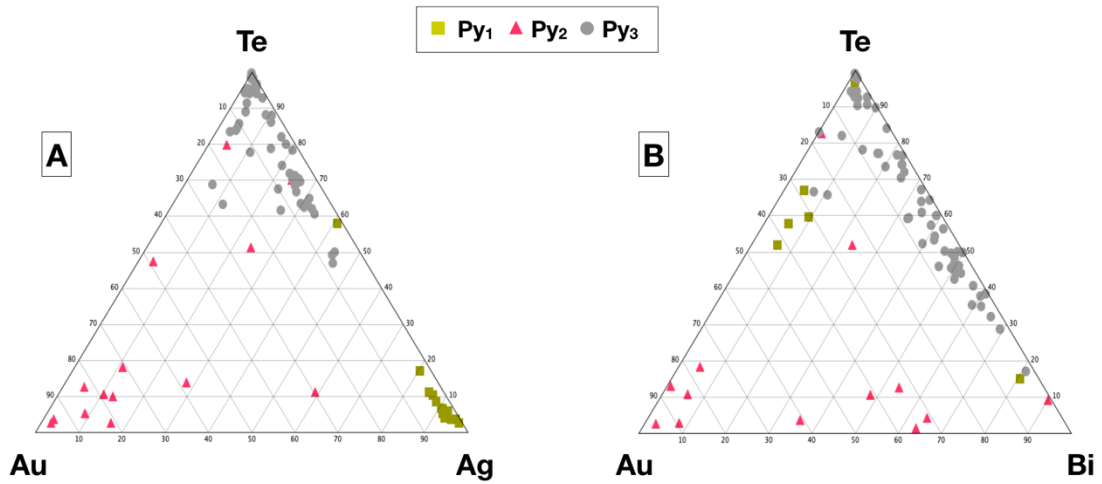


Figure 5.12. Ternary diagrams for precious metals of economic interest, tellurium and bismuth, obtained by LA ICP-MS in-situ spot analyses of phases Py₁-Py₃: (A) Te-Au-Ag and (B) Te-Au-Bi.

5.11.iii. Cataclastically deformed Py₃

The third phase of pyrite (Py₃) hosted by the swarm of shear-veins cross-cutting the S₂/S₃ fabric (Figure 5.4B) exhibits variability in both Ni (IQR = 16.3 - 337 ppm) and Co (IQR = 17.0 - 216 ppm). An average Co/Ni ratio of 2.59 is observed for this phase, with a wide dispersion of values comparable to Py₂. All Au/Te values (mean = 0.07) lie <1, while Au/Ag with a mean value of 0.94 plots closest to the Au/Ag=1 line of the three datasets (Py₁₋₃). Au contents in this phase have a median value of 0.31 ppm (IQR = 0.08 - 0.66 ppm), indicating that there is not a significant refractory component to this generation of pyrite. A positive correlation of Au is observed with Ag ($\rho = 0.69$), Bi (0.63), Te (0.60) and Pb (0.51). Py₃ is also relatively enriched in Te compared with earlier phases with a median value of 5.21 ppm (IQR = 2.15 - 10.6 ppm) (Table 5.4 and Figure 5.12). Signatures suggest that while Au is relatively depleted in this phase, Py₃-stage hydrothermal fluids were likely sourced from a distinctive reservoir fertile for auriferous and argentiferous phases. This may suggest stabilisation of a system source prior to the mobilisation of the late fluid. An observed Te

anomaly (Figure 5.12) provides evidence that this phase may be a possible source for telluride inclusions and later Te- phases.

LA-ICP-MS element mapping (Figure 5.15) confirms oscillatory element variations (e.g. Co, Ni) in crystal growth, radial from cores (c. 100 ppm Co, <10 ppm Ni) to outer zones (>1000 ppm Co, >100 ppm Ni). Elevated Au levels and coincident As, Cu, Te and Bi, along with discrete auriferous particles occur independently of lattice bound Co-Ni signatures in Py₃ cross-cutting earlier phases with oscillatory growth zones.

5.11.iv. Late stage gold emplacement

Laser Ablation ICP-MS spot analyses and element mapping, supporting petrographic observation of sequential precipitation of Au- and telluride minerals, provide evidence for a late-stage introduction of an auriferous fluid, responsible for the precipitation of Au particles along with Bi- and Ag- telluride phases at Curraghinalt (designated 'Stage II'). Micro-fractures opened during brittle deformation of pyrite grains in all observed phases (Figure 5.13, Figure 5.14 and Figure 5.15) show elevated contents of Cu (>10 ppm), Ag (>10 ppm), Te (>5 ppm) and Au (>1 ppm) supporting petrographic observations of visible metalliferous phases (see Figure 5.7, Figure 5.8 and Figure 5.9); additional enrichments are observed within late fractures for Mn compared with the grain background (>10 ppm) and Pb (>1 ppm). Pyrite is not observed precipitating within micro-fractures.

For Py₁ and Py₂, micro-fracturing cross-cuts earlier phases (Figure 5.14) but also preferentially enriches Py₁-Py₂ grain (phase) boundaries (Figure 5.13 and Figure 5.14); concentrations of >1 ppm are observed for Py₂, though at these boundaries where fluid has exploited a pre-existing weakness, concentrations are >10 ppm. Particles of Au are observed at the Py₁-Py₂ interface (Figure 5.16), observable using linear scaling of the data and confirmed through inspection of ICP-MS signals. Micro-fractures are observed to cross-cut

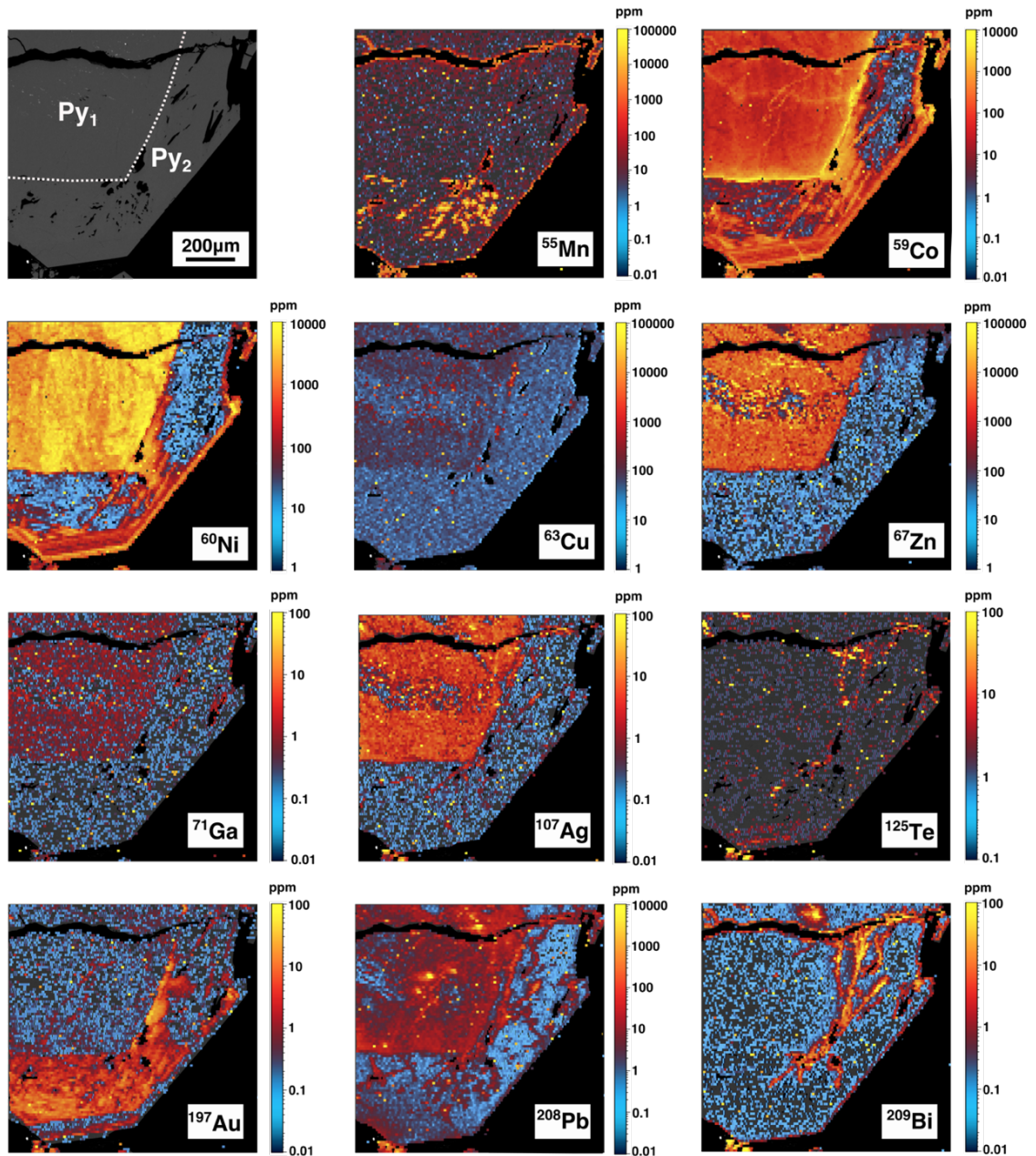


Figure 5.13. Laser Ablation ICP-MS raster element map showing trace element distribution within a 1mm x 1mm region of pyrite hosted by quartz-ankerite in sample CT12 (drill-hole 11-CT-99, 819.04-819.24m) at the eastern extent of the vein swarm. The grain is composed of two phases, Py₁ and Py₂. The internal phase, Py₁, exhibits elevated Co, Ni, Cu, Zn, Ga, Ag and Pb, with Ni revealing an internal structure approximately top to bottom in the image. Au is relatively enriched in Py₂. Bi and Te exploit an area of weakness at the boundary of Py₁. The rim of Py₂ also exhibits elevated contents of Co and Ni. Localised enrichments located approximately top-right to bottom-left within the mapped area of Py₁ denote ablated inclusions of galena.

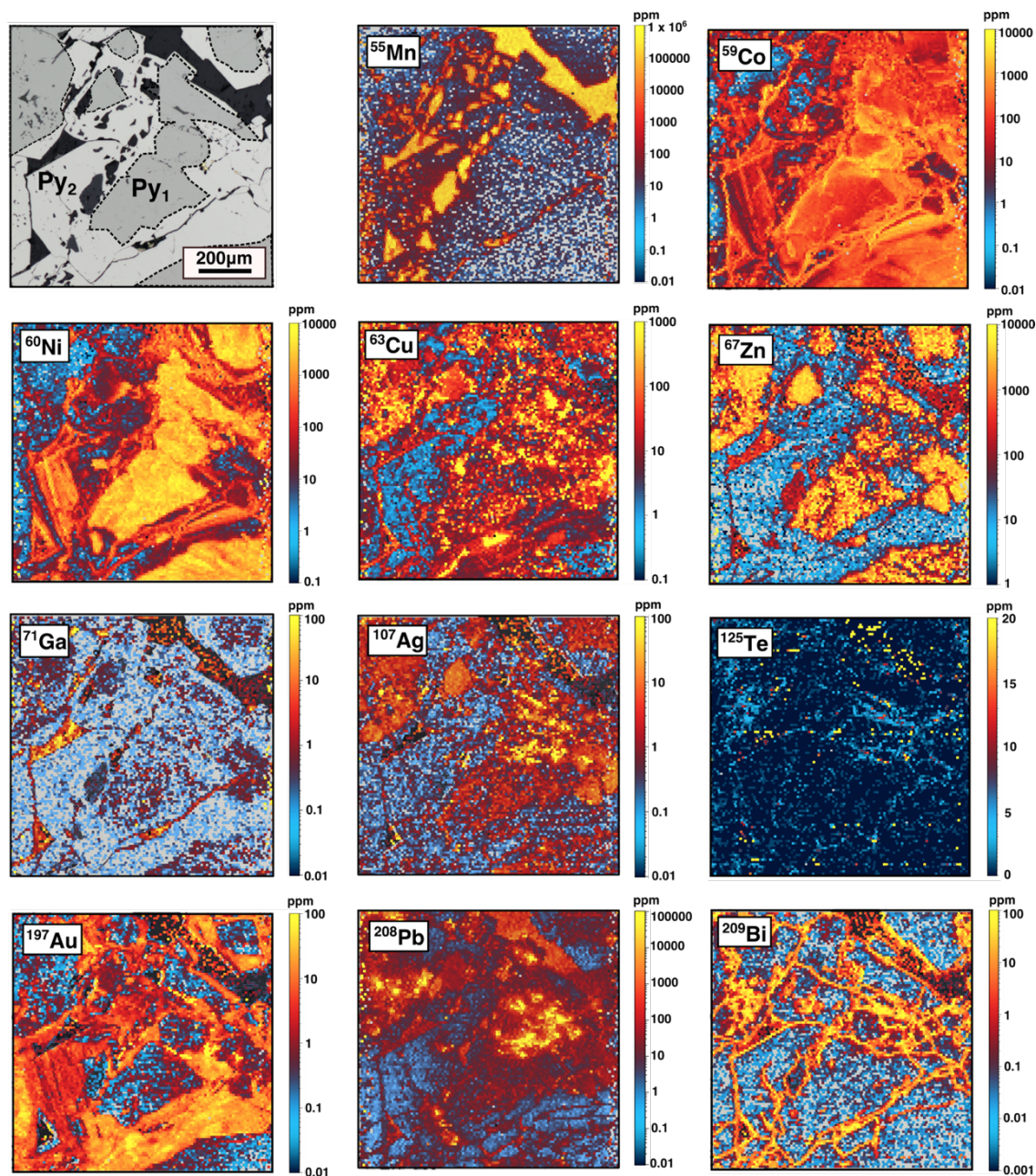


Figure 5.14. A second region of Py₁-Py₂ in sample CT12 (drill-hole 11-CT-99, 819.04-819.24m), mapped using Laser Ablation ICP-MS. Pyrite is hosted in this region by ankerite, confirmed by the presence of elevated concentrations of Mn which substitutes for Fe and Mg. Internal Py₁ exhibits comparable concentrations of Co and Ga to Py₂, while relatively elevated in Ni, Cu, Zn, Ag and Pb, in broad agreement with trends observed in the mapped area for Py₁ in the previous figure. Py₂ exhibits relatively elevated Au with oscillatory zonation of Co and Ni. Galena is observed as localised elevated concentrations within Py₁. Raster element mapping reveals a complex network of microfractures cross-cutting both phases, carrying elevated contents of Bi and Te.

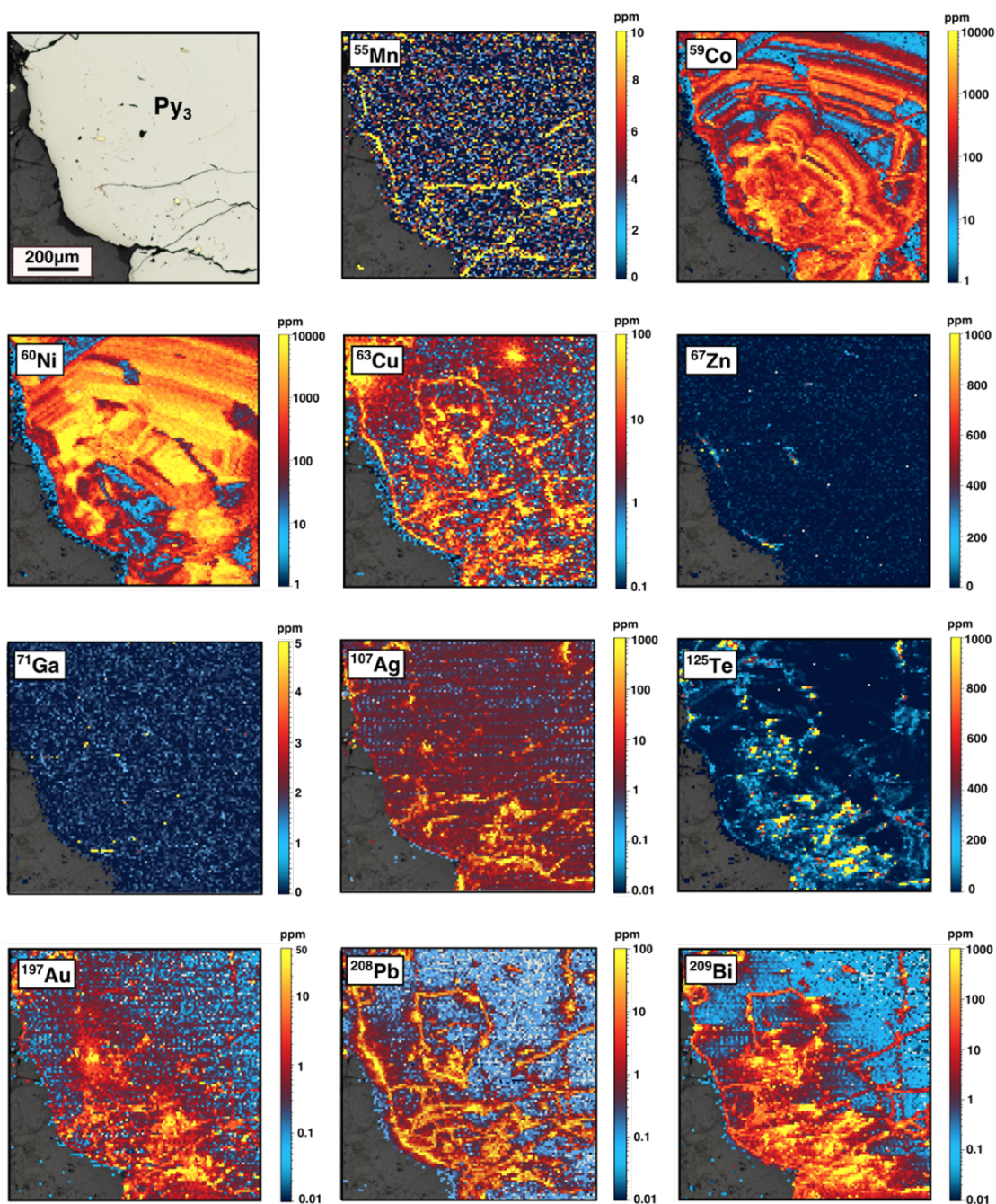


Figure 5.15. Trace element distribution within an area of Py_3 in sample CT20 (drill-hole 16-CT-342, 199.83–199.93m, ‘Grizzly’ vein), which appears broadly homogeneous in reflected light microscopy. Element raster mapping by Laser Ablation ICP-MS reveals complex oscillatory zonation of Co and Ni emanating from a central core, with relative depletion in other analytes. Fractures visible in reflected light (top-left image) at the bottom of the grain approximately left to right are characterised by elevated contents of Mn, however a more intricate network of micro-fractures is also revealed, carrying elevated concentrations of Cu, Ag, Te, Au, Pb and Bi. Local enrichments are observed for Au and Ag coincident with auriferous particles located within these networks, with local enrichments of Bi and Te indicating the presence of tellurides.

earlier concentric zonation of Py_3 , (e.g. of Co and Ni) providing evidence of relative timing, post-dating growth zones (Figure 5.15). Micro-fractures are typically enriched at concentrations >10 ppm Au consistent with observations in LA ICP-MS mapping of Py_1 and Py_2 . The distribution of micro-fractures in both Py_1 - Py_2 and Py_3 porphyroblasts is

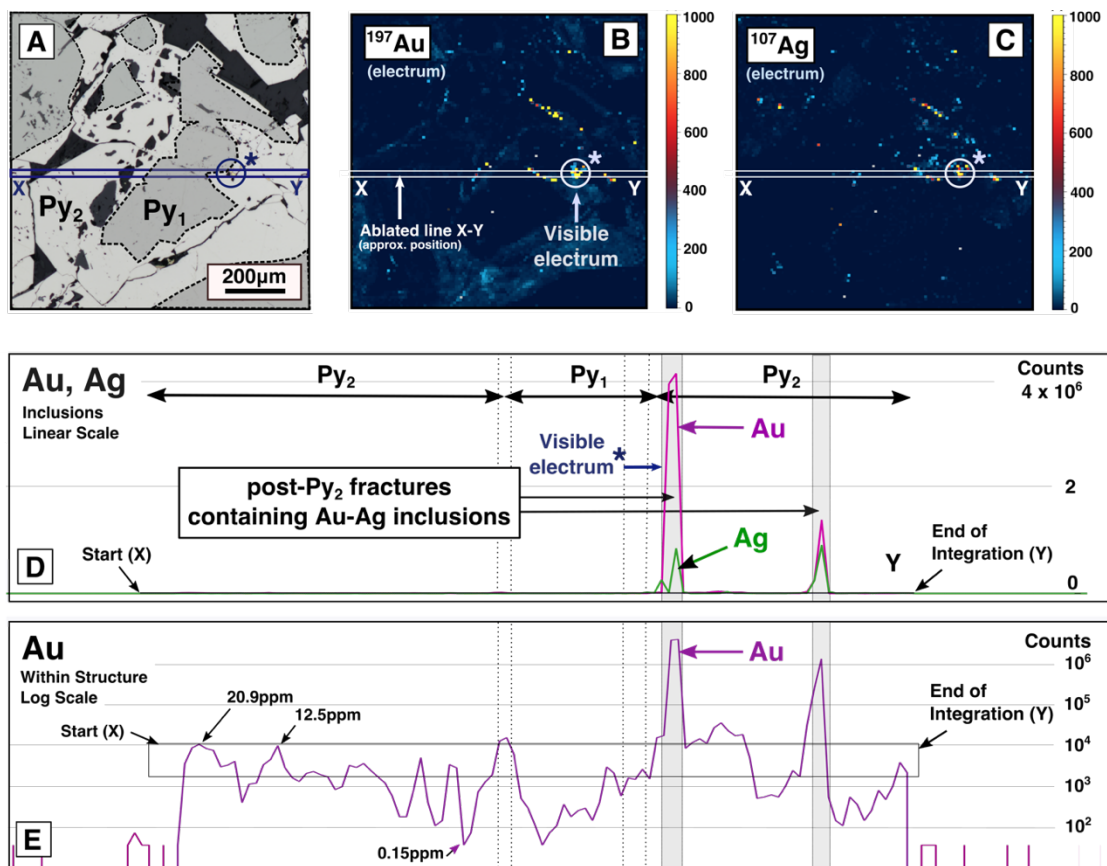


Figure 5.16. (A) The region of interest bound by blue lines marks the position of ablated line 62 (of 110) (X-Y) for the area of Py_{1-2} (element concentrations for other analytes are presented in Figure 2.14). (B) and (C) present Au and Ag with concentrations presented using a linear scale (ppm), revealing micro-scale Au particles (*designated as electrum); particles are positioned both along the boundary of Py_1 and within micro-fractures cross-cutting Py_1 and Py_2 . Raw counts received by mass spectrometer detector for Au and Ag are shown in (D), represented in linear scale: Au and Ag peaks are coincident where inclusions are present, the second of which lies within Py_2 , confirming that fractures bearing auriferous particles cross-cut this phase. while Au within the structure of pyrite is shown in part (E), represented in logarithmic scale: elevated Au within Py_2 is evident >0.15 ppm.

controlled by cataclasis and brittle deformation of grains interpreted to be coincident with collapse of the orogen.

5.11.v. Au and deleterious elements: As, Sb and Hg

The presence of deleterious elements (often referred to as ‘penalty elements’ due to financial penalties applied by smelters, or ‘impurities’) has implications for gold ore processing, due to the limited ability of smelters to treat concentrates which contain them; deleterious elements may include Sb, As, Bi, Cd, Cl, F, Pb, Hg, U and Zn (Adams, 2005).

Concentrations of As, Sb and Hg are recorded in Laser Ablation ICP-MS spot analyses at Curraghinalt, though in relatively low abundances for mineralisation-hosting Py₃ within shear-veins constituent of the estimated resource. Contents of As are most elevated in Py₂ overgrowths (within the earliest observed ‘syn-deformational’ veins) and is recorded in all spot analyses (median 14,680 ppm; IQR = 8,250 – 20,800 ppm; n=35). As in this phase exhibits a positive correlation with Au ($\rho = 0.89$; Spearman rank), also correlating positively with Ni ($\rho = 0.52$) and Co ($\rho = 0.50$), and negatively with Mo ($\rho = -0.66$). Within Py₁, arsenic is present at a median concentration of 15.6 ppm (IQR = 3.80 – 29.5 ppm; n=15), also correlating positively with Au ($\rho = 0.66$) and Ni ($\rho = 0.74$) though not with Co ($\rho = -0.19$). Py₃ records the lowest As concentrations of the three populations with a median abundance of 3.77 ppm (IQR = 2.44 – 6.15; n=126) where it correlates positively with Ag ($\rho = 0.62$), Pb ($\rho = 0.54$), Bi ($\rho = 0.54$), Sb ($\rho = 0.5$). The element does not show correlation with Te within tested phases. The identification of elevated Au correlating with As in Py₂ is indicative of a syn-deformation pressure equivalent to hypozonal formation depths (>12km) (Goldfarb et al., 2001) during growth of this phase and coincident metalliferous emplacement, at intermediate greenschist to amphibolite facies metamorphic conditions.

Both Sb and Hg contents show median abundances <2 ppm in Py₁ (median Sb = 1.04 ppm, IQR = 0.48 – 2.30 ppm, n=30; median Hg = 1.73 ppm, IQR = 1.37 – 2.22 ppm, n=35), and <1 ppm in Py₂ and Py₃. For the two elements, positive correlation with Au is only observed for Sb within analyses of Py₃ ($\rho = 0.52$).

5.12. Discussion

5.12.i. Overview

This section presents a detailed interpretation of findings from this study in the context of its principal objectives: (i) to develop an augmented paragenetic sequence of metalliferous emplacement at Curraghinalt which includes new petrographic and geochemical findings, and (ii) to consider the relationship between gold mobility, metamorphism and deformation.

A revised paragenetic sequence is presented in Table 5.5 which includes two Au mobility stages (I and II); supporting evidence is discussed along with how this model relates to previously presented models (*Sections 5.12.ii., 5.12.iii. and 5.12.iv.*). The implications of this study's findings that (i) evidence does not support the hypothesis that auriferous particles are associated with the growth of pyrite (*Section 5.12.v.*), (ii) Au, Ag, Bi and Te phases are not observed in textural equilibrium with pyrite (*Section 5.12.v.*), (iii) pyrite is absent within micro-fractures of Py₃ themselves (*Section 5.12.v.*) (iv) early base metal mobility is observed (*Section 5.12.vi.*) and (iv) evidence supports late introduction of Au and Te to the Curraghinalt vein network (*Section 5.12.vii.*) are discussed. The mobility of Au⁰ nanoparticles under retrograde conditions as indicated by supporting geochemical concentrations of Au and As is considered in *Section 5.12.viii.* Certain ore-forming processes are interpreted, including Au nucleation on fracture walls (*Section 5.12.ix.*) and bi-sulphide Au complexing in late transporting fluids, based on study observations and fO_2 and temperature conditions (*Section 5.12.x.*). It is proposed that Bi-Te-Au-Ag signatures, as discovered within Py₃ micro-fractures

in this study, are not atypical of gold deposits formed in orogenic terranes (e.g. Kalgoorlie, Western Australia; the Ashanti gold district, West Africa; Cripple Creek, Colorado, USA) (*Section 5.12.xi.*). Pyrite is a stable porphyroblast in metamorphic terranes which can archive concentrations of trace elements and therefore provide detailed insight into the mobility of those elements, petrographically constrained to deformation phases (*Section 5.12.xii.*).

5.12.ii. A revised paragenesis

High-precision techniques including Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Spectroscopy (EDS/EDX) and Laser Ablation Inductively Coupled Plasma - Mass Spectroscopy (LA ICP-MS) have enabled the gathering of geochemical data for trace elements within vein-hosted pyrite phases at low concentrations. Geochemical evidence is presented, supported by petrographic observations using optical microscopy, of gold mobility during two distinct metalliferous events at Curraghinalt: syn-deformational ‘Stage I’ corresponding to lattice-bound Au enrichment in Py₂, and late-orogenic ‘Stage II’, an event within cross-cutting shear-veins characterised by visible gold particles (as inclusions and aggregated particles). A revised chemically supported paragenetic sequence (a central objective of this contribution) is presented in Table 5.5, integrating petrographic and geochemical observations from this study. A schematic model of mobility at the grain-scale is proposed in Figure 5.17.

5.12.iii. Earlier models

Previous work in determining a paragenetic sequence for mineralisation at Curraghinalt by Earls et al. (1996), Wilkinson et al. (1999) and Parnell et al. (2000) were interpreted

Vein type		Ankerite-quartz-sulfide	Ankerite-quartz-sulfide	Quartz-sulfide 'shear-veins'	Fracture-infill of all previous phases
Relationship to fabrics		S ₂ /S ₃ fabric-parallel	S ₂ /S ₃ fabric-parallel	Cross-cutting	Cross-cutting
Deformation		Syn-D ₃	Syn-D ₃ (late)	Late orogenic	
Metamorphism		Peak (Upper GS)		Retrograde Path	
Timing		c. 468 Ma	c. 468 Ma	462.7 – 452.8 Ma *	
Key pyrite phase		Py ₁	Py ₂	Py ₃	-
Fluid phase		Ankerite, Q ₋₁	Ankerite, Q ₀	Ank, (Q ₁), Q ₂ **	Q ₃ -Q ₄ **
Au mobility Stage		-	I	-	II
Inclusions and entrained minerals	Au-Ag				
	Bi-telluride (Bi ₂ Te ₃)				
	Galena incl. (PbS)				
	Sphalerite (ZnS)				
	Muscovite				
	Ag-telluride (Ag ₂ Te)				
Synchr.	Chalcopyrite				
	Tetrahedrite				
Trace element concentrations	Mn				
	Co				
	Ni				
	Cu				
	Zn				
	Ag				
	Sn				
	Te			Early Te	Late Te
	Au				
	Pb				
	Bi				

Table caption overleaf

Table 5.5. Paragenetic sequence for tested vein types. * Rice et al (2016), ** Earls et al (1996), Wilkinson et al (1999), Parnell et al (2000). Line strength as a means to visualise data: >1 ppm = width of 1; >10 ppm = 2; >100ppm = 4; >1000ppm = 6.

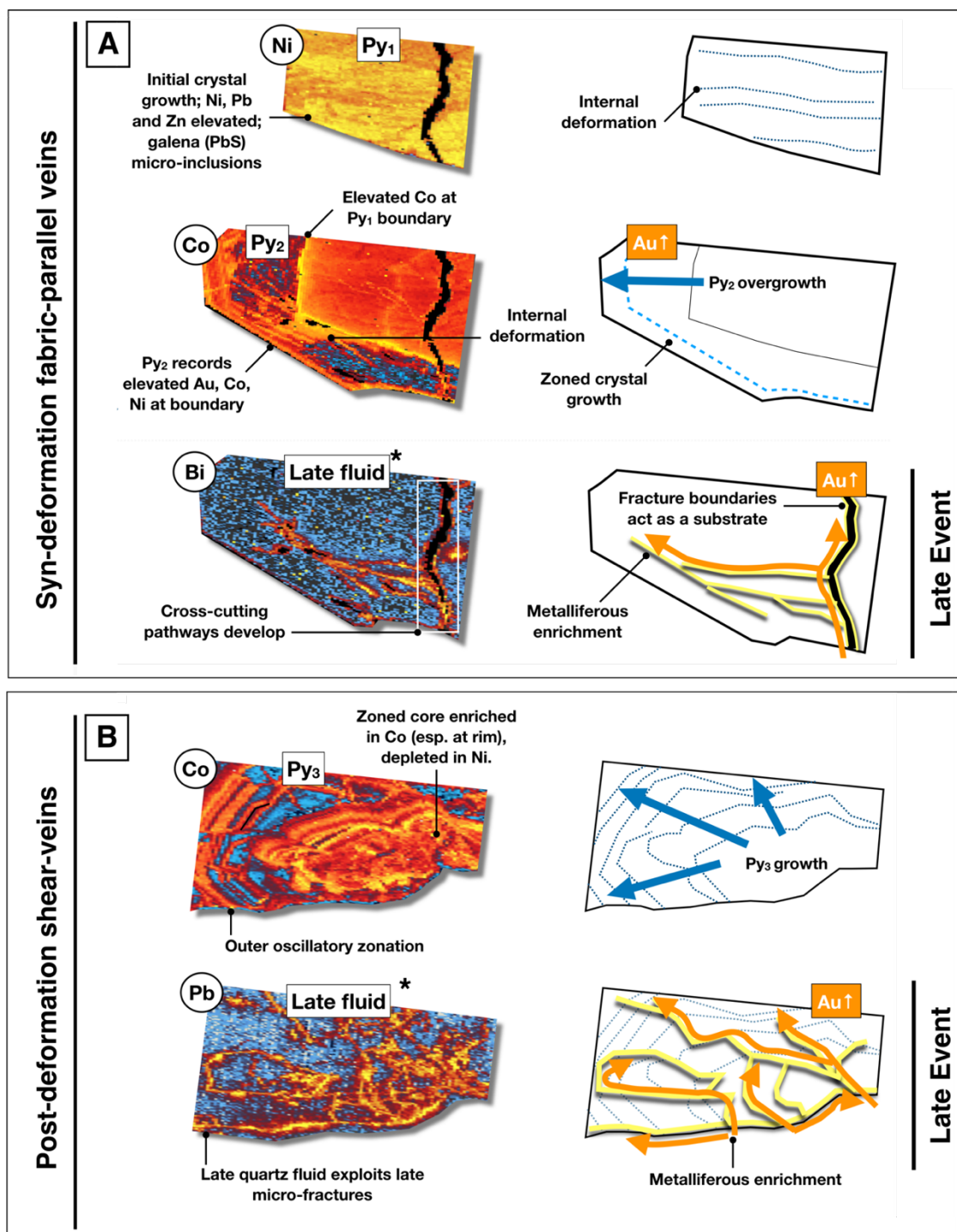


Figure 5.17. Schematic model of fluid interaction with pyrite phases and metalliferous emplacement at the grain-scale, based on Laser Ablation ICP-MS raster element mapping (Figure 5.13 and Figure 5.15). (A) early Py₁ and Py₂ phases, (B) resource-associated Py₃.

predominantly using petrographic evidence, fluid inclusions and additional microscopic studies (e.g. cathodoluminescence in relation to quartz), along with ^{34}S isotope signatures of host pyrite within shear-veins cross-cutting regional S_2/S_3 deformational fabrics. Four quartz phases (Q_{1-4}) within these veins form the framework for their interpreted sequence, along with the key observation of two specific electrum (Au-Ag) morphologies: ‘ e_1 ’ bound within pyrite grains (equivalent to Py_3 from this study, attributed to Q_2) and ‘ e_2 ’ located dominantly within fractures of those grains (attributed to fluid mixing of two end-members represented by Q_3 and Q_4); Q_1 was determined to be barren with respect to auriferous mineralisation. Interpretation of fluid compositions form the basis for source interpretations, leading some authors to suggest a magmatic reservoir for the initial fluid phase of Au (‘primary gold’; e_1 carried by Q_2) and the mixing of a surface-derived formation water (Q_3) with a basinal brine (Q_4) carrying ‘late Au’ (e_2). The favoured emplacement model for e_2 was the dissolution and remobilisation of primary e_1 into cataclastic fractures (disproved herein) by the Q_3 - Q_4 fluid or ‘late brine’, however their interpretation was open to the idea of the younger brine also introducing new Au to the system (Wilkinson et al, 1999).

5.12.iv. Initial Au mobility

The earliest recognised phase of Au within the Curraghinalt system observed in the results of this study pre-dates previous models, which were focused entirely on veins cross-cutting penetrative S_2/S_3 Grampian fabrics. This study reveals an earlier phase of regional Au mobility which was emplaced synchronous with fabric development. This event is defined herein as Stage I, and is characterised by lattice-bound Au at concentrations <10 ppm (median 3.69 ppm; IQR = 2.02 – 10.1 ppm; $n=34$) within Py_2 . The discovery of this emplacement phase adds a potential 6 Myr of Au mobility to the 10 Myr interval within the Ordovician proposed by Rice et al (2016) (462.7 – 452.8 Ma), which may be therefore

considered the final stage of Au emplacement which initiated synchronously with peak deformation (D₃; c. 468 Ma).

The internal structure of Py₁ and Py₂ is preserved (evidenced through Laser Ablation ICP-MS mapping particularly of Co and Ni, see Figure 5.13 and Figure 5.14), therefore it is not considered feasible that Py₂ was itself a source for Au within visible auriferous particles associated with subsequent pyrite generations. It would be expected that there would be disturbance of geochemical growth zones which is demonstrably absent, therefore Au migration from within syn-deformational Py₂ may be discounted.

5.12.v. Pyrite hosted auriferous particles

For shear-hosted veins (within envelopes associated with the estimated resource, e.g. ‘Crow’, ‘106-16’), the results presented in this study challenge the concept of an ‘e₁’ Au emplacement phase synchronous with pyrite growth (attributed in this study as Py₃). Laser Ablation ICP-MS element raster mapping demonstrates that optically visible particles, previously considered to be ‘e₁ inclusions’, form at the intersections of a cryptic network of cataclastic micro-fractures exploited by a late fluid exhibiting a Bi-Te-Ag-Au-Pb-Cu signature infiltrating Py₃ (see Figure 5.15) along with earlier phases Py₁ and Py₂ (see Figure 5.13, Figure 5.14 and Figure 5.16). This chemical association is supported by the petrographic observation of intergrowths of auriferous particles with Bi- and Ag- tellurides observed within these micro-fractures.

While gold particles are observed optically within pyrite grains and those particles are more argentiferous, this observation by previous workers is most likely linked to the introduction of a late fluid; an ‘e₁’ or ‘e₂’ phase cannot be paragenetically distinguished by this study as two separate events. Evidence suggests simply that auriferous particle formation occurs as a single late event (Stage II), which has the effect of decoupling Au emplacement from the host pyrite development entirely and suggests a late fluid origin. In light of there

being no clear evidence from this study to support auriferous electrum as paragenetically linked to the growth of pyrite phases; Au(-Ag) particles associated with the principal gold deportment, in the view of this study, entirely post-date development of all pyrite phases Py₁₋₃. Furthermore, examination of micro-fractures hosting Au show no evidence of any textural equilibrium between Au-Ag-Bi-Te phases and pyrite, and the fractures are notably void of pyrite.

5.12.vi. Zn, Ni and Pb mobility during early Grampian arc-continent collision

Results provide evidence that elevated concentrations of Zn and Ni were emplaced by hydrothermal fluids prior to the earliest instance of observed Au (Py₂; Stage I). This study identifies elevated Zn and Ni contents within the earliest encountered pyrite phase (Py₁). This precursor phase, along with Stage I Au in Py₂, is encountered within veins hosted within S₂/S₃ fabrics, which likely correspond to metamorphic veins described by Parnell et al (2000) which were considered at that time to be barren. Results suggest a quartz phase preceding those identified by Wilkinson et al. (1999) and Parnell et al. (2000), Q₀, which has been imaged using cathodoluminescence showing that Py₁₋₂ grains incur upon and replace this phase of quartz (Figure 5.5). Prograde base-metal signatures are encountered in pyrite (largely framboidal varieties) within orogenic systems, for example within the Otago Schist of New Zealand (Hu et al., 2016; Pitcairn et al., 2010). Hu et al (2016) note enrichment of Ni, Co, Pb, Zn along with As, V and Cd within ‘polyframboids’ which may be a source of metals in mineralising fluids. Carbonaceous shales present a possible source for Zn and Ni signatures; as an example, a linear correlation between the two elements is observed in organic-rich marine shales of Devonian and Carboniferous age in the mid-western United States (Desborough et al., 1991). Carbonaceous shales are recorded in lower Dalradian Supergroup stratigraphy in County Donegal (Atkin, 1979). An alternative source for base-

metals is the outboard arc which records numerous Zn occurrences (Spencer, 2012). However, the early syn-deformational timing of Py₁ suggests that a remobilised Laurentian margin source is a more likely candidate.

5.12.vii. Py₃ is an unlikely source of Au or Te

With respect to the post-Py₃ late fluid which this study proposes transported the most significant amounts of Au into late micro-fractures, Laser Ablation ICP-MS spot analysis and chemical mapping (e.g. Figure 5.15) and Scanning Electron Microscopy (SEM) (e.g. Figure 5.8) confirm the commonly observed (Boyle, 1979) Te-Bi-Au-Ag association, along with elevated Cu. Results presented using these techniques provide information on the mobility of Au and Te during evolution of the system. For the principle host mineral phase, Py₃, data from this study (Table 5.4) demonstrate that Te is relatively enriched (at concentrations $\approx$ 1-100ppm, med. 5.21 ppm) compared with earlier phases, and that Te is anomalous in Py₃ with respect to Au ($\approx$ <0.5 ppm), Ag and Bi (Figure 5.12). Au conversely does not show elevated contents (med., 0.31 ppm; IQR = 0.08 – 0.66 ppm; n=69). Auriferous particles are positioned within a framework of cryptic micro-fractures, precipitating in a constrained sequence prior to Ag- and Bi- tellurides, while the zonation of crystals (particularly evidenced through Co and Ni distributions) are undisturbed and demonstrate little distortion of host pyrite lattices.

While there is potential for Py₃ to be a source of Te, and not of Au, it is unlikely that either phase contributed to the deportment of Au particles or tellurides observed within late micro-fractures. If Au or Te were to be exsolved from pyrite, significant elevated contents of Au within the pyrite lattice would be required in order to form a deposit of significant magnitude (Taylor, 2015) and one would expect to observe distortion of the outer zones of chemically mapped pyrite phases, neither of which are the case in tested samples. This study

proposes therefore that Au was introduced natively to pyrite fractures carried by late fluid. Over-pressurising may be responsible for injection of the aqueous fluid into pyrite fracture networks, along with changes in solubility (Akinfiyev and Diamond, 2009) which precipitated quartz. Subsequent changes in the physio-chemical environment led to supersaturation of the fluid with respect to Au, and later Te and Bi. Cook and Ciobanu (2005) and Boyle (1979) suggest an overall late overall timing for Te emplacement in auriferous deposits which broadly agrees with the data herein. This sequence of events is identified at deposits of the Grass Valley Gold District of California, where auriferous fluids infiltrating late fractures of pyrite grains is well established (Knaebel, 1931); Au in the district is found to precede the precipitation of tellurides within pyrite micro-fractures (Taylor, 2015).

5.12.viii. Au/As: Late fluid super-saturation: supporting evidence

Plotting Au/As (converting ppm values to mol %) and considering the positions of results relative to the solubility curve of Deditius et al. (2014) ($C_{Au} = 0.004.C_{As} + 2 \times 10^{-7}$) appropriate for orogenic systems, this study observes that data for Py₁ and Py₂ ('syn-deformational') phases generally plot below this curve, indicative of Au¹⁺ in solution, while data for Py₃ plot above the curve confirming the presence of Au⁰ nanoparticles. For Py₂, analyses show higher concentrations of both Au and As than for Py₁, suggesting a prograde model of nanoparticle dissolution and incorporation of Au into the pyrite lattice during heating and burial. The relative position in Au-As space of Py₃ values above the solubility curve demonstrates that Au⁰ nanoparticles were mobile under retrograde conditions, which aggregated as colloids within late micro-fractures. This evidence supports the model of a late super-saturated fluid emplacing Au along with Bi, Ag and Te phases.

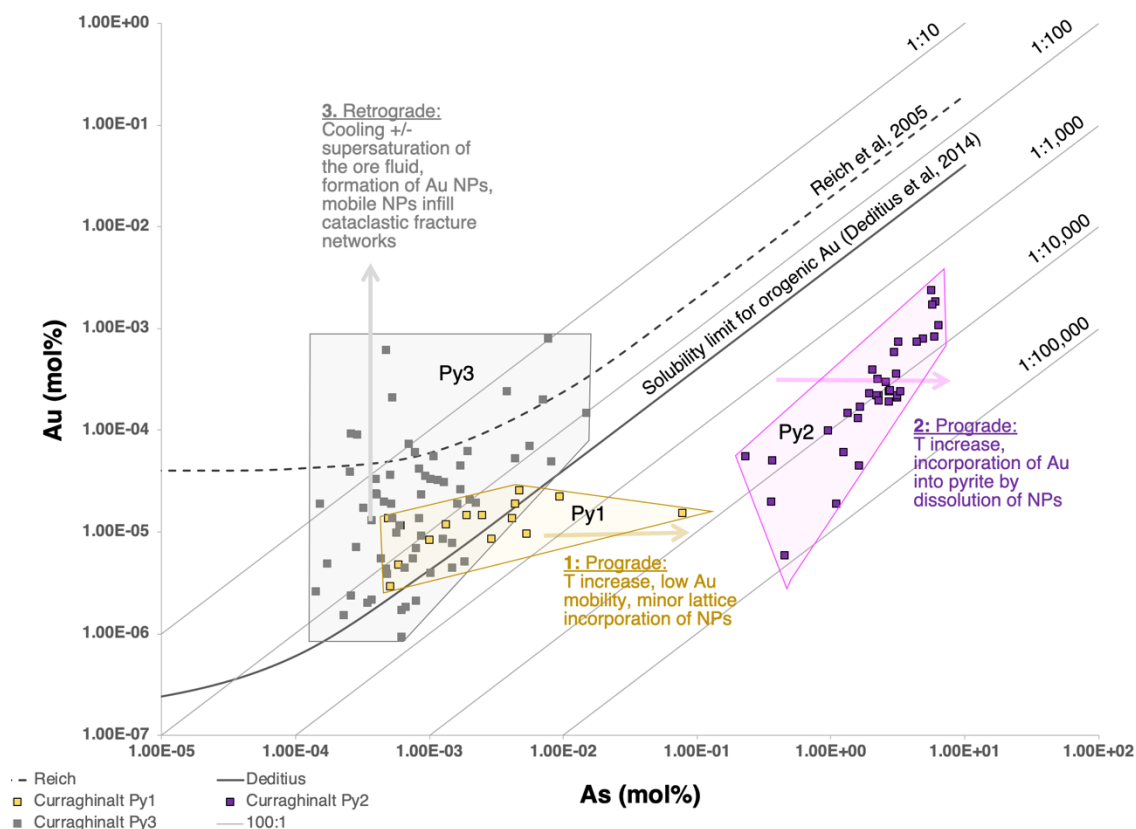


Figure 5.18. Au/As plot of Laser Ablation ICP-MS spot analyses for pyrite generations Py₁, Py₂ and Py₃, with the solubility curves of Deditius et al. (2014) and Reich et al. (2005).

5.12.ix. Nucleation of Au on fracture-wall surfaces

Observations from this study suggests that Au along with tellurides nucleated within the walls of Py₃ micro-fractures, introduced by a late auriferous fluid; it is likely that this was instigated by changes in pH resulting in locally reducing conditions, and that pyrite surface reactions and monomer diffusion are key enabling mechanisms for nucleation.

The chemistry of gold crystal nucleation has been studied by notable scientists including Faraday, who experimented with the nucleation of Au colloids as early as 1856-1857 (Thanh et al., 2014), famously forming them by accident [he observed a cone effect (known as the ‘Faraday-Tyndall effect’) when shining a light through a fluid, which he discovered was related to the suspension of gold particles too small to observed at the time (The Royal Institution, 2019)]. Thanh et al (2014) emphasise a thermodynamic perspective

for the formation of nuclei on surfaces; supersaturation, temperature and surface free energy are identified as critical experimental parameters, with the largest impact on the rate of nucleation being derived from supersaturation. They identify surface reactions and the diffusion of monomers (molecules which may bond with an identical molecule to form a polymer chain, or three-dimensional network) to surfaces as key mechanisms for Au particle nucleation.

5.12.x. Au complexing and the role of late orogenic fluids

Summary of pertinent observations

A late fluid infiltrating micro-fractures of Py₃ forms the ore-stage at Curraghinalt; evidence characterising the emplacement of metalliferous particles and the geochemistry of this event is provided high resolution SEM imaging of veins where Au is observed to have been emplaced in sequence with Bi- and Ag- tellurides along with later chalcopyrite (Au → Ag → Te → Bi → Cu; see *Section 5.8*), cathodoluminescence (CL) which demonstrated quartz infiltrating micro-fractures (see *Section 5.8*) and LA ICP-MS raster element mapping, wherein (i) the full extent of micro-fracturing has been revealed through elevated contents of Cu, Ag, Te, Au, Pb and Bi, and (ii) it has been confirmed through the lack of any disturbance to cyclical growth zones (e.g. of Co and Ni) that this fluid did not source gold from the internal structure of pyrite grains themselves (see *Section 5.11*). These findings have implications for the genetic model in terms of (i) gold complexing within carrier fluids, and (ii) the *role* of late fluids at Curraghinalt.

Au complexing overview

Chloride and bi-sulphide complexes are the two principal carriers of Au within hydrothermal fluids (Pokrovski et al., 2014); the solubility of Au within fluids is controlled principally by temperature, pH and redox conditions (fO_2). Taking into account the mineral paragenesis, textural evidence and previous fluid inclusion studies (Wilkinson et al., 1999; Parnell et al., 2000), this study proposes the main Au emplacement stage at Curraghinalt was facilitated by bi-sulphide (HS^-) complexes of Au in a late fluid which infiltrated during the fracturing of 'ore-stage' Py_3 . This is consistent with the view expressed in previous studies (wherein bi-sulphide complexes were favoured over the introduction of chloride complexes) under lower-temperature conditions, however the perspective offered by new information requires a revised interpretation of the prevailing model.

A revised interpretation in support of bi-sulphide complexing

In suggesting bi-sulphide complexes carrying Au within this late fluid rather than chloride complexes, the prevailing model of Wilkinson et al. (1999) favours the interpretation that the dissolution of pyrite is considered to have resulted in elevated bi-sulphide activity and accessing of Au 'locked' within pyrite crystals. This interpretation is problematic in the context of aforementioned microanalytical and geochemical findings of this study which show that Au was introduced from an external source, and not liberated from within pyrite itself. This information was acquired from LA ICP-MS raster element mapping of Py_3 . Dissolution of pyrite is not observed and is discounted as a mechanism, however a reinterpretation can be offered which does support bi-sulphide complexing. There are three components to this analysis: (i) petrographic evidence (relating to sulphide) and phase relations (temperature - fO_2 ; involving a re-examination of fluid inclusion data from the literature and (ii) geochemical evidence (with regards solubility of Au).

The observation of abundant pyrite (Py₃) within ‘ore-stage’ veins (cross cutting the S₂/S₃ fabrics) supports widespread reducing conditions prior to the cataclasis and the introduction of those fluids. This study observes that pyrite is not present within microfractures of Py₃ hosting Au; however, sulphide stability is supported by the observation of chalcopyrite sealing those fractures. Plotting this data in fO_2 – temperature space, from which fO_2 is inferred by relative reducing vs. oxidising conditions, temperature data provided by aforementioned fluid inclusion data and the stability of sulphide inferred from the observation of pyrite and chalcopyrite, a field representing those conditions can be approximated (see Figure 5.19). The lowering of the temperature within that field (indicated by a red arrow) and the traverse of the ‘solubility cliff’ effects the saturation of Au in fluids and the precipitation of Au particles which nucleate on reactive surfaces within microfractures (solubility contours for Au(HS)₂⁻ fluid is shown using blue dashed lines in the referenced figure).

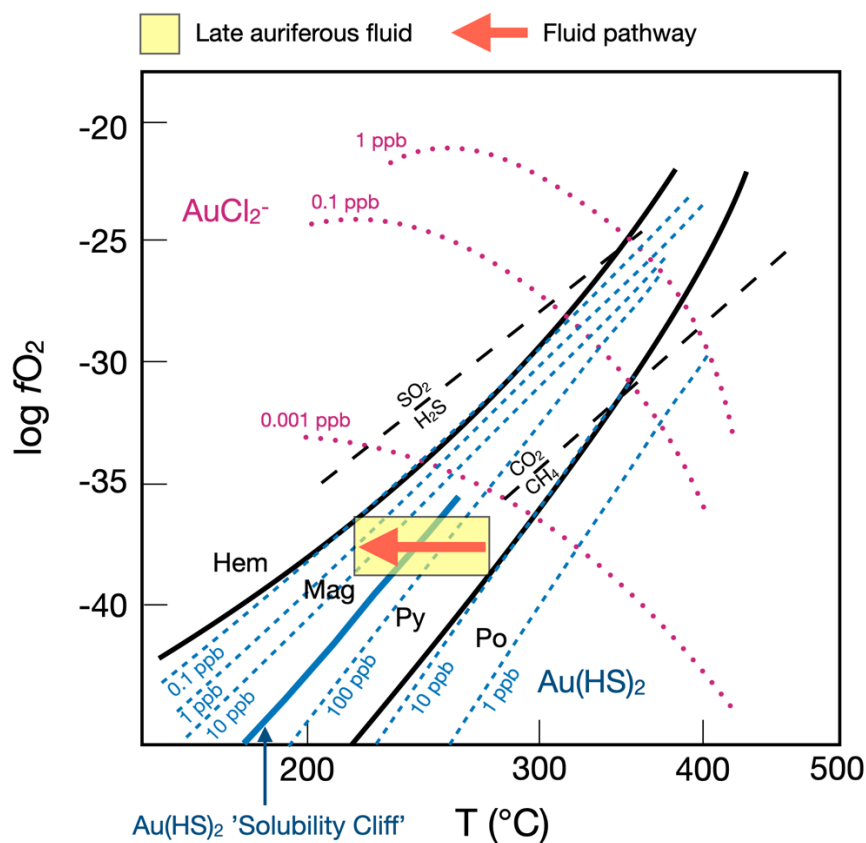


Figure 5.19. Estimated fluid pathway and $\log f\text{O}_2$ – temperature field for late auriferous fluids at Curraghinalt based on homogenisation temperatures (see previous figure) and observed stability of pyrite. Localised change in temperature may force the fluid over the ‘solubility cliff’ (attributed on figure), wherein the solubility of Au decreases significantly with a minor change in temperature (~ 50 °C) and particles become available which may nucleate within pyrite fractures. Conditions favour bisulphide complexing as opposed to chloride complexing: temperature conditions would need to be significantly higher (not supported by reported data or observations in this study). Modified after Klein (2014); diagram conditions: 6 wt.% NaCl, pH 6, 320 ppm S.

As aforementioned, pyrite is not observed healing micro-fractures of Py_3 (interpreted from element abundances recorded through LA ICP-MS raster mapping and SEM imaging): one potential explanation is the increased stability of Fe-chloride complexes associated within late fluids (Q_3 and Q_4 brines). Iron may be retained within the saline fluids rather than being available for the precipitation of pyrite. In chloride-rich solutions FeCl_2 becomes stable at 200 °C, increasing Fe solubility and possibly limiting the precipitation of pyrite (Heinrich and Seward, 1990).

A late fluid was also proposed by Wilkinson et al. (1999) and Parnell et al. (2000); examination of fluid inclusions enabled the characterisation of the ‘late quartz’, considered to be derived from the mixing of fluids (Parnell et al., 2000; Wilkinson et al., 1999); these observations are consistent with findings from this study. Salinity and homogenisation temperature data is presented by Wilkinson et al. (1999) relating to the Q_3 (formation water) and Q_4 (basinal brine) quartz phases. For the Q_3 fluid, a salinity of 0.1 to 15.4 wt.% NaCl equiv and a homogenisation temperature (T_h) of 92-276 °C is presented, while Q_4 inclusions have a salinity of 11.9-26.2 wt.% NaCl equiv while T_h of 42-230 °C. The late fluid event is characterised in their study as ‘ Q_3 - Q_4 ’, resulted from a mixing of the two fluids. A revised interpretation of the *role* of previously characterised late fluids is necessitated by this study. An important modification to the previous model is that while elevated NaCl is associated with a component to ‘ Q_3 - Q_4 ’, its contribution to Au emplacement was likely limited to the

lowering of fluid temperatures during mixing with auriferous metamorphic fluids. This would have the effect of forcing saturation (Figure 5.20) and eventual precipitation of Au. This study therefore favours transport of Au within bisulphide complexes: more oxidising and higher temperature conditions would be required for the supersaturation of AuCl_2^- under the temperature conditions suggested, and is not supported by observed vein mineral assemblages and fluid inclusion data.

The introduction of external Au, and revision of the remobilisation hypothesis

Wilkinson et al. (1999) acknowledge a lack of clarity as to whether the infiltration of late fluid (including a brine component) introduced new Au, or remobilised Au from pre-existing mineralisation, propose that Au was solubilised, transported and reprecipitated by the late brine. This study is of the view that the hypothesis of remobilisation of pre-emplaced Au from within pyrite by the late fluid can be discounted as this is not supported by petrographic or geochemical evidence. Future fluid inclusion work to characterise the properties of fluids carrying gold within observed infiltrating pyrite micro-fracture networks is recommended by this study.

5.12.xi. Are Bi-Te-Au-Ag signatures typical of orogenic gold deposits?

Bismuth and tellurium minerals are commonly associated with gold emplacement in a range of deposit types, with a Te-Bi-Au(-Ag) chemical relationship frequently encountered. Telluride emplacement is also observed to be consistently late in the depositional cycle of quartz-sulphide deposits, and the age of systems themselves appears to be largely irrelevant with respect to this correlation, with tellurides observed within auriferous deposits from the Precambrian to the Tertiary (Boyle, 1979). Cook and Ciobanu (2005) agree with Boyle (1979)

in pointing out that this chemical relationship is not specific to one deposit classification, but observed in systems across the magmatic-hydrothermal and metamorphic spectra. Examples of the range of deposits and deposit-types where tellurides are observed in association with Au include the giant orogenic Golden Mile deposit, Kalgoorlie, Western Australia (Boyle, 1979; Cook and Ciobanu, 2005; Shackleton et al., 2003); Ashanti, Ghana, which is theorised to have a granitoid-intrusive component (Bowell et al., 1990) and Cripple Creek, Colorado, USA (Boyle, 1979; Goldfarb, 2014; Kelley and Ludington, 2002).

5.12.xii. Pyrite as a vectoring tool

Key advantages of pyrite are its abundance and stability as a rigid porphyroblast throughout the development of veins; timing of pyrite growth has been shown in this study to be linked to deformation fabrics. This study demonstrates that pyrite trace element geochemistry has utility in assessing the mobility of trace elements coincident with phases of deformation when supported by robust petrographic constraints.

The abundance of Au observed within early syn-deformational Py₂ provides evidence that Au was mobile at an early stage in the deformation history synchronous with peak metamorphic conditions, and as such provides an indicator of Au fertility. It is considered that the discovery of such enriched phases in a greenfields exploration setting may be of strategic use in evaluating regional prospectivity, when considered in the context of localised structural and rheological complexity. Results demonstrate that cataclastically deformed pyrite is a suitable trap for Au and telluride phases, and that bounding surfaces within micro-fractures provide a substrate for Au particle nucleation. Examination and quantification of pyrite morphology and deformation textures within orogenic belts may provide a useful vector. Calculation and plotting of Au/As ratios with respect to a solubility curve suitable for orogenic systems allows for the interpretation of Au chemical state and the inference of respective processes. In a mineral exploration context, such calculations may

prove of value in determining the relative position of observed pyrite within an evolving system (e.g. prograde vs. retrograde, deformation context).

5.13. Conclusions

While orogenic gold systems display many characteristics which are broadly observable across the deposit-class spatially and through geological time, many exhibit local peculiarities specific to their physio-chemical environment. Curraghinalt is such an example; multiple metal emplacement events are observed through its visible mineral phases and trace element signatures. This study has demonstrated using a microanalytical approach that the principal stage of Au emplacement post-dates the development of quartz veins which cross-cut deformation fabrics, is decoupled from the growth of pyrite generations and synchronous with a period of post-deformational cataclasis, and presents evidence in favour of Au being transported within this stage by a late supersaturated fluid under retrograde metamorphic conditions. This study also presents evidence of precursor phases of Zn-Ni and Au mobility, associated with veins which formed during the development of a Grampian schistosity within host formations. It is not suggested by the results that locally there is any link between early lattice-bound Au and ore-stage Au deposition; evidence supports their derivation from distinctive sources.

The determined sequence of events is as follows:

1. Synchronous with the development of prograde S_2 schistositities in Dalradian Supergroup host-rocks, base-metal transporting fluids were mobile which exploited weaknesses parallel to this new fabric. Zn and Ni anomalies are recorded within the earliest phase of pyrite Py_1 , hosted by quartz-ankerite veins. This event may be

considered to be broadly coincident with peak-metamorphism at upper-greenschist facies conditions. Such fluids may be sourced from carbonaceous shales formations lower in the stratigraphy.

2. While prograde S_3 fabrics developed, an auriferous fluid was mobile locally to Curraghinalt. A second generation of pyrite, Py_2 , developed as overgrowths within fabric-parallel quartz-ankerite veins. A switch occurred from Zn-Ni transporting fluid to an auriferous signature, therefore this fluid is likely to have a distinct composition, and was likely emplaced following a reconfiguration of structural pathways during the early stages of orogenic collapse. This is likely to be an orogenic fluid associated with the dehydration of host formation minerals.
3. Within a distinctly retrograde metamorphic environment, shearing and dilation resulted in cross-cutting structures penetrating Grampian S_2/S_3 fabrics, resulting in the development of the principle quartz-ankerite-sulphide vein envelopes associated with the Curraghinalt resource. Pyrite (Py_3) is precipitated from the fluid, recording elevated Ni (and to an extent, Mn, Co and Te). While Te within this phase is anomalous in comparison to earlier phases, Au is depleted, evidence that Py_3 itself was not a viable source of gold.
4. An episode of brittle deformation resulted in cataclasis and fracturing of Py_3 . During this phase, a saline orogenic fluid carrying Au, Ag, Bi, Te and Pb exploited these structural weaknesses infilling grain micro-fractures and enveloping grain boundaries (a magmatically derived model for this stage is neither required nor supported by the findings of this study). Au was likely carried as bisulphide complexes associated with the dehydration of continental shelf sediments. Fluctuations in pressure-temperature

conditions and episodic opening and closing of the system are reflected in oscillatory Co and Ni variations in Py₃ growth phases. There is some evidence of Bi- tellurides forming during the growth of Py₃, which most likely sourced Te (and Bi) internally.

5. Au(-Ag) particles formed within micro-fractures, preferentially at junctions (physical micro-scale traps), and at grain boundaries where host quartz is weakest. These particles may have been mobilised during further synchronous cataclastic episodes to become 'free gold'. An argentiferous signature for particles along micro-fractures spatially constrained 'within' grains is accounted for by secondary Ag precipitation, additionally forming enveloping Ag- and Bi- tellurides. Te may be sourced from the Py₃ grains themselves, or enriched by the saline fluid. The timing of this episode is not altered from the findings of previous workers (late Ordovician), however the previously argued concept of argentiferous Au-inclusions is not supported. This episode also affects the earlier Py₁ and Py₂ carrying phase, where Au(-Ag) grains are also observed in late micro-fractures bearing the same Ag-Bi-Te-Pb signature.
6. A subsequent Cu emplacement phase of chalcopyrite flooding occurs, infilling remaining space within micro-fractures and partially enveloping pyrite grains in all veins types.

The geochemical examination of petrographically constrained grains of pyrite from the Curraghinalt deposit has revealed that fluids were mobile at an early stage which carried Au synchronous with deformation suggesting the orogen was fertile, however that a late separate Au event late in the orogenic history and associated with a super-saturated fluid was responsible for the large-scale mobilisation of nano-particles and emplacement of visible phases. With regards implications for exploration, this study suggests that pyrite can provide

insight into the mobility of metals with time, which may confer indications of metal prospectivity.

Chapter Six: Targeting orogenic gold in north-west Ireland: the paragenesis and geochemical signature of vein-hosted pyrite at Cloonacool, County Sligo

6.1. Abstract

The scarcity of economic near-surface metal deposits presents an increasingly challenging environment for explorers; while much can be learned from traditional prospecting techniques and drilling, new tools are required. Analyses of the trace-element geochemistry of sulphide minerals hosting mineralisation offer insight into the evolution of complex mineral systems. Petrographically supported paragenetic sequences may illuminate discrete macro-scale emplacement events which may be linked to the local and regional deformation history, and help to explain variations both within deposits themselves and with adjacent systems. Cloonacool is a vein-hosted Au prospect in the west of Ireland set within a Neoproterozoic terrane (Ox Mountains Central Inlier, Dalradian Supergroup), deformed during the Palaeozoic Grampian orogenic event, c. 475-460 Ma. The occurrence is hosted by comparable stratigraphy and adjacent to the same tectonostratigraphic boundary as gold resources that are the current focus of economic activity along-trend in Northern Ireland at

Curraghinalt and Cavanacaw (Sperrins Inlier, Dalradian Supergroup). This contribution details the results of analyses of pyrite samples from drill-core across the prospect, using Scanning Electron Microscopy (SEM) techniques including Energy Dispersive X-ray Spectroscopy (EDS/EDX), coupled with Laser Ablation Inductively Coupled Plasma – Mass Spectroscopy (LA ICP-MS) in-situ methods. This study has been conducted with a view to extracting geochemical information which may enable interpretation of the deposit-scale paragenetic history of host pyrite, and the identification of potential trace-element pathfinders for Au within the Ox Mountains Central Inlier. Shear and branching extensional veinlets are observed, with breccias associating with structurally weakened zones on the scale of the examined drill-core. Tested quartz-sulphide veins have an association with composite S_2/S_3 regional fabrics, exploiting weaknesses between grains of a coarse semi-pelitic to psammitic quartz-albite-chlorite-muscovite host assemblage. These pathways have been opened at multiple stages by fluids carrying differing chemical signatures as evidenced by pyrite analyses. SEM imaging and EDS/EDX results reveal compositional zonation of pyrite, confirming a multi-phase geochemical evolution. Two vein types are observed; early Type I veins (200-1,000 μm scale) principally associated with quartz, Ti-oxides (ilmenite and rutile) and zoned pyrite (Py_1), with only rare auriferous inclusions encountered. Type II veins which are broader (cm-scale) and utilise the same pathway network hosting coarse, anhedral and brittlely deformed pyrite masses (Py_2) carrying Au(-Ag) and galena inclusions, while euhedral ancillary grain assemblages (Py_3) carry diagnostic sphalerite. Ti-oxides and rare apatite are also associated with this vein type. Visible Au phases are present in the form of inclusions within pyrite grains themselves and proximal to grain boundaries (avg. 76.9 wt.% Au, $n=18$), as ‘free gold’ (avg. 71.74 wt.% Au, $n=2$) and as late micro-fracture infill (avg. 64.11 wt.% Au, $n=1$). The average Au:Ag ratio for the acquired visible phase dataset within Type II veins is 3.7 : 1 ($n=21$). LA ICP-MS in-situ spot analyses of Py_1 , Py_2 and Py_3 ($n=107$) reveal median Au contents within tested Cloonacool pyrite of 0.59 ppm (IQR = 0.23 – 1.35

ppm, n=94) with a minimum of 0.04 ppm and a maximum concentration of 11.8 ppm; average Au/Ag is 1.4 ($2\sigma = 8.39$, n=87). Average Co/Ni for the pyrite dataset is 0.69 ($2\sigma = 4.02$, n=100), with a broad range observed between 0.006 and 20.08, confirming variability of Co and Ni contents across and potentially within different pyrite classes. Median enrichments >100 ppm are observed for Ni (255 ppm, IQR = 54.5 – 700 ppm, n=105) and As (950 ppm, IQR = 52.8 – 5,278 ppm, n=106). Spot analyses demonstrate internal chemical variation within Py₂ masses, with elevated Ni, As, Au, Te and Bi and relatively depleted Cu, Ag and Pb contents toward the edges of tested regions. Combining observations from petrography, LA ICP-MS spot data and raster element mapping of Py₂ confirms 4 internal generations: Py_{2a} (an early Zn event), Py_{2b} (euhedral zoned cores containing oscillatory Co and Ni), Py_{2c} (associated with early Au emplacement and visible Au phases) and Py_{2d} (bearing relatively elevated Co, Ni, Ag, Sb, Te and Pb, associated with inclusions of galena).

It is considered that while tested veins show a general petrographic association between Au, Pb and Zn within pyrite, geochemical analyses show that Cloonacool Au mineralisation is principally associated with a discrete Au-As enriched pyrite generation (Py_{2c}), and a later fluid event which infilled grain micro-fractures post-deformation. Pyrite concentrations of 0.01-10 ppm of Mo, Ga, Sn, W and Tl, 0.1-1ppm of Mn, 1-10ppm of Ag, Sb, Te, Au, Hg and Bi, 10-100ppm of Co, Ni, Cu, Zn, Se and Pb and >1000ppm As are presented as a potential pathfinder framework for auriferous Py_{2c} (Au event I), though late Au post-dating all pyrite generations (Au event II) is also an important constituent of this prospect.

6.2. Introduction

6.2.i. Discovery of gold in the Ox Mountains

Gold exploration in the north-west of Ireland led to the discovery of new deposits during the 1980s; one mine is actively producing at Cavanacaw, and a >6 Moz deposit is at an advanced stage of development at Curraghinalt. Both of these are located in County Tyrone, Northern Ireland. Prospecting has also been undertaken along the trend of the associated major structure, the Fair Head-Clew Bay Line (FH-CBL), to the south west: Au in the Central Ox Mountains Inlier was discovered in 2016 (Playfair Mining Ltd., 2016), principally using traditional geological methods. This included mapping of a 4.5 km x 200 m E-W trending target structure, coincident with the faulted boundary of the Lower Lismoran and Ummoon Formations (within the Argyll Group). This structure is identifiable in Tellus (inter-governmental survey) geophysical data as a conductor. A faulted contact of the Inlier is present with Carboniferous stratigraphy to the north, while to the south the Dalradian-Carboniferous boundary is present as an unconformity. Quartz and sulphide-bearing float was recovered from the target area which carried grades of up to 9.8 g/t Au; 2016 drilling confirmed gold-in-bedrock (with grades up to 2.8 g/t) within the NW-SE trending 'Furze' vein, and the presence of a 100-150m thick Cloonacool Alteration Zone (CAZ), characterised by silicification, chloritisation and bleaching of the host formation. Preliminary geochemical assay results suggested an association of Au with Te.

6.2.ii. Pyrite as an archive of geochemical events

Pyrite, as one of the most common sulphide minerals in the lithosphere, is intimately associated with metal emplacement in hydrothermal ore systems (Ciobanu et al., 2012; Craig and Vokes, 1993; Keith et al., 2018). In metamorphic terranes, it preserves both protracted hydrothermal signatures and deformation textures which may be diagnostic of specific events (Craig et al., 1998; Craig and Vokes, 1993). Pyrite also has the ability to retain a robust geochemical record of elements mobile during geologic events (Large et al., 2012; Large et al., 2009; Li et al., 2019; McClenaghan et al., 2004; Shao et al., 2018; Steadman et al., 2015; Thomas et al., 2011), this presents an opportunity for workers to greatly enhance their understanding of prospects and where intercepted sulphide mineralisation may lie within the broader chemical context of a multi-faceted mineralising system. Studies have demonstrated the capacity of pyrite in a diverse array of settings to retain an archive of chemical signatures, for example Co, Ni, Cu, Zn, As, Mo, Ag, Sb, Te, Au, Pb, Bi and platinum-group elements (Keith et al., 2018; Large et al., 2012). Parameters which may act as controls on mineralisation in hydrothermal systems may include pH, pressure, temperature and fO_2 conditions; formation mechanisms include boiling, conductive cooling, redox variations and sulphidation resulting from wall-rock interactions (Keith et al., 2018). Trace element ratios of mineral phases can provide insight into such processes and the nucleation of metalloid particles. Co/Ni ratios may enable the discrimination of diagenetic and hydrothermal pyrite and indicative of ore-forming processes (Bralia et al., 1979; Large et al., 2009), Au/As provides information on the solubility of Au in fluids (Deditius et al., 2014; Reich et al., 2005), while Te and Se ratios have recently been evaluated to elucidate the process of their incorporation into pyrite lattice and the formation of tellurides (Keith et al., 2018).

6.2.iii.Laser ablation ICP-MS in mineral systems research

Emerging in situ Laser Ablation Inductively Coupled Plasma – Mass Spectroscopy (LA ICP-MS) techniques including spot analyses and raster element mapping have the capacity to retrieve high precision trace element data from sulphide minerals at low abundances (Ulrich et al., 2009). Such data from cores and growth zones may be used make determinations as to the mobility of elements within transporting fluids, to inform interpretations of geochemical paragenesis elucidating the relative timing of metal emplacement and geochronology. In-situ analysis of sulphides by LA ICP-MS have been deployed in a range of systems including orogenic and Carlin-type Au deposits (Cave et al., 2017; Large et al., 2009; Li et al., 2019), intrusion-related Au deposits (Nutt and Hofstra, 2007), volcanogenic massive sulphide (VMS) (McClenaghan et al., 2009) and stratiform ore deposits (Brodbeck et al., 2019).

6.2.iv. Scope of study and project objectives

This study examines the trace element geochemistry of pyrite at the Cloonacool Au prospect, supported by petrographic microscopic observations (SEM, EDS/EDX). A total of 107 LA ICP-MS in-situ spot analyses with supporting semi-quantitative raster element mapping of a targeted regions of interest were undertaken using a G2 193 nm Excimer ArF laser (Teledyne Cetac, USA) with a HelEx II 2-volume cell coupled to an Elemental iCapQs mass spectrometer (ThermoFisher Scientific, USA) at the Geochemistry Laboratories, Trinity College Dublin. This dual technique enables the acquisition of a robust trace-element dataset at low detection limits, and visual confirmation of discrete generational phases.

The objectives of this contribution are to: (1) enhance our understanding of potential ore-forming processes and Au mobility in the Central Ox Mountains Inlier, Ireland, through the development of a robust paragenetic sequence, (2) relate chemical signatures to

deformation events associated with collisional orogenesis, and (3) to elucidate geochemical pathfinders for exploration: a critical dimension to this research is a demonstration of the utility of geochemical methods for exploration targeting and de-risking in orogenic terranes.

6.3. Geological Setting

6.3.i. The Ox Mountains Inlier

Cloonacool is located within the Ox Mountains Inlier (Figure 6.1) which has a NE-SW strike and extends from Castlebar, County Mayo to Manorhamilton, County Leitrim (Phillips et al., 1975). Domains of the Inlier have been divided into three distinct tectonostratigraphic units (Southwest, Central and Northeast) and it is bound by Carboniferous rocks to the north and southeast, with down-faulted Devonian sedimentary rocks at its south-western margin; Cloonacool vein mineralisation is constrained to the Central domain. Successions are characterised by meta-sedimentary formations of the Dalradian Supergroup, a metamorphic sequence of Neoproterozoic marine shelf sediments, tillites, volcanics and turbidites which are exposed in the Grampian Terrane across north-west Ireland and central Scotland (Alsop and Jones, 1991; Chew et al., 2009b). The Inlier is one of five exposed in Ireland, the other four (from SW to NE) are located in Connemara, NW Mayo, Donegal and the Sperrin Mountains, and NE Antrim (Chew et al., 2009b).

6.3.ii. Tectonic context and deformation

Dalradian Supergroup stratigraphy exposed in Ireland exhibits multiple phases of deformation consistent with the Grampian Orogeny (Chew et al., 2009b), during which an intra- oceanic island arc was subducted beneath the Laurentian continental margin. The

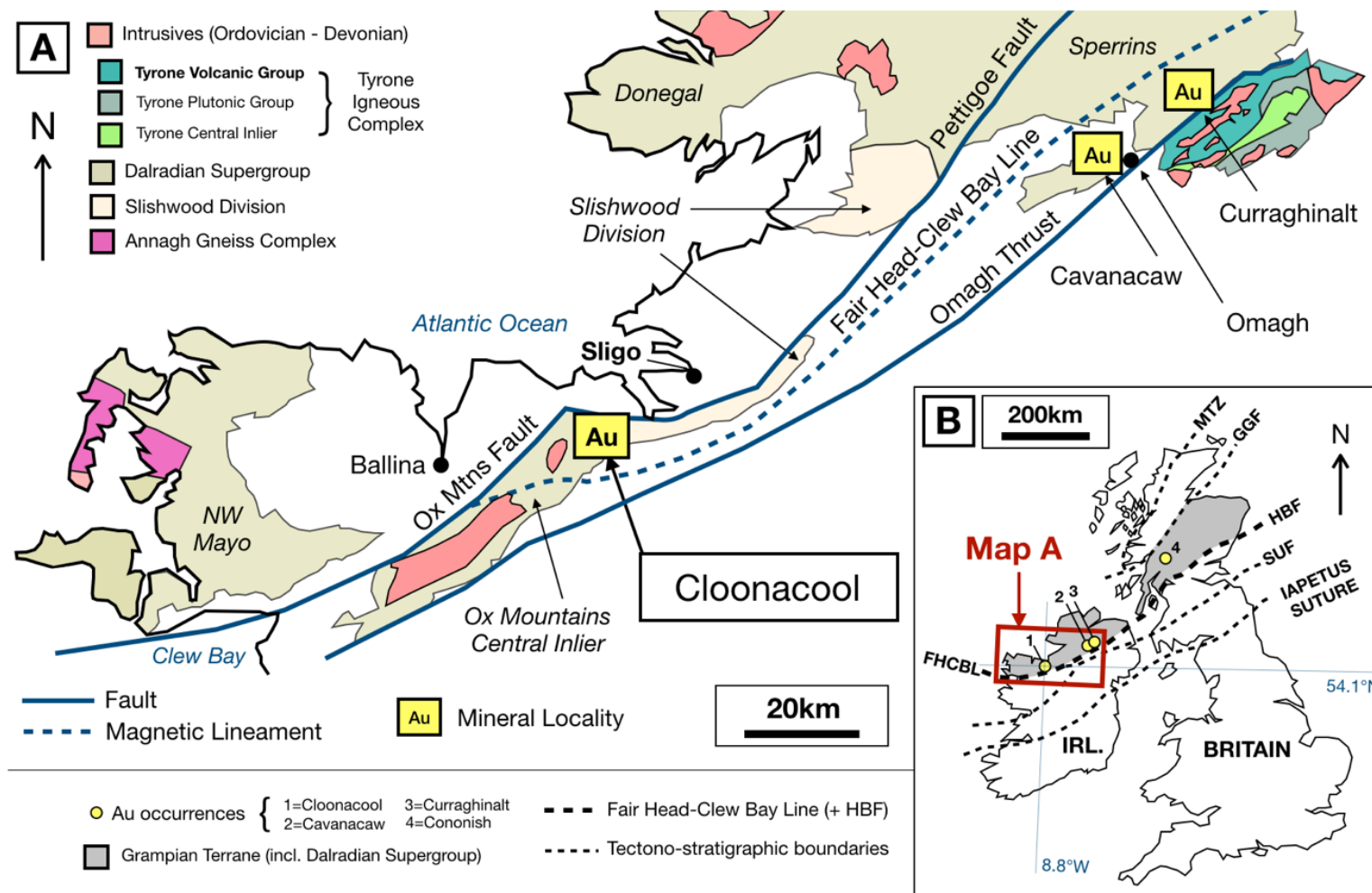


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Figure 6.1. (previous page) (A) Schematic map showing the location of the Cloonacool Au occurrence within the Ox Mountains Central Inlier in north-west Ireland (Dalradian Supergroup), proximal to the western boundary of the Slieve Donard Division, and its relative position with respect to the Cavanacaw and Curraghinalt deposits within the Sperrins Inlier (Dalradian Supergroup) to the NE. The principle geological units of interest to the study are shown, derived from the Geological Survey of Ireland 'Bedrock Geological Units' 1:1,000,000 and 1:500,000 datasets (Geological Survey of Ireland, 2019). The SW-NE trending Ox Mountains Fault and contiguous Pettigoe Fault are displayed, along with the WSW-ENE trending Omagh Thrust marking the suture of the Grampian orogenic event (c. 475-460 Ma). The approximated position of the Fair Head – Clew Bay Line, a major tectono-stratigraphic boundary, is shown based on interpretation of magnetic lineations (Chew and Schaltegger, 2005); (B) A schematic map of Ireland and Britain, with the location of 'Map A' shown using a red box. WSW-ENE to SW-NE trending tectono-stratigraphic boundaries north of (and including) the Iapetus Suture are displayed (MTZ = Moine Thrust Zone; GGF = Great Glen Fault; FHCBL = Fair Head-Clew Bay Line, HBF = Highland Boundary Fault; SUF = Southern Uplands Fault) (Ingham et al., 1999). Au occurrences of active economic interest within the Grampian terrane (shown in dark grey) are designated using yellow circles; in addition to the occurrences shown in Map A, the position of Cononish in Scotland is also included.

timing of the collision has been constrained by previous workers to the Lower Ordovician Arenig epoch (478.6 ± 1.7 and 471.8 ± 1.6 Ma) (Dewey and Shackleton, 1984 cited by Chew et al., 2009), while subsequent deformation during the Middle Ordovician led to peak metamorphism (lower amphibolite) at c.468 Ma (Chew et al., 2009b). During the Lower Ordovician, Laurentia was progressively approaching the micro-continent of Avalonia to the south; the final collisional stage which closed the Iapetus Ocean during the Early Devonian is known as the Acadian event (or 'Acadian Orogeny') (Chew et al., 2009b). The suture of the orogen is demarcated by the Fair Head – Clew Bay Line (FH-CBL) in Ireland (Figure 6.1) and the Highland Boundary Fault (HBF) in Scotland. This event resulted in significant uplift and deformation of the Dalradian (D_1 - D_4 , with D_3 representing peak metamorphic conditions) and is represented within the Ox Mountains structural record by an S_3 fabric dated to 470-460 Ma.

	Tectonic Event	Ox Mountains	Sperrin Mountains
485 Ma (Tremadoc)	Onset of subduction and collision, ophiolite obduction.		
478.6-471.8 Ma (Arenig)	<u>Onset of Grampian Event:</u> Collision of arc with continental margin. Thickening of the succession due to foreland-directed thrusting.	Blueschist-facies conditions pervasive. D ₂ deformation (recognized in Connemara to the south). MP ₂ and MS ₂ assemblages.	Syn-D ₂ fabric development.
470-462 Ma (Arenig to Llanvirm)	Collisional thickening.	Blueschists transferred back to foreland. S ₃ fabric development. Lough Talt antiform. Greenschist-amphibolite facies conditions (MS ₃ -MP ₃).	D ₃ Deformation, prograde metamorphism. Peak at c.468 Ma. Greenschist-facies conditions.
462-452 Ma (Llanvirm to Caradoc)	Rapid uplift and cooling (retrograde conditions).	Uplift and exhumation, cooling	Curraghinalt Au deposit: vein emplacement.
c.412 Ma		Ox Mountains Granodiorite emplaced.	

Table 6.1. Summary of tectonic and metamorphic and structural events. Information retrieved from Alsop and Jones (1991), Chew and Schaltegger (2005) and Chew et al. (2009).

This time interval, which has also been proposed for the juxtaposition of the Dalradian succession with the adjacent Slieve Donard Division, is interpreted as contemporaneous with D₃ deformation associated with the Omagh Thrust in the Sperrin Mountains to the NE (Flowerdew et al, 2000, cited in Chew et al, 2009).

6.3.iii. Local and regional metamorphism

Peak metamorphic conditions within the western Irish Dalradian Supergroup associated with the Grampian event ranged from greenschist to amphibolite facies. Experimental work and interpretation of assemblages by Yardley et al. (1987) reveal Barrovian metamorphism at peak pressure-temperature conditions of c. 410-620 °C and < 7 kbar in the Ox Mountains Inlier (greenschist-amphibolite facies; peak within staurolite-kyanite zone near Zion Hill (<5 km W of Cloonacool) at 600-620 °C and 6-7 kbar, with decreasing temperatures westward). East of Zion Hill (likely corresponding to the Cloonacool area) lies a zone of retrogressed formations, characterised by chloritoid greenschists, where staurolite and kyanite have been replaced by Na-poor muscovite, paragonite and margarite; the temperature of comparable retrogressed rocks in the western Ox Mountains Inlier (between Castlebar and Newport, County Mayo) has been calculated by Yardley et al. (1987) using the paragonite-muscovite solvus as 460 °C +/- 50 °C.

These conditions were superimposed on a previous regional metamorphism at 6-10 kbar, considered by Yardley et al. (1987) to have been at blueschist grade or at the blueschist-greenschist transition. Evidence of blueschist-facies meta-basites from South Achill (NW Mayo) at the western extremity of the terrane support this model. High-pressure blueschist facies metamorphic conditions within the terrane are associated with D₂ deformation, and are interpreted by Chew et al. (2009) to have been present within distal Dalradian sediments and the Clew Bay Complex accretionary wedge during the mid-Arenig (c. 475 Ma), as thickening of the succession commenced due to thrusting directed toward the foreland. This event occurred approximately 5-10 Myr prior to the regional metamorphic D₃ peak (c. 468 Ma) wherein, the blueschist facies succession was transferred to the over-riding plate and thrust back toward the foreland.

6.3.iv. Structures and proximal intrusives

The two dominant structures that define the orientation and shape of the Ox Mountains Central Inlier succession are the F₂ Lough Anaffrin Anticline (which may include preserved S₁ features) and the D₃ Lough Talt Antiform which defines the overall orientation of the succession (Chew et al., 2009). A series of intrusives are present within the Inlier known collectively as the Ox Mountains Igneous Complex: these include the Ox Mountains Granodiorite which has been temporally constrained to 412.3 ± 0.8 Ma (Early Devonian), using U-Pb dating of zircon from a tonalite facies of the pluton, and are hence considered contemporaneous to large Irish batholiths such as the Leinster Granite and the Newry Igneous Complex (Chew and Schaltegger, 2005). The Ox Mountains Granodiorite was previously considered to be contemporary with late-D₂ event deformation (e.g. Long and Max, 1977).

6.3.v. Local stratigraphy

Cloonacool veining is constrained within the Lower Lismoran Formation, a c.400 m thick succession within the Argyll Group (Alsop and Jones, 1991) (see Figure 6.2). The formation is characterised by interlayered grey-green semi-pelites and psammites, with feldspathic psammites recognised occasionally as >1m intervals. Collectively, the Lower Lismoran Formation and the underlying Ummoon Formation exhibit both amphibolite and greenschist facies metamorphic assemblages (Phillips et al., 1975). The earliest assemblage (MP₁), attributed to the Precambrian D₁ deformation event, contains kyanite, staurolite, diopside and K-feldspar. This assemblage is common within the Ummoon Formation, however staurolite and kyanite are considered to be absent from Lower Lismoran Formation rocks (Jones et al., 1988). Phillips et al. (1975) describe MS₂ and MP₂ as amphibolite-facies assemblages, associated with D₂ deformation; MS₂ is a mica schistosity (hornblende +

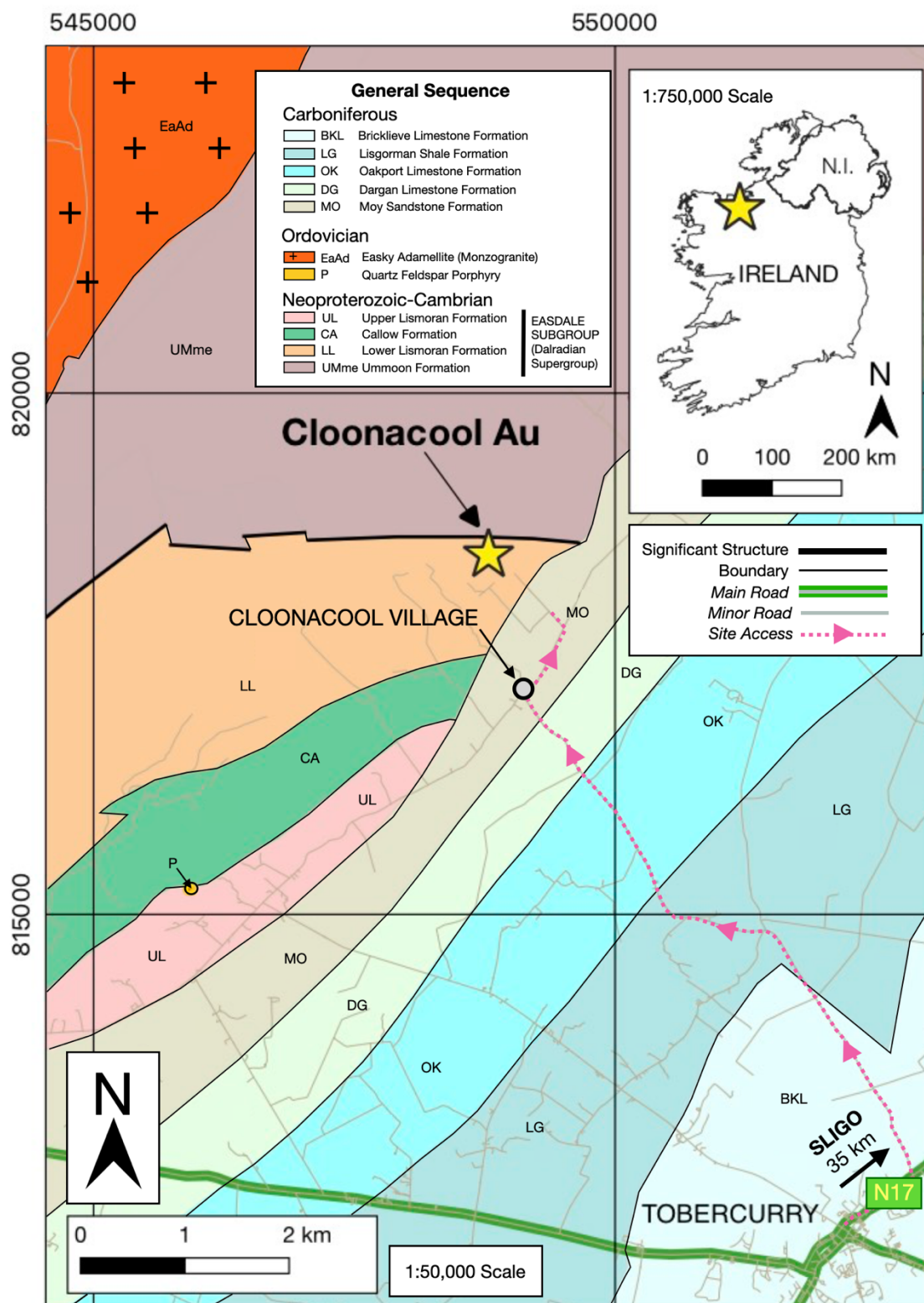


Figure 6.2. 1:50,000 scale map of geological formations local to the Cloonacool gold occurrence in County Sligo Ireland; inset map of Ireland and Northern Ireland for context. This map is based on 1:100,000 bedrock data from Geological Survey Ireland (GSI), with road and settlement information obtained from Ordnance Survey Ireland. General sequence information is included from Alsop and Jones (1991) and Dixon (1972). Co-ordinates (in metres) are in Irish Transverse Mercator (ITM) grid.

oligoclase + muscovite + 'brown biotite'), while the MP₂ assemblage comprises garnet + staurolite + oligoclase + muscovite. MS₃ and MP₃, associated with D₃ Grampian deformation are greenschist assemblages which include epidote and a 'green biotite' which replaced earlier MS₂-MP₂ 'brown biotite' within parts of the Lower Lismoran Formation. Later D₄ and D₅ deformational events are recorded within the central domain of the Ox Mountains Inlier, though specifically within the Cloonygowan Formation which is stratigraphically younger than the Lismoran Formations.

Phillips et al (1975) observe that the Lower Lismoran Formation underwent cataclasis and suggest that it is noteworthy for its retrogressive greenschist facies metamorphism. However, Jones et al (1988) consider its grade to be of 'epidote-amphibolite' facies, noting the presence of a quartz-albite-epidote-almandine assemblage and the presence of <5 mm garnets (characteristic of MP₂). It may be considered that the assemblage observed by Jones represented the MP₂ assemblage present prior to the aforementioned replacement, as this formation traversed the greenschist-amphibolite transition following peak Grampian metamorphism (D₃) on a retrograde path. The Ummoon Formation is considered by Jones et al. (1988) to include kyanite and staurolite, characteristic of early MP₁ assemblage, suggesting that it was less impacted by post-D₁ metamorphic conditions than the Lower Lismoran.

Cloonacool veins are spatially proximal to the lower stratigraphic boundary of the Lower Lismoran Formation with approximately 600m-thick semi-pelite and pelite-dominated Ummoon Formation. Winchester et al. (1987) have suggested based on geochemical evidence that these formations may belong to separate terranes, however Phillips et al. (1975) note their petrographic similarity, and suggest that the Lower Lismoran Formation may be a retrogressed equivalent of the Ummoon Formation.

Dalradian		Central Ox Mtns. Inlier		Sperrin Mtns.		
Southern Highland Group			Callow Shear Zone	★ Curraghinalt, Cavanacaw Au	Broughderg	
					Mullaghcarn	
					Glengawna	
					Glenelly	
					Dart	
Argyll Group	Tayvallich	★ Cloonacool Au	Upper Lismoran		Dungiven Limestone	
			Callow			
	Crinan		Lower Lismoran		Newtownstewart	
	Easdale		Glenawoo Slide*			
			Meelick Member*			
			Newantrim Member			
			Slievenagark Member			
			Lough Talt Slide			
	Islay		Leckee Quartzite			
			Tawnyshane Tillite			

Figure 6.3. The stratigraphic context of the Cloonacool Au prospect within the host framework of the Neoproterozoic Upper Dalradian Supergroup present in north-west Ireland, deformed during the Caledonian-Appalachian orogenic cycle (475-405 Ma). Cloonacool veins are hosted by the Lower Lismoran Formation at the boundary with underlying formations, constituent of the Argyll Group. This formation lies at a lower stratigraphic level to occurrences within the Sperrins Inlier to the north-east, host formations of which are considered to be part of the Southern Highland Group. Correlative stratigraphy has been modified after Chew et al. (2001) which draws on previous work by Harris et al. (1994) and Long and McConnell (1999). The Ummoon Formation may be considered in the context of presented stratigraphy as comprising the Glenawoo Slide and Meelick Member components marked with an asterisk (*).

The two formations were described by Taylor (1968a) who considered them to be separated by a zone of intense strain called the Glenawoo Slide; Phillips et al (1975) note that while they are similar, the fundamental difference between the two being that the Lower Lismoran Formation is more psammitic: the transition between them being a psammite band of <1m thickness. Jones et al (1988) confirm the original transitional contact, precluding the formations as belonging to separate tectono-stratigraphic terranes, this interpretation is also proposed by Alsop and Jones (1991).

6.4. Materials and Methods

6.4.i. Sampling

Following reconnaissance of the locality in the field (Figure 6.4 and Figure 6.5), visual inspection of drill-core from the Cloonacool Au occurrence identified intercepts of interest to the study (Figure 6.6). A total of 17 representative samples of mineralised vein and wall-rock material were retrieved from three drill-holes (DDH 3382-001, - 002 and -009). All sampled drill-holes intercepted an envelope of significant veining close to surface, of which six samples were retrieved and analysed: BC06 (drill-hole 3382-009), BC11 (drill-hole 3382-002), BC13 and BC16 (drill-hole 3382-001). An additional 11 samples were taken from sulphide-bearing material below this horizon within areas which may constitute additional vein envelopes at depth. Three-dimensional visualisation of the drill-hole geology was enabled through the use of operator-provided spatial data and drill-logs, with data modelled using the Leapfrog Geo software package (Seequent, New Zealand). Aerial imagery was attained using Google Earth (following their guidelines for non-commercial use; copyright Google & Maxar Technologies).



Figure 6.4. Andrew Bowden, discoverer of the Cloonacool Au occurrence, with an exposed outcrop of the mineralised 'Furze' vein (photograph by author).

6.4.ii. Thin sections and reflected light microscopy

Slabs were cut from drill-core sections, from which polished thin sections ($n=25$) measuring 5.1×2.5 cm at $60 \mu\text{m}$ thickness were prepared at Thin Section Lab (Toul, France). Petrographic analysis was carried out at iCRAG Lab@TCD, Trinity College Dublin, using a Nikon Eclipse LV100 microscope with reflected-light capability coupled with a high-resolution camera system. Representative reflected light images of visible gold, lead and zinc occurrences and associated pyrite were retrieved, along with stitched images of thin sections.

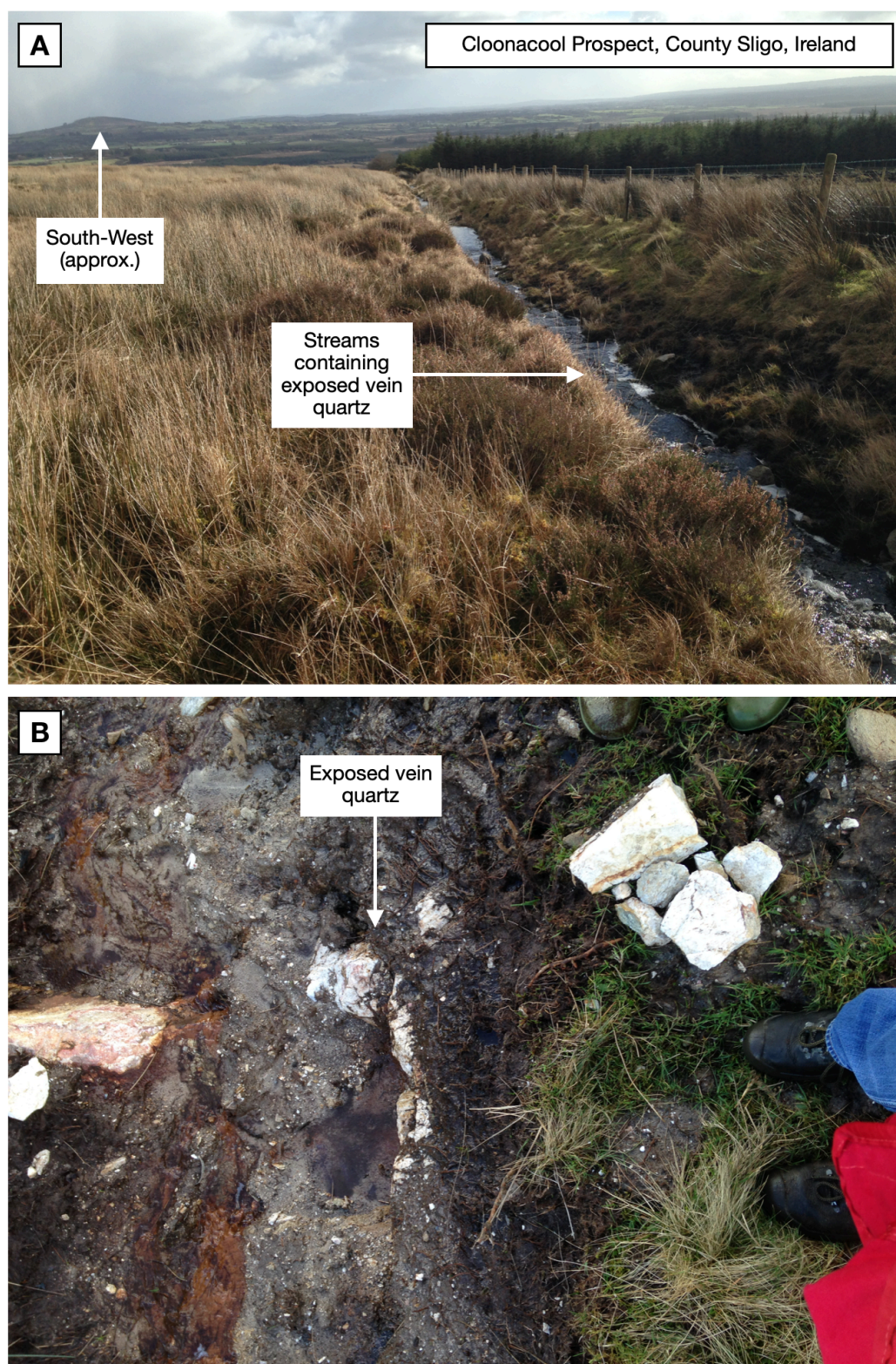


Figure 6.5. (A) A stream traversing the Cloonacool area within which mineralised vein material was encountered; (B) exposed vein quartz within the stream (boots in image for scale at right-hand side). Photographs by author.

Drill-holes and core sampling

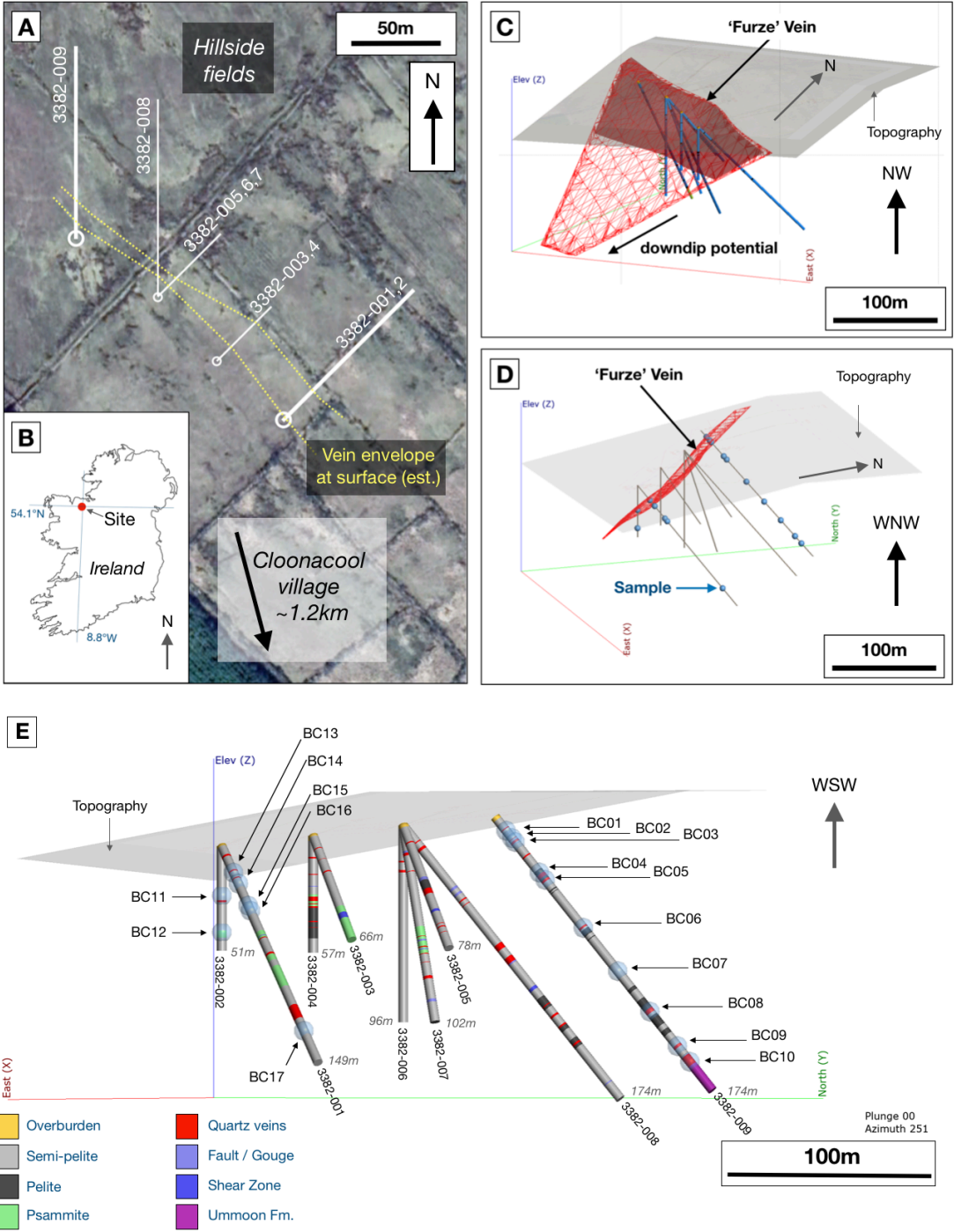


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Figure 6.6. (A) Traces of Cloonacool drill-holes superimposed upon an aerial photograph of the area (copyright 2019 Google: Maxar Technologies), with the surface-exposed mineralised vein envelope indicated using a dashed line, and an arrow marking the bearing toward Cloonacool village to the SSE; (B) inset map of the island of Ireland showing the location of Cloonacool; (C) 3-dimensional model of the vein envelope looking toward NW, showing drill-holes and local topography; (D) model orientated with a view toward WNW with the locations of study samples marked using blue spheres; (E) a 3-dimensional view of the drill-holes looking WSW, with operator logging depicted using a colour-scale (see legend). The locations of samples are shown using semi-transparent blue spheres, with their sample identifier included in annotation. Modelling was completed using Leapfrog Geo (Seequent, New Zealand).

6.4.iii. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS/EDX)

A Mira XMU Variable Pressure Field Emission Scanning Electron Microscope (FE-SEM; Tescan, Czech Republic) enabled collection of high-resolution raster images of specific areas at high magnifications. The Backscattered Electron (BE/BSE) method was preferred. A high voltage of 20 keV was used, at a working distance of 15-20 mm. Using an equipped X-ray detector (Oxford Instruments, United Kingdom), Energy Dispersive X-ray Spectroscopy (EDS/EDX) analysis was carried out on target areas $<1\ \mu\text{m}$ in size. Generated spectra allow for the estimation of elemental compositions and spatial distribution of abundances using a raster mapping technique, with performance monitored using a Cobalt pellet standard (MAC #217). Standardisation of results was carried out using custom block (#217) by Micro-Analysis Consultants (MAC) Ltd. (U.K.), and block MINM 25-23 by Astimex Standards Ltd. (Canada).

6.4.iv. Laser Ablation Inductively Coupled Plasma – Mass Spectroscopy (LA ICP-MS)

In-situ Laser Ablation Inductively Coupled Plasma – Mass Spectroscopy (LA ICP-MS) techniques were used to resolve trace element compositions for vein and wall-rock pyrite. Analyses were performed using a G2 193 nm Excimer ArF laser (Teledyne Cetac, USA) with a HelEx 2-volume cell, coupled to an Elemental iCapQs mass spectrometer (ThermoFisher Scientific, USA) at the Trinity College Dublin Geochemistry Laboratories, Pearse Street, Dublin. For both spot analysis and raster element mapping, a variable volume device developed in-house is retrofitted linking the ablation cell to the ICP-MS torch. This enables smoothing of the signal between the laser and mass spectrometer, enhanced signal sensitivity and reduced formation of oxide via the introduction of a 3-10 ml/min flow of N₂ to the sample-gas mixture (see Zhou et al., 2017). Data were calibrated with analyses of NIST-610 and NIST-612 (National Institute of Standards and Technology, USA), BCR-2G (United States Geological Survey, USA) and MUL-ZnS (Montanuniversität Leoben, Austria) standards and a MASS-1 sulphide standard (United States Geological Survey, USA). Processing of data was carried out using Iolite 3.0 (Wavemetrics, USA) and IoGAS (Reflex, Australia).

6.5. Petrography

6.5.i. Drill-core observations

Acquired drill-core samples exhibit shear-veins, branching millimetric veinlets, and breccias in faulted zones. Veins typically comprise quartz, albite and pyrite, and may anastomose suggesting multi-phase interactions between vein-sets. Observed shear-veins within the ‘Furze’ vein envelope may be millimetric to centimetric in scale and are associated with the

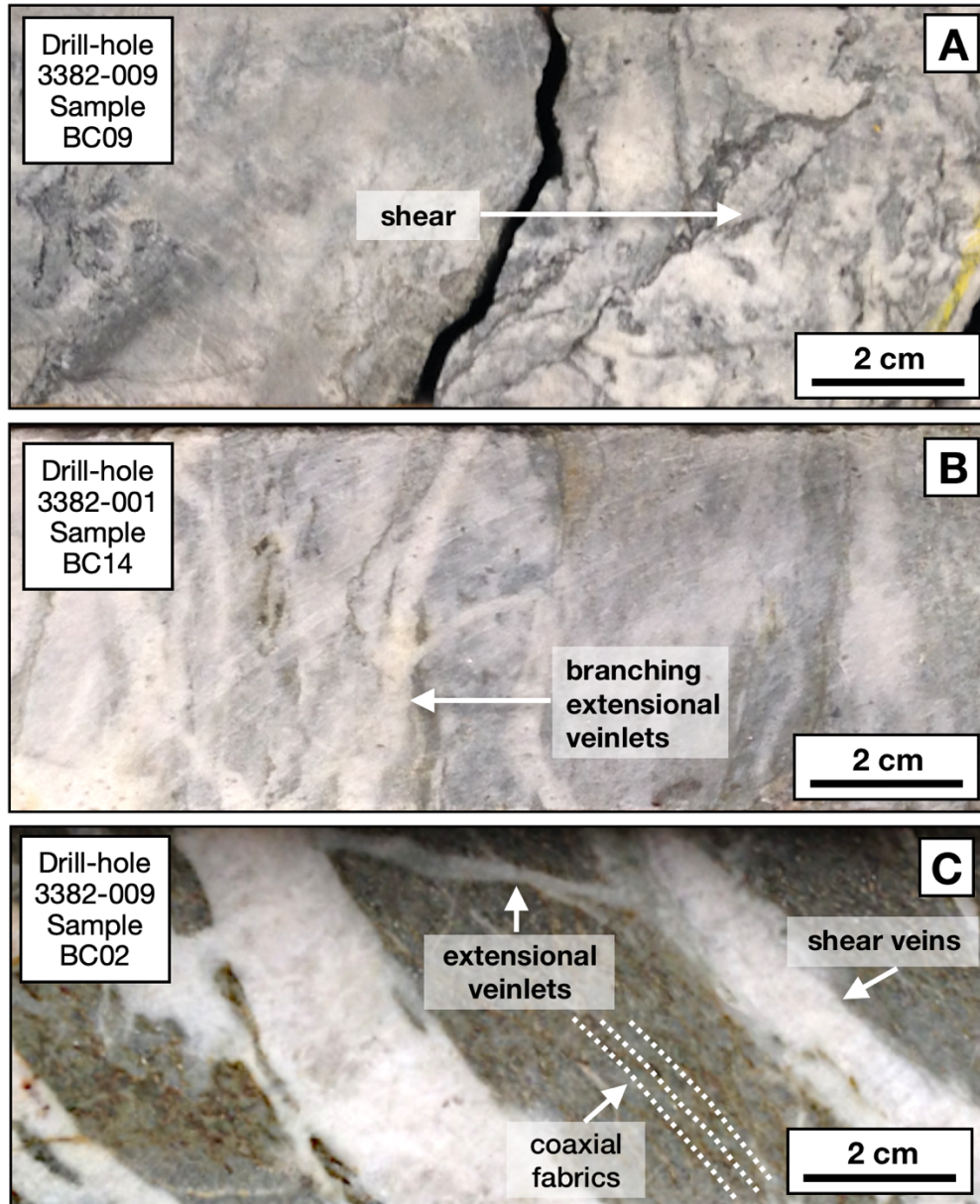


Figure 6.7. (A) Structurally deformed zone in a half-core sample (drill-hole 3382-009, 145.83-145.96m; sample BC09) containing albite and quartz veins, with dark bands containing abundant pyrite bearing dendritic textures observed; (B) narrow (<0.25cm) anastomosing extensional veinlets with a milky appearance are observed within sample BC14 (drill-hole 3382-001, 25.65-25.85m), visually branching at acute to c.45° angles from larger <1 cm veins). Veins show an affinity for the main fabric of the silicified host assemblage and are coincidentally folded, suggesting subsequent local to regional deformation; (C) quartz-albite shear veins (1-5cm range) and branching veinlets (<1cm) observed in sample BC02 (drill-hole 3382-009, 13.35-13.48 m).

schistosity of siliceous semi-pelitic to psammitic host assemblages. These veins contain pyrite and are hypothesised to be the principle carrier of mineralisation. Within shear zones associated with localised structural movements, these veins may exhibit dendritic textures (Figure 6.7A). Shear veins are anastomosing, suggesting that the same pathways were exploited episodically by the influx of fluids. Extensional veinlets which branch from the main vein-sets (Figure 6.7B) appear to be compositionally similar.

Veins are hosted by grey to dark-grey semi-pelites and coarse psammities with intermittent graphitic pelitic horizons. Host rocks exhibit a strong fabric, which may kink and fold within shear zones. Host rocks contain feldspar and muscovite, are highly chloritised indicative of greenschist facies conditions; rare garnet also encountered suggests conditions approaching the greenschist-amphibolite facies transition.

6.5.ii. Microscopic vein classification and pyrite phases

Samples from the main 'Furze' vein envelope were examined using reflected light and Scanning Electron Microscopy (SEM), with mapping using Energy Dispersive X-ray Spectroscopy (EDS/EDX) conducted to identify mineral phases.

Two principle vein types of interest within shears have been classified: designated *Type I* and *Type II* (see Figure 6.8). Type I veins represent an early limited influx of sulphur-bearing fluids during an initial opening of fabric-parallel pathways, preceding the later Type II protracted event with a higher fluid volume carrying metals of interest. These vein types are distinguished by size, composition, deformation and their relationship with gangue minerals. Vein classification does not include all vein types from the project, but rather focuses on the evolution of the principle types encountered considered to represent the ore-stage. Type I veinlets contain Py_1 pyrite grains bearing a temporal relationship with ilmenite and rutile, while Type II veins consist of gold and galena-bearing Py_2 deformed masses (comprising arsenian pyrite infill, Ap_1), and a late sphalerite-bearing pyrite phase, Py_3 .

Type I veinlets (see Figure 6.8 and Figure 6.9) are on average 250 μm ($2\sigma = 460 \mu\text{m}$, min. 35 μm , max. 1,065 μm , $n=50$) in width, and extend along the boundaries of coarse grains within the host assemblage. They exhibit preferred orientations with frequent parallel veinlets (Figure 6.9A) observed and may branch along the boundaries of grains adjacent to this principle alignment (Figure 6.9C), filling in available space. They commonly contain quartz, ilmenite, Fe-oxides and pyrite. Pyrite grains (Py_1) are euhedral to subhedral, disseminated and average 73 μm in width ($2\sigma = 140 \mu\text{m}$, min. 6 μm , max. 335 μm , $n=50$). The position of veinlets, closely following the boundaries of albite and quartz grains within the host matrix, suggests these are prograde, exploiting the geometric configuration of those grains and structural weaknesses between them. Py_1 post-dates a phase of ilmenite (Figure 6.9B), which is unevenly distributed within veinlets: it may be only a minor constituent of the vein composition ($<10\%$), or a more significant component ($>60\%$). Cyclical zonation is suggested by the presence of inclusion trails within a subset of these grains (Figure 6.9B and Figure 6.11), suggesting the retention of a complex internal chemical record. Type I veinlets are observed throughout the collected sample suite suggesting widespread distribution. Py_1 grains within the vein type contain rare auriferous inclusions, though this is not widely observed. Both ilmenite and rutile are observed as composite grains confirming a variable distribution of Fe within those minerals.

Type II veins (see Figure 6.8C and Figure 6.9D-F) represent the principle stage of mineralisation in tested samples. They contain quartz, pyrite, chlorite (chamosite), muscovite and minor monazite, with abundant visible auriferous inclusions (and galena) associated with sulphides. In thin section these veins are on average an order of magnitude larger in width than Type I veinlets (Figure 6.8C), with a mean width of 3,630 μm ($2\sigma = 3,985 \mu\text{m}$, min. 640 μm , max. 6,315 μm , $n=12$). Their size and geometry sub-parallel to the precursor Type I network suggest that they may be associated with a disruptive brittle deformation event which expanded existing viable pathways to accommodate larger fluid volumes.

Polycrystalline masses of locally equigranular pyrite (Py_2) conjoined by arsenian pyrite infill, and later euhedral growths observed at the extremities of these masses (Py_3) are the main sulphide components to this phase. Homogeneous in appearance at their cores, evidence suggests that euhedral Py_2 grains, ranging between 40 and 180 μm in width (avg. 100 μm , $2\sigma = 75 \mu\text{m}$, $n=20$), competed for space with adjacent grains during their growth cycle (Figure 6.9E). Where these grains impinge upon each other within masses, micro-inclusion trails and deformation textures are observed and infill of arsenian pyrite (Ap_1).

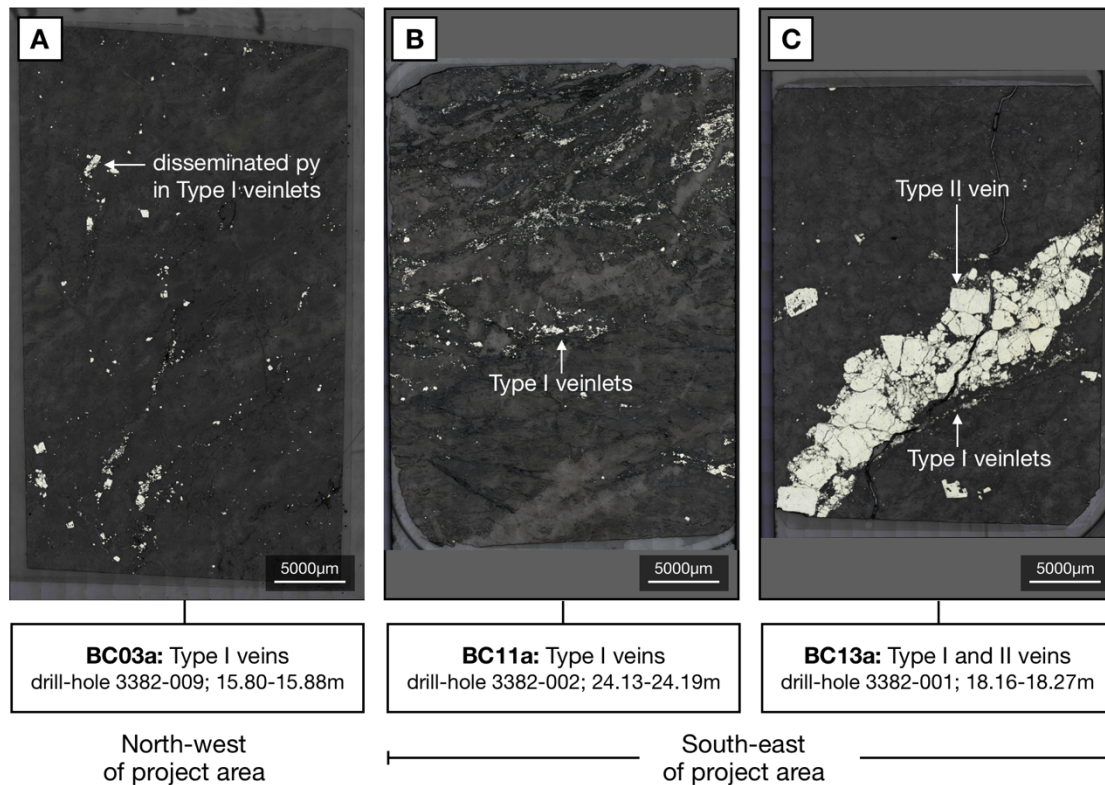


Figure 6.8. (A) Disseminated pyrite within Type I veinlets (NW of project area); (B) Type I veinlets (SE of project area); (C) sub-parallel interaction of Type I and Type II veinlets (SE of project area).

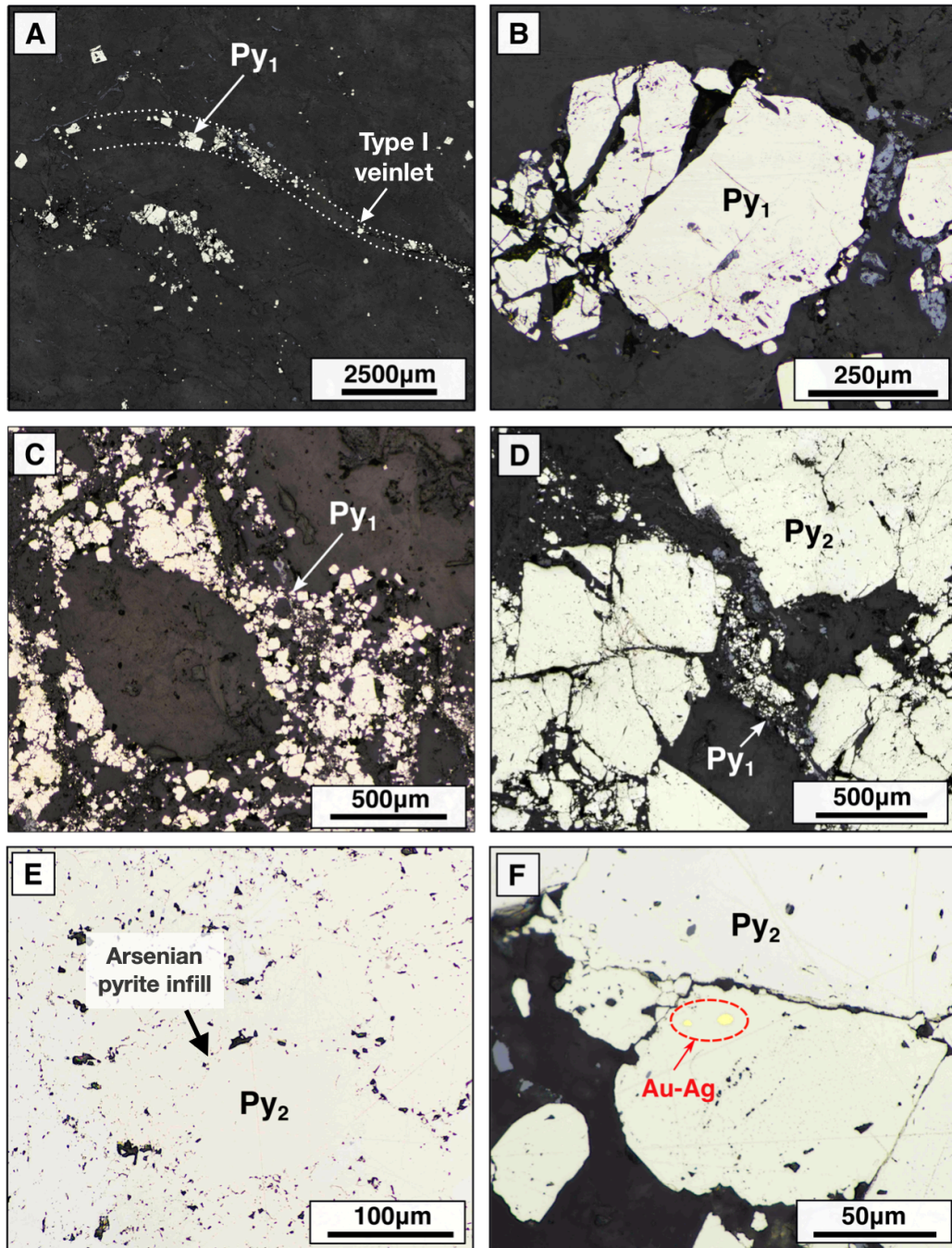


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Figure 6.9. (A) Py_1 within *Type I* veinlets (sample BC03, drill-hole 3382-009, 15.80-15.88m): this vein type is commonly observed across the sample suite and is characterised by the replacement of Ti-oxides by Py_1 , which have later endured brittle deformation. They represent a fluid injection permeating along coarse psammitic grain boundaries within the host matrix resulting in a semi-erratic geometry, however they do show an overall preferred alignment suggesting that they are associated with the dominant schistosity; (B) a magnified view of typical Py_1 grain within a *Type I* veinlet (sample BC03, drill-hole 3382-009, 15.80-15.88m): these are fragments of a single grain which has fractured subsequent to its precipitation replacing Ti-oxide, as evidenced by the presence of inclusion trails suggesting cyclic chemical zonation within the outer 20% of the grain; micron-scale auriferous inclusions are observed within this outer region; (C) branching of *Type I* veinlet along the boundary of an albite grain (sample BC11, drill-hole 3382-002, 24.13-24.19m): subhedral Py_1 dominates the photographed region; fluids have followed a path of least resistance along the host grain boundary; (D) replacement of a *Type I* vein by a Py_2 mass within a *Type II* assemblage sample (sample BC13, drill-hole 3382-001, 18.16-18.27m): a key temporal relationship is revealed as Py_2 growths replace earlier Py_1 ; (E) fragmental Py_2 within *Type II* vein (sample BC13, drill-hole 3382-001, 18.16-18.27m): growth has been impeded by proximity to neighbouring grains within the mass, leading to adjoinment; micro-inclusion trails and arsenian pyrite infill denote the limits of growth. These masses are characteristic of sulphide within this vein type and are observed to overgrow earlier *Type I* vein assemblages. They contain trace inclusions of visible gold and galena; (F) a Py_2 mass within *Type II* veins (sample BC13, drill-hole 3382-001, 18.16-18.27m): recrystallisation textures are observed at boundaries. Both phases have experienced cataclasis and fracturing; auriferous particles are visible.

Commonly rectangular in appearance and averaging $150\ \mu\text{m}$ in width ($2\sigma = 160\ \mu\text{m}$, min. $45\ \mu\text{m}$, max. $340\ \mu\text{m}$, $n=16$), rare Py_3 grains within the *Type II* vein assemblage are characterised by the presence of visible sphalerite inclusions, implying a late Zn event. They are located along the edges of Py_2 masses and have been considered separately due to the presence of sphalerite inclusions and recrystallisation textures (these are best observed in Scanning Electron Microscope raster imaging: see Figure 6.10).

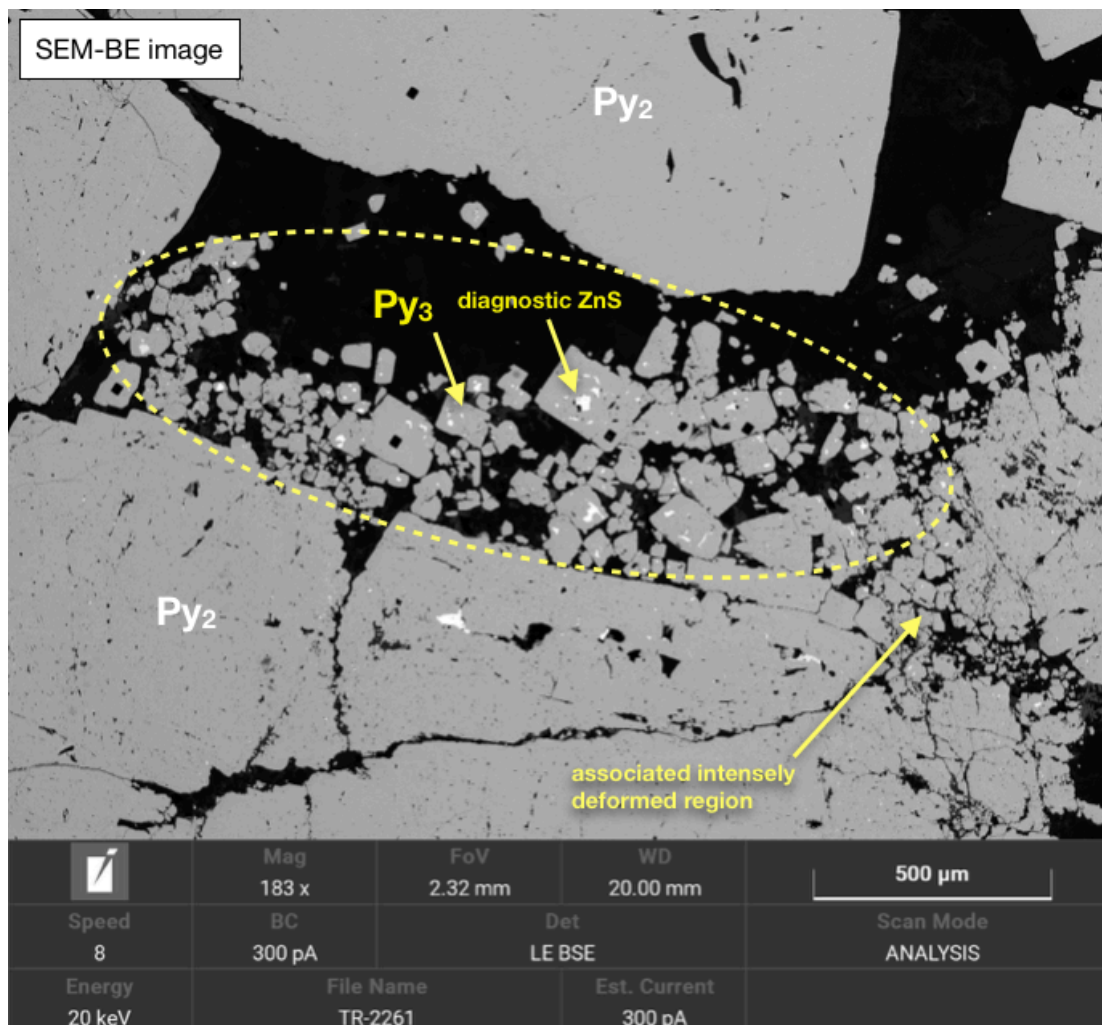


Figure 6.10. Rare euhedral Py₃, hosting abundant rounded sphalerite particles which appear reflective compared to host pyrite using a Scanning Electron Microscope (SEM) in Backscattered Electron mode (BE) (sample BC13, drill-hole 3382-001, 18.16-18.27 m). Scans were completed at an accelerating voltage of 20 kV and a working distance of 15 mm, using a 300 pA current.

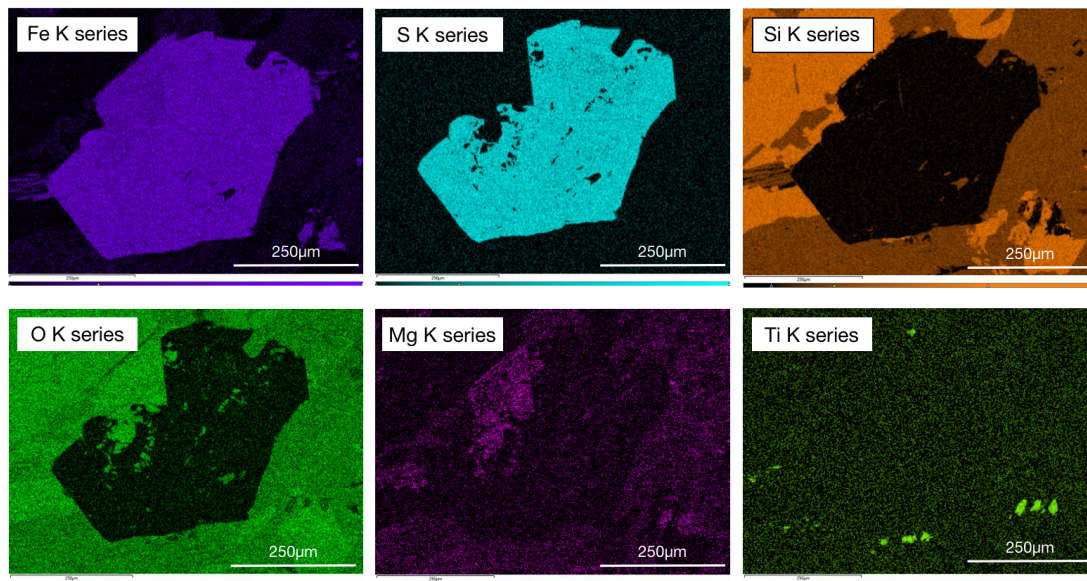
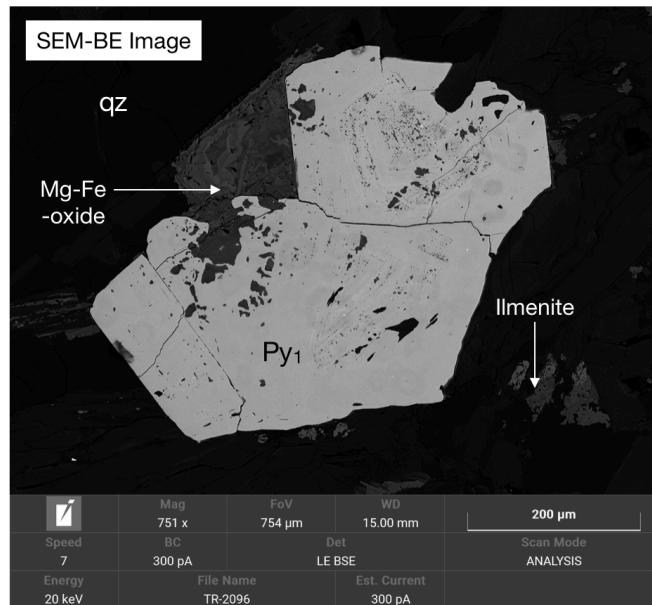


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Figure 6.11. Conjoined crystals of a 395 x 545 μm Py_1 grain within a Type I veinlet (sample BC01; drill-hole 3382-009, 8.62-8.74m), imaged using a Scanning Electron Microscope in Backscattered Electron mode (SEM-BE), exhibits a strong zonation indicative of oscillatory chemical zonation. Grains show evidence of brittle deformation and are show trails of quartz-filled pores cross-cutting the zonation, thereby suggesting disruption due to a fluid event subsequent to Py_1 development. The rim of the grain shows evidence of recrystallisation. Immediately adjacent to the euhedral pyrite grains is a Mg- Fe- oxide mineral that has been replaced by the pyrite. This may be magnesioferrite spinel, associated with a high temperature metamorphic event preceding Au emplacement. Energy Dispersive X-ray Spectroscopy (EDS/EDX) mapping shows the relative abundances of major elements across the region of interest; coincident Ti and Fe within minor grains to the lower right of the grain confirm accessory ilmenite within the gangue.

6.5.iii. Host assemblages

Samples hosting Type I and Type II veins are characterised by a semi-pelitic to psammitic inequigranular groundmass containing albite and quartz, with silicates occupying regions between those grains. Polygonal albite represents approximately 50% of grains, varying in size between 55 and 420 μm ($n=20$), while quartz grains (c. 30%) vary between 30 μm and 225 μm ($n=20$). These grains exhibit a weak schistosity. Seriate silicate grains (c. 20%), compositionally muscovite and chlorite, are most commonly aligned with veinlets.

6.5.iv. Gold particles

Visible gold is principally observed within the outer regions of Py_2 grains in Type II veins (Figure 6.12 and Figure 6.13), with rare inclusions found within Py_1 in preceding Type I veinlets. Particles may be rounded, elongate or angular and are typically pitted. Four optically discriminated classes of visible gold (typically <10 μm in diameter) are observed: Category 1: *inclusions* (entirely bound by pyrite; Category 2: inclusions which have an interface with the host vein assemblage (*inclusions at boundaries*); Category 3: *free gold*, which occurs entirely within the host vein assemblage and Category 4: *microfracture-hosted gold*. The largest measured

occurrences are of the fourth type: elongate particles observed within open micro-fractures or at the confluence of micro-fractures ($<65\text{ }\mu\text{m}$, long axis; Figure 6.12B). The composition of particles was confirmed through analyses using Scanning Electron Microscope (SEM) and quantitative EDS/EDX analysis (Figure 6.14 and Table 6.2), retrieving data from spots using as large a field of view as possible within the available surface area, typically $<10\text{ }\mu\text{m}$ ($n=21$; sample BC13, drill-hole 3382-001, 18.16-18.27m) (Figure 6.13). A silver component to all particles was observed; Au:Ag was an average of 3.7 : 1 within measured particles. Category 1 particles are the most auriferous of those tested. Au averaged 78.3 wt.% ($2\sigma = 12.0\text{ wt.}\%$; $n = 16$), while Ag is present at an average concentration of 21.7 wt.% ($2\sigma = 12.0\text{ wt.}\%$). The maximum Au:Ag ratio in inclusions of this type was 9.7 : 1 (Au, 90.7 wt.%; Ag, 9.3 wt.%), with 9 of 16 values demonstrating Au concentration $> 80\text{ wt.}\%$. One tested particle of this category records a 0.4 wt.% Te concentration. A bimodal distribution suggests that some tested particles may cryptically have an association with micro-fracturing (in addition to Category 4), a hypothesis supported by the observation of fine dark linear features in Scanning Electron Microscope raster imaging (Figure 6.12C). Inclusions which are partially exposed to the surrounding vein matrix (Category 2) are argentiferous relative to Category 1 particles tested (avg. 73.9 wt.% Au, $2\sigma = 1.2\text{ wt.}\%$; avg. 26.1 wt.% Ag, $2\sigma = 1.2\text{ wt.}\%$; $n=2$). Au : Ag for this type is 2.8 : 1. Free gold particles (Category 3) contain comparable silver (avg. 73.5 wt.% Au, $2\sigma = 1.2\text{ wt.}\%$; avg. 26.1 wt.% Ag, $2\sigma = 1.2\text{ wt.}\%$; $n=2$), with a Au : Ag ratio of 2.6 : 1. In one analysis of visible Au identified within a micro-fracture (Category 4) (e.g. Figure 6.12C), Au is present at a concentration of 68.3 wt.%, while Ag is recorded at 31.7 wt.%. Results show that where particles appear to be locked within pyrite crystal structure, they tend to be more auriferous, while particles which have an interface with the surrounding assemblage and may be later in the mineralisation sequence have a higher Ag

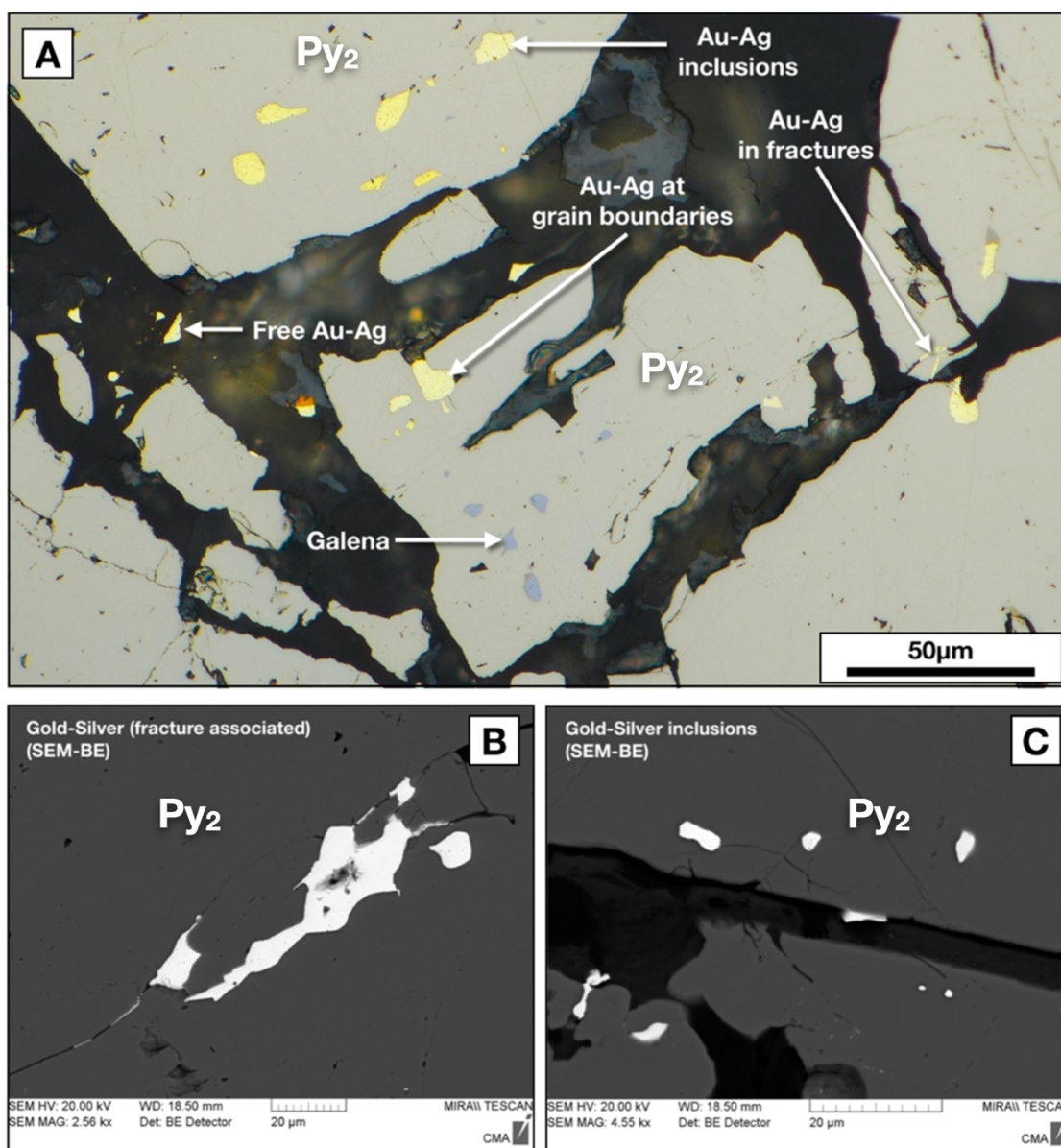


Figure 6.12. (A) Visible gold types observed within *Type II* veins at the Cloonacool Au occurrence and associated galena within and surrounding grains of pyrite (Py₂) (sample BC13, drill-hole 3382-001, 18.16-18.27m, reflected light with image saturation increased by ~10% in post-processing; (B) SEM raster image retrieved using the Backscattered Electron detector (BE) (sample BC13, drill-hole 3382-001, 18.16-18.27m): Au occupies available space within a Py₂ grain fracture; (C) inclusions of reflective Au are observed within the Py₂ grains themselves and along the grain boundary in this SEM-BE raster image (sample BC13, drill-hole 3382-001, 18.16-18.27m). Observed micro-fractures within grains suggests widespread cataclastic deformation, which may have liberated inclusions into the surrounding *Type II* vein host.

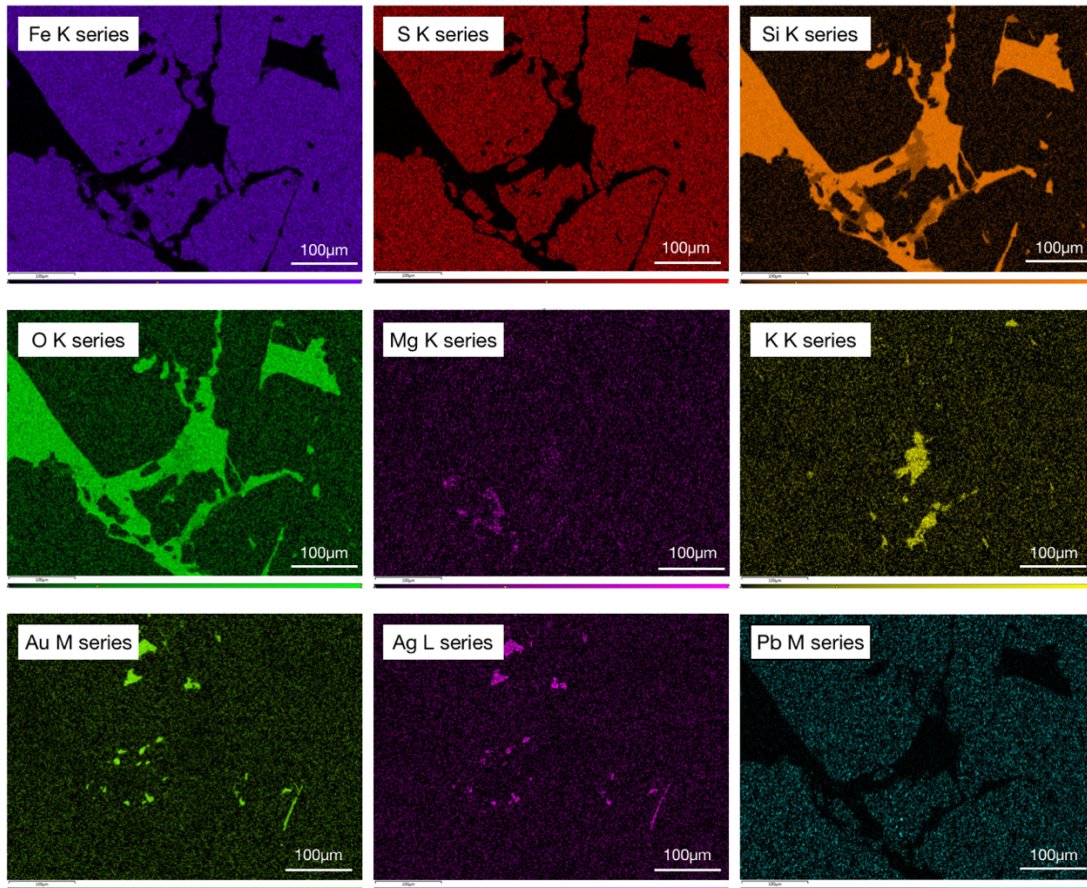
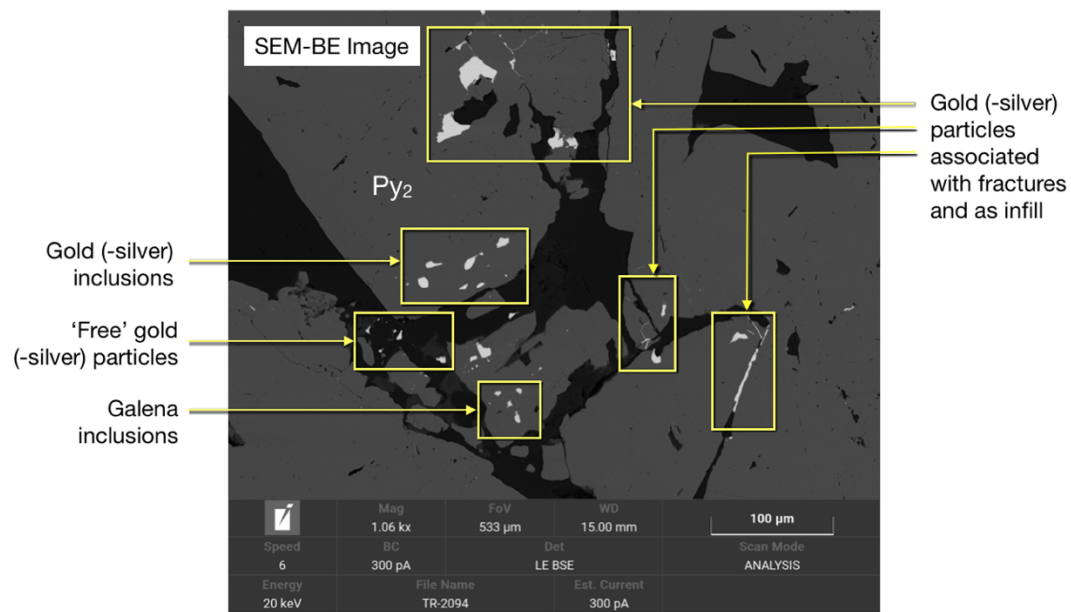


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Figure 6.13. Backscattered Electron (SEM-BE) image of adjoining subhedral Py_2 within a quartz(-phyllosilicate) matrix (sample BC13; drill-hole 3382-001, 18.16-18.27m) demonstrating the diversity of auriferous particles morphologies (and galena) present within tested ‘ore-stage’ veins at Cloonacool. Evidence of Au-Ag inclusions, particles in close proximity to micro-fractures, fracture-infill and ‘free gold’ are observed, along with inclusions of galena. The range of grain morphologies suggests multiple phases of auriferous emplacement, while galena is distinctly associated with the Py_2 grains themselves (in the absence of cryptic micro-fracturing detectable using alternative methods, e.g. LA ICP-MS).

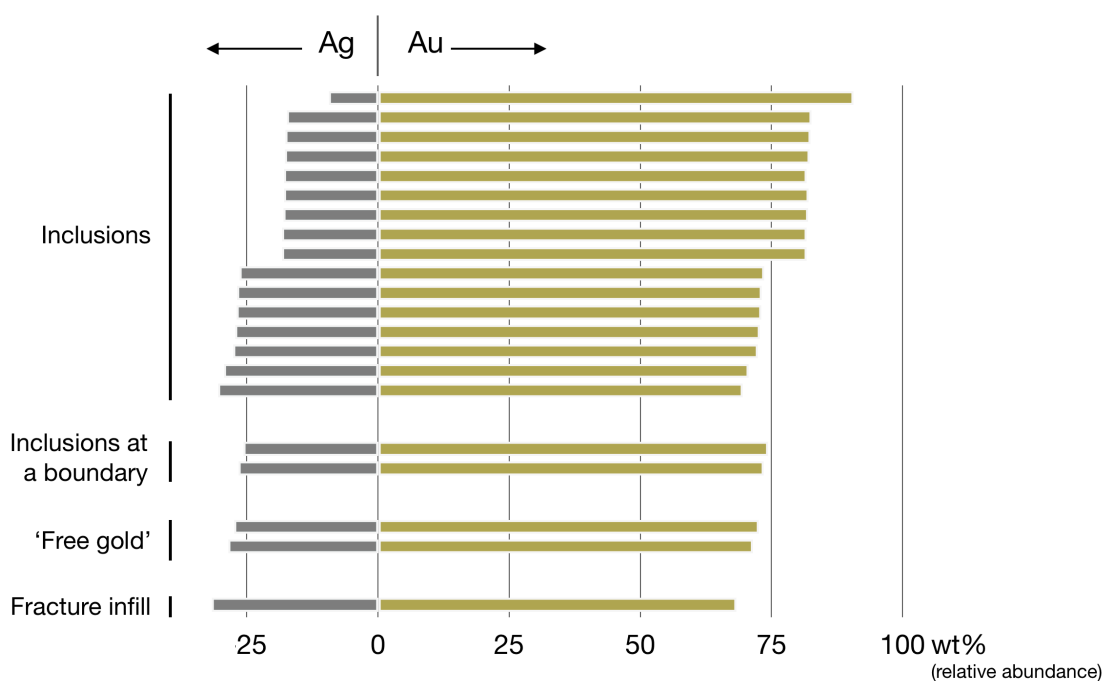


Figure 6.14. Analyses of Au vs. Ag concentrations within particle categories associated with Py_2 within Type II veins, acquired using Energy Dispersive X-ray Spectroscopy (EDS/EDX) (sample BC13; drill-hole 3382-001, 18.16-18.27m; $n=21$). Results demonstrate the propensity of inclusions bound within pyrite to be more auriferous.

Category	Particle location	Au	Ag	Te	Au/Ag
1	Inclusion	90.7	9.3	0.0	9.7
1	Inclusion	82.7	17.3	0.0	4.8
1	Inclusion	82.4	17.6	0.0	4.7
1	Inclusion	82.2	17.8	0.0	4.6
1	Inclusion	81.7	17.9	0.4	4.6
1	Inclusion	82.1	17.9	0.0	4.6
1	Inclusion	82.0	18.0	0.0	4.5
1	Inclusion	81.7	18.3	0.0	4.5
1	Inclusion	81.7	18.3	0.0	4.5
1	Inclusion	73.6	26.4	0.0	2.8
1	Inclusion	73.2	26.8	0.0	2.7
1	Inclusion	73.0	27.0	0.0	2.7
1	Inclusion	72.8	27.2	0.0	2.7
1	Inclusion	72.4	27.6	0.0	2.6
1	Inclusion	70.6	29.4	0.0	2.4
1	Inclusion	69.6	30.4	0.0	2.3
2	Inclusion at boundary	74.3	25.7	0.0	2.9
2	Inclusion at boundary	73.5	26.5	0.0	2.8
3	Free gold	72.6	27.4	0.0	2.6
3	Free gold	71.4	28.6	0.0	2.5
4	Microfracture	68.3	31.7	0.0	2.2

Table 6.2. Individual results of EDS/EDX analyses (n=21) of auriferous particles associated with Py₂ within Type II veins (sample BC13, drill-hole 3382-001, 18.16-18.27 m) within the region of interest imaged in Figure 3.12.

component. Follow-up testing in two distal areas of Py₂ within Type II veining (see Figure 6.15) supports this hypothesis: a silver-rich particle associated with the boundary of a pyrite grain is presented in the first region of interest recording a Au : Ag ratio of 2.73 : 1, while two inclusions in a second region retained Au : Ag ratios of 4.59 : 1 and 4.57 : 1, respectively.

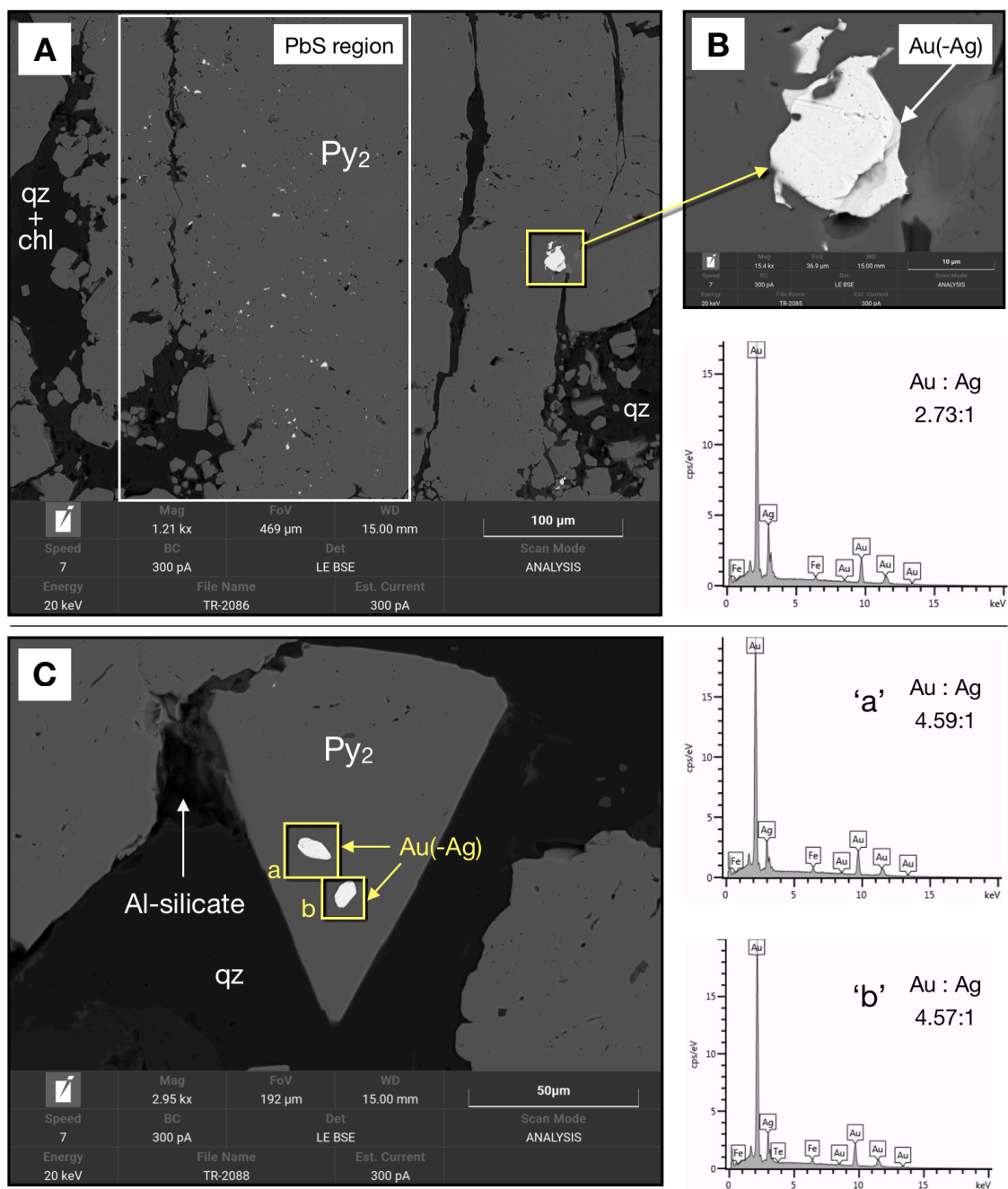


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Figure 6.15. (A) Aligned anhedral Py_2 grains; Backscattered Electron image (SEM-BE). A highlighted region is characterised petrographically by the presence of micro-scale inclusions of galena (range $0.48\ \mu\text{m}$ - $5.09\ \mu\text{m}$, mean $1.99\ \mu\text{m}$; $n=15$), while a Au-Ag particle ($16.3\ \mu\text{m} \times 16.6\ \mu\text{m}$) is observed bound by pyrite proximal to a cross-cutting an area absent of PbS micro-inclusions. The observed auriferous particle records a 2.75 : 1 ratio of Au : Ag (71.1 wt.% : 25.8 wt.%). Aligned fractures cross-cut grains approximately sub-parallel to the orientation of host psammite grains and the orientation of the vein itself. Proximal gangue mineralogy comprises quartz with minor chlorite; (B) Au-Ag particle of interest from region 'A' highlighted; the grain exhibits a rounded morphology with spurs which suggests a feeder mechanism or dispersion into the adjacent micro-fracture to the right in the image; (C) euhedral Py_2 grain (undifferentiated) with the shape of a radial segment which impinges on an adjacent grain. Similar to the grain in region of interest 'A', the grain shows a faint porosity (infilled with quartz) and contains two Au-Ag inclusions with no observed micro-fracturing. Gangue mineralogy in the vicinity of the grain is principally quartz with minor Al-silicate at the deformed zone between the grain of interest and its neighbour to the left in the image. The inclusions (marked with a lower-case 'a' and 'b') are more auriferous than tested particle 'B': both have a Au:Ag ratio of 4.34 : 1. Scans were completed in Backscattered mode at an accelerating voltage of 20 kV and a working distance of 15 mm, using a 300 pA current (sample BC13, drill-hole 3382-001, 18.16-18.27 m).

6.5.v. Galena and sphalerite

Characteristically light-grey galena inclusions (Figure 6.12) may also be observed proximal to auriferous particles within Py_2 . Imaging using SEM and analyses using EDS/EDX demonstrate that galena may be widely distributed within specific internal zones of Py_2 . Within a selected region of interest (Figure 6.15A) galena is observed (range $0.48\ \mu\text{m}$ - $5.09\ \mu\text{m}$, mean $1.99\ \mu\text{m}$; $n=15$) occurring within a constrained zone to the left of the grain, while the area to the right is devoid of visible inclusions. Sphalerite is observed within the cores and outer zones of euhedral Py_3 clusters (see Figure 6.10), which may be considered diagnostic of this phase.

The results of reflected light microscopy and SEM (including EDS/EDX) analysis, suggest a temporal association between Pb mineralisation and auriferous (Category 1) inclusions, while sphalerite inclusions (visible, micron-scale) are observed within overgrowth

Py₃. A sequence is suggested, whereby an early hydrothermal fluid carrying Au and Pb was active within the system contemporary with the formation of Py₂; this preceded a minor Zn event (increased Zn precipitation) synchronous with rare Py₃ formation; a second Au event associated with higher Ag concentrations is likely to have occurred late, associated with late micro-fractures in brittlely deformed grains.

6.5.vi. Fe standardisation for LA ICP-MS spot analysis

EDS/EDX analyses of Fe (n=27) (Table 6.3) were conducted on pyrite to determine an appropriate internal standardisation value for follow-up Laser Ablation ICP-MS quantitative analyses. An average value of 46.7 wt.% ($2\sigma = 0.9$ wt.%) was acquired. Pyrite is considered to be dominantly stoichiometric for the purposes of quantification, with minor Si, Ti, Zn and As values encountered. Totals for analyses averaged 100.05 wt.%. (range. 98.83 – 101.57 wt.%).

#	Sample	Si	S	Ti	Fe	Zn	As	Total
1	BC13	-	52.64	-	46.25	-	-	98.89
2	BC13	-	53.18	-	47.47	-	0.77	101.43
3	BC13	-	53.72	-	46.71	-	-	100.42
4	BC13	-	53.03	-	47.07	-	-	100.10
5	BC13	-	52.85	-	46.91	-	-	99.76
6	BC13	-	52.71	-	46.40	-	-	99.11
7	BC13	-	52.43	-	46.40	-	-	98.83
8	BC13	-	53.01	-	46.44	-	0.91	100.36
9	BC13	-	53.31	-	46.55	-	0.90	100.76
10	BC13	-	54.22	-	47.32	-	-	101.54
11	BC13	-	53.38	-	47.05	-	-	100.44
12	BC13	-	52.90	-	47.14	-	-	100.04
13	BC13	-	53.23	-	46.94	-	-	100.18
14	BC13	-	53.62	-	47.95	-	-	101.57
15	BC13	-	53.16	-	46.04	1.64	-	100.83
16	BC13	-	52.79	-	46.81	-	-	99.60
17	BC13	-	53.37	-	46.62	-	-	100.00
18	BC13	-	53.07	-	46.68	-	-	99.74
19	BC13	-	52.21	-	46.85	-	-	99.05
20	BC13	0.30	53.21	-	46.72	-	-	100.23
21	BC13	-	52.57	-	46.89	-	-	99.46
22	BC11	-	53.26	-	46.87	-	-	100.13
23	BC11	-	53.11	-	46.51	-	-	99.61
24	BC11	0.34	53.45	0.56	46.12	-	-	100.47
25	BC11	-	53.16	-	46.40	-	-	99.56
26	BC11	-	53.47	-	46.90	-	-	100.37
27	BC11	-	52.39	0.47	46.00	-	-	98.86

Table 6.3. Fe and S concentrations of pyrite for Fe internal standardisation of Laser Ablation ICP-MS spot analyses, derived from Energy Dispersive X-ray Spectroscopy (EDS/EDX) (n=27); the average concentration was 46.7 wt.%.

	Host	Type I		Type II		Late Fractures
Albite	————					
Muscovite	————					
Chlorite	————			-----		
Garnet	-----					
Quartz	————	————	————	————	————	————
Ti-oxide (Rutile, Ilmenite)		————		-----		
Mg-Fe- oxide		-----				
Monazite				-----		
Py ₁			————			
Py ₂				————		
Arsenian pyrite infill (Ap ₁)					————	
Py ₃						————
Galena				-----		————
Au-Ag			-----	————		————
Sphalerite						————
Au			————→			
Pb				————→		
Zn					————→	

Table 6.4. Mineralogical framework, as observed petrographically at the Cloonacool Au occurrence. The host formation is characterised by albite, silicates and quartz, with two vein types (*Type I-II*) intersecting the formation. All vein types contain Ti-oxides which were subsequently replaced by pyrite. *Type I* veins are characterised by relatively fine, disseminated pyrite (Py₁), which commonly exhibits zonation, while *Type II* veins are larger in width and comprise pyrite masses (Py₂) and a minor late phase, Py₃, which exhibits diagnostic sphalerite and recrystallisation textures. Py₂₋₃ are associated with inclusions of visible Au and galena, with trace monazite observed. Au-Ag is observed within late fractures of pyrite within Type II veins.

6.6. Laser Ablation ICP-MS spot analysis

6.6.i. Overview and experimental approach

This study has determined that differences in morphology are observed between pyrite generations; variations in trace element abundances are observed in the results of LA ICP-MS in-situ spot analyses. In order to obtain the most representative data from tested samples, 107 spot analyses were targeted on Type I and Type II vein pyrite phases Py₁ – Py₃. Analyses included 72 spots on the earliest recognized form of pyrite, Py₁ (samples BC03, BC11 and BC13), 30 analyses of Py₂ (sample BC13), with 5 analyses of rare sphalerite-bearing Py₃ (sample BC13). Ablated spots (pits) are square in cross-section and 20 x 20 µm in size.

The objectives of the phase of work were (i) to investigate trace element signatures and Au contents for petrographically identified pyrite generations for a suite of elements appropriate to the mineral deposit type and observed inclusion phases (e.g. Zn, Pb); results are principally represented in figures by median values and interquartile ranges); (ii) determination of the physical properties of gold in tested analyses using Au and As (e.g. inclusions vs. lattice-bound Au); (iii) determinations of critical ratios (e.g. Co/Ni, Au/Ag); (iv) confirming the stability of signatures within petrographically-defined early pyrite (Py₁) and ‘ore-stage’ Py₂ in order to elucidate possible internal variation and (v) to determine correlations of tested analytes using Spearman rank methodology. Results are presented for ⁵⁹Co, ⁶⁰Ni, ⁶³Cu, ⁶⁶Zn, ⁷¹Ga, ⁷⁵As, ⁷⁸Se, ⁹⁵Mo, ¹⁰⁷Ag, ¹¹⁸Sn, ¹²¹Sb, ¹²⁵Te, ¹⁸²W, ¹⁹⁷Au, ²⁰²Hg, ²⁰⁵Tl, ²⁰⁸Pb and ²⁰⁹Bi. No attempt has been made to remove the possible effect of micro-inclusions on presented results. A value of 46.7 wt.% was used for internal standardisation of Fe in Iolite processing of pyrite analyses using an average value derived from EDS/EDX analyses.

6.6.ii. Gold solubility in pyrite

Au concentrations are recorded in 94 analyses across the dataset; the average detection limit was 0.034 ppm (n=107). For all generations, median Au was determined to be 0.59 ppm (IQR = 0.23 – 1.35 ppm, n=94). The maximum individual value for Au was 11.8 ppm, observed in an analysis of early Py₁. Across phases, Au is depleted in Py₁ (median 0.54 ppm, IQR = 0.16 – 1.3 ppm, n=59) and Py₂ (median 0.76 ppm, IQR = 0.28 – 1.36 ppm, n=30) compared to late Py₃, which records a median value of 2.22 ppm (IQR = 0.37 – 5.23 ppm, n=5). Across the dataset, Au correlates positively with As, with a calculated Spearman rank coefficient of $\rho = 0.57$ (n=106), this is most pronounced in Py₃ ($\rho = 0.99$) however only 5 of the 10 spot analyses are taken into consideration for this calculation. Median As contents for all phases are 950 ppm (IQR = 52.8 – 5,278 ppm, n=106). Within Py₃ which shows relatively elevated Au levels, contents of As are also high compared with earlier generations, a median of 4,990 ppm is determined (IQR = 2,780 – 14,010 ppm, n=5). Converting ppm values to mol% and using log-log compositional space, 7 analyses of Py₁ and 7 analyses of Py₂ lie above the solubility curve of Deditius et al (2014) for orogenic gold systems, predicting that ablated Au for these analyses takes the Au⁰ nanoparticle form. The balance of analyses lie below the solubility curve indicating that concentrations are in solution and of the Au¹⁺ variety. Early Py₁ and Py₂ individual analyses are positioned in a similar range (Au, c. 0.01 – 10 ppm; As, c. 10 - >10,000 ppm), while Py₃ values are more clustered toward the right of the chart (Au, c. 0.1 – 10 ppm; As, c. 1,000 - >10,000 ppm). The ratio of Au : As for the overall dataset is an average of 1 : 221. Particles of the Au¹⁺ species have large atomic radii, and are incorporated due to significant structural distortion of the host crystal lattice. A proposed mechanism for the incorporation of Au into the lattice of the crystals themselves include the substitution of Au for Fe within octahedral locations which have experienced distortion, creating vacancies (Deditius et al, 2014). The prediction of soluble

Au^{1+} within a sub-set of Py_2 coinciding with visible Au-Ag micro-scale inclusions and Py_3 suggests an availability of mobile Au^0 nano-particles which could be incorporated into pyrite structure, synchronous with deformation.

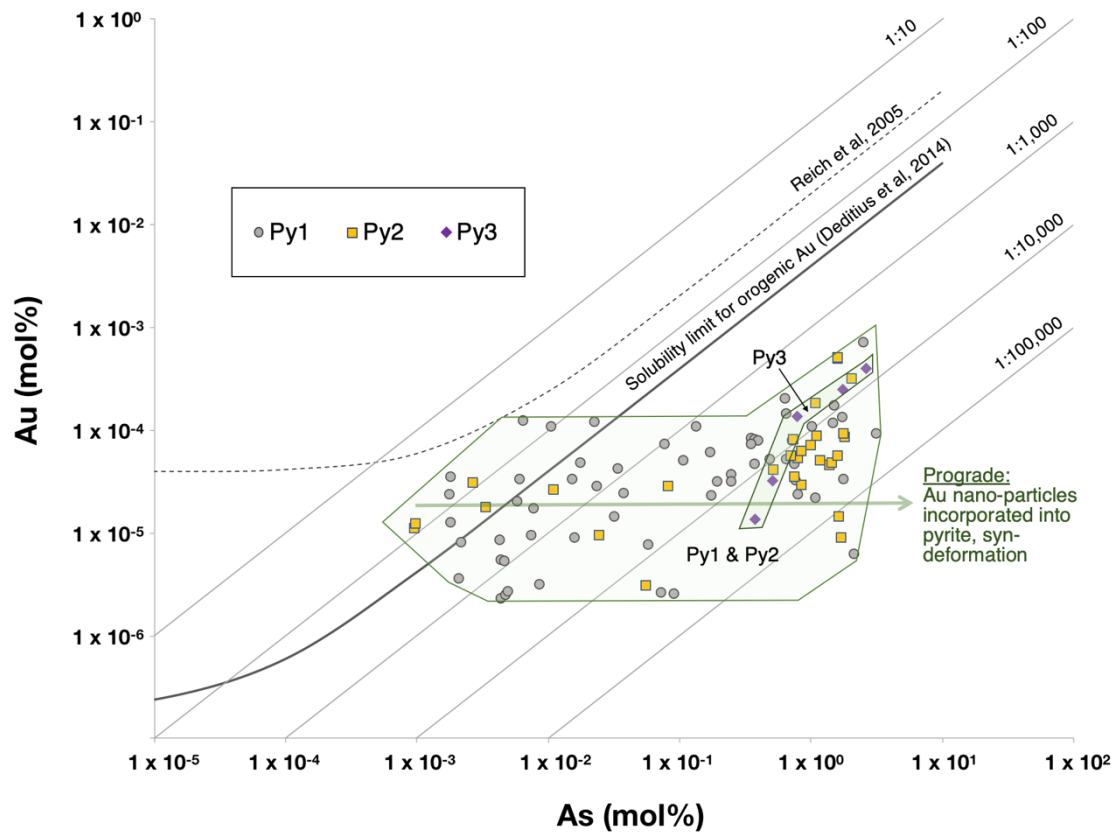


Figure 6.16. Scatter plot of Au/As concentrations ($n=93$) for Py_1 , Py_2 and Py_3 generations, expressed as mol %. The general solubility curve for arsenian pyrite in hydrothermal deposits derived by Reich et al (2005) is shown ($C_{\text{Au}} = 0.02 \cdot C_{\text{As}} + 4 \times 10^{-5}$) as a reference, with the more applicable solubility curve calculated by Deditius et al (2014) for orogenic systems formed at higher temperatures (appropriate to greenschist facies conditions) ($C_{\text{Au}} = 0.004 \cdot C_{\text{As}} + 4 \times 10^{-7}$).

6.6.iii.Py₁ (within Type I veinlets)

The earliest form, Py₁, shows higher concentrations of Co and Ni (and a wide interquartile range of Mo values) compared to later generations, while showing lower values of As and Hg; additional analytes show less striking deviations (Figure 6.17). Using the >100ppm definition of enrichment, this phase is elevated in Co (median 141 ppm; IQR = 32.5 – 442 ppm; n=72), Ni (median 444 ppm; IQR = 177 – 938 ppm; n=72) and As (median 233.5 ppm; IQR = 38 – 2,448 ppm; n=72). Co shows an affinity in bivariate plots for Ni ($\rho = 0.79$), while additionally Ni positively correlates with Se ($r = 0.56$). Arsenic shows a positive correlation (see Table 6.6) within this generation with both Au ($\rho = 0.57$) and Te ($\rho = 0.53$). Plotting Co vs. Ni (Figure 6.18A), a clear separation is observed between Py₁ and Py₂ results. Both cluster proximal to the Co/Ni = 1 line, however Py₁ reports notably higher values. Individual Au/Ag ratios for this phase are dominantly <1 (mean = 0.89) (Figure 6.18B). A signature of subsidiary interest derived from Spearman correlation matrices (see Table 6.6) is between Zn and Sn ($\rho = 0.95$), Tl ($\rho = 0.89$) and Hg ($\rho = 0.54$); while Pb correlates positively with Sb ($\rho = 0.8$), Bi ($\rho = 0.8$), Ag ($\rho = 0.7$), Te ($\rho = 0.69$), Cu ($\rho = 0.68$) and Hg ($\rho = 0.54$). Within Pb-Zn space (Figure 6.19E), Py₁ values are generally widely spread <100 ppm Zn and <1,000 ppm Pb, while Zn values form a narrow cluster >1,000ppm Zn and <100 ppm Pb.

Spatial variation of Py₁ trace element concentrations within near-surface samples between two localities, the collars of which are separated by 200m, was tested by sub-division of results into two sample populations from the north-west and south-east of the drill pattern (see Figure 6.6). The first population (NW) consists of 30 analyses of Py₁ from sample BC03 within drill-hole 3382-009 (15.80-15.88m) at the far north-west of the project area, while the second population (SE) consists of 42 Py₁ analyses from two drill-holes at the south-eastern extent of the area: BC11 (drill-hole 3382-002, 24.13-24.19m) and BC13 (drill-hole 3382-001;

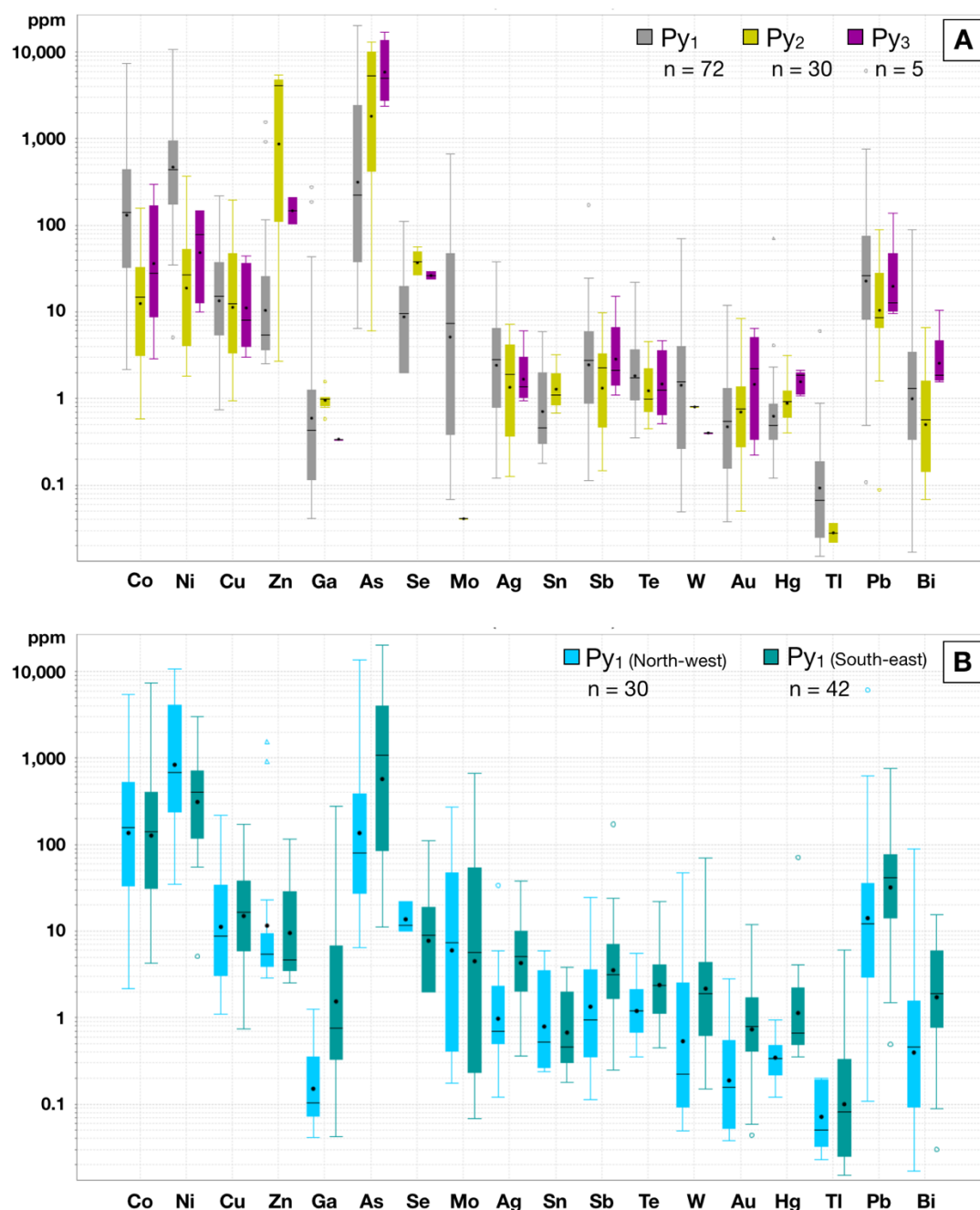


Figure 6.17. Box and whisker plots of concentrations of Co, Ni, Cu, Zn, Ga, As, Se, Mo, Ag, Sn, Sb, Te, W, Au, Hg, Tl, Pb and Bi. (A) presents data for Py₁, Py₂ and Py₃, while (B) shows Py₁ data subdivided by spatial location (derived from drilling at the far north-west and south-east extremities of the tested area). Central boxes represent the middle 50% of data from Q1 to Q3 (the interquartile range); an outlier is $> 1.5x$ (Q3-Q1) from the box, while triangles denote values $> 3x$ (Q3-Q1). Whiskers indicate extreme values which are not outliers.

18.16-18.27m). Box and whisker plots of results are presented in Figure 6.17B, within which similarities are observable in the concentrations of certain elements (e.g. Co) alongside differences in others (e.g. Ga). Using an independent sample two-tailed t-test (for testing the differences between means assuming equal variance and therefore proposed with a degree of caution), it is determined that there is no significant difference between the mean of populations at the 95% confidence level ($P=.05$) for Co ($P=.64$), Cu ($P=.89$), Zn ($P=.17$), Ga ($P=.16$), As ($P=.17$), Se ($P=.84$), Mo ($P=.38$), Sn ($P=.54$), Sb ($P=.34$), W ($P=.83$), Au ($P=.06$), Hg ($P=.27$), Tl ($P=.52$), Pb ($P=.35$) or Bi ($P=.83$). There is however a significant difference observed between the mean of the two populations at this level for Ni ($P=.0003$), Ag ($P=.02$), Te ($P=.02$). These results show there is broad consistency in the data with spatial variation in different drilled locations. Within the north-west population, median Ni concentration is 679 ppm (IQR = 238 – 4,130 ppm; $n=30$), while for south-east samples, a lower median of 404 ppm Ni (IQR = 118 – 705 ppm; $n=42$) is recorded. Ag is relatively elevated to the south-east; median abundances of 0.69 ppm (IQR = 0.51 – 2.3 ppm; $n=25$) in the north-west and 5.11 ppm (IQR = 2.02 – 9.95 ppm; $n=40$) are observed at the south-east. Te also shows relative enrichment in south-eastern sampling: the north-west group reports 1.21 ppm Te (IQR = 0.68 – 2.11 ppm), while median values of 2.36 ppm (IQR = 1.12 – 4.05 ppm; $n=40$) were retrieved in the south-easterly group.

6.6.iv. Py₂ (within Type II veins)

Py₂ ($n=30$) which forms the dominant masses of pyrite within Type II veins, associated with visible Au particles and galena, shows median enrichments >100 ppm in Zn (4,090 ppm; IQR = 1,747 – 4,830 ppm; $n=9$) and As (5,300 ppm; IQR = 429 – 10,060 ppm; $n=29$) (Figure 6.17A). Since it is observed that 21 analyses report below detection for Zn (avg. limit of 4.53 ppm), it may infer that these elevated values are influenced by the presence of micro-

inclusions, however an alternate hypothesis pursued in this study is that Py₂ contains multiple subsidiary generations associated with discrete metalliferous events (tested in later LA ICP-MS raster element mapping). Concentrations >10 ppm are observed for Co (median 14.7 ppm; IQR = 3.1 – 32.3 ppm; n=23), Ni (median 27.1; IQR = 4.1 – 53.2 ppm; n=28), Cu (median 12.4 ppm; IQR = 3.4 – 48 ppm; n=25) and Se (median = 38 ppm; IQR = 27.5 – 49 ppm; n=9), while all presented heavier isotopes are recorded in this phase at median values <10 ppm. The range of values in Co-Ni space (Figure 6.18A) is lower for Py₂ (Co/Ni avg. 0.62; 2 σ = 1.06) is than Py₁ (Co/Ni avg. 0.68; 2 σ =4.7); due to their high abundance within pyrite, Co and Ni results may be interpreted as supporting petrographic evidence that Py₁ and Py₂ are separate generations.

Zn in Py₂ correlates positively (see Table 6.7) with Cu (ρ = 0.68; Spearman rank), Ga (ρ = 0.57) and Ag (ρ = 0.58), and negatively with As (ρ = -0.74) and Ni (ρ = -0.63). Arsenic, while correlating positively with Au (ρ = 0.58; Spearman rank), also shows negative correlation with Ag (ρ = -0.66), Cu (ρ = -0.55) and Hg (ρ = -0.51). Lead, evident in visible particle form within this phase, is present in median concentrations of 8.6 ppm (IQR = 6.6 – 28.2 ppm), maximum Pb is 89.9 ppm. Pb does not show positive correlations with tested trace elements (ρ > 0.50), however a negative correlation with Cu (ρ = -0.51) is observed. A bivariate plot of Pb versus Zn (n=9) shows a separation of values (Figure 6.19E), with two analyses with low Zn < 10ppm and the balance (n=7) positioned in a small cluster >1,000ppm Zn (Pb for all analyses within the 1 – 100ppm range). Pb/Zn provides additional evidence of internal sub-phases. Au/Ag for this phase is an average of 2.52 (2 σ = 8.66), with wide dispersion of results away from the Au/Ag = 1 line in log-log compositional space (Figure 6.18B). Analyses of Py₂ are dominantly positioned below the Au/Pb = 1 (Figure 6.19A), proximal to and surrounding the Au/Te = 1 line (Figure 6.19C), entirely below the Au/Zn = 1 line (Figure 6.19D), and above the Pb/Bi = 1 line (Figure 6.19F).

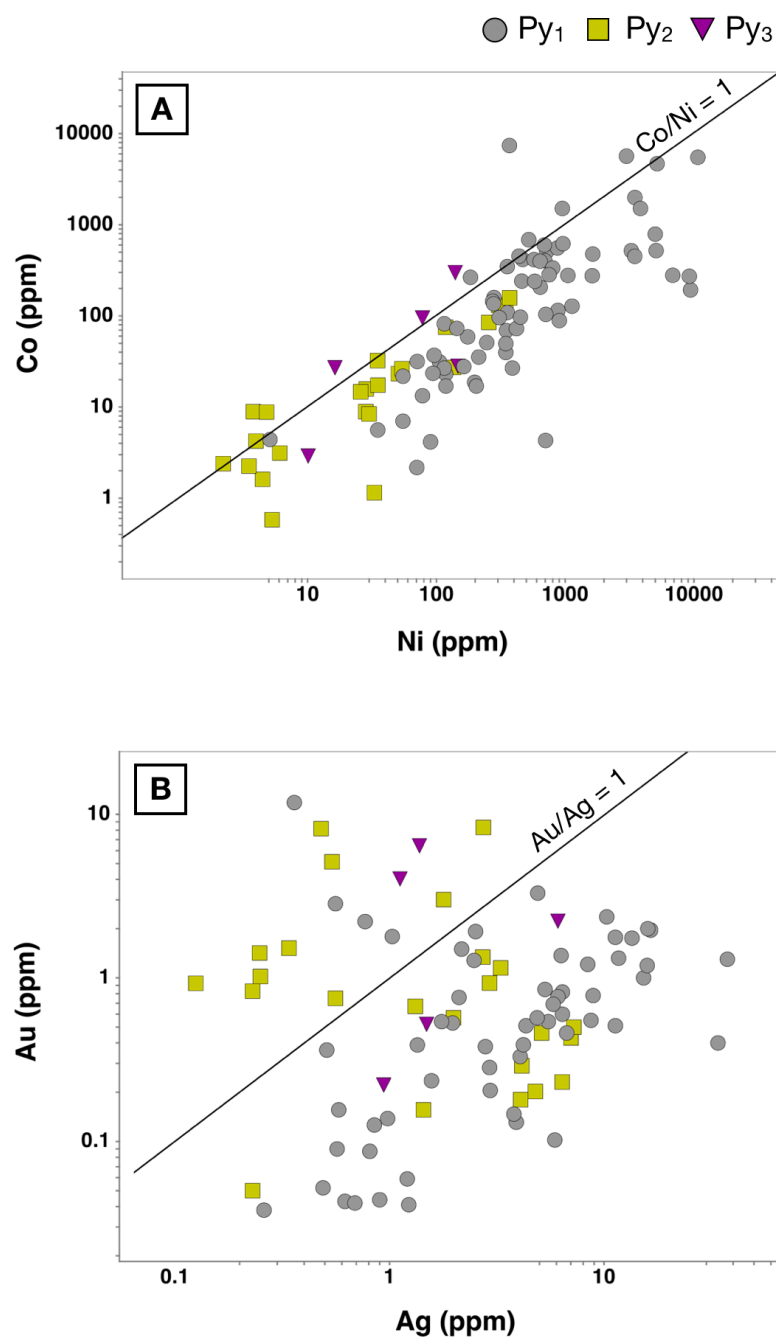


Figure 6.18. (A) Scatter-plot of Co/Ni for phases Py₁, Py₂ and Py₃ showing close proximity to the Co/Ni = 1 line and a dominant Co/Ni < 1 trend. Results show that Py₁ plots in a field bearing higher Co and Ni values than Py₂, while Py₃ values are more dispersed; (B) Scatter-plot of Au/Ag for tested phases showing wide dispersal of data; 93.1% of Py₁ values (n=58), 58.3% of Py₂ values (n=23) and 60% of Py₃ values (n=5) plot below the Au/Ag = 1 line.

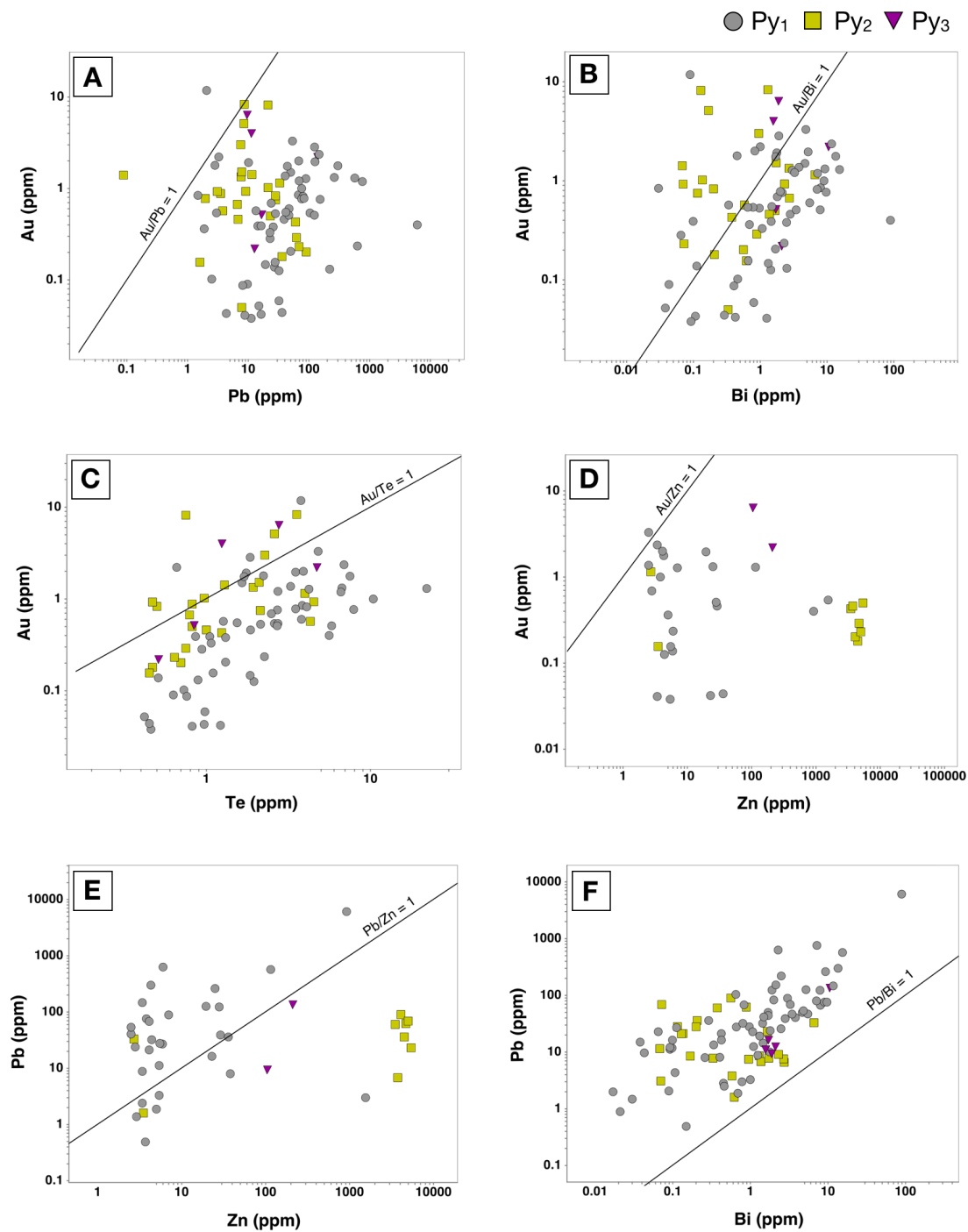


Figure 6.19. Scatter plots of selected Py_1 , Py_2 and Py_3 analyses. (A) Au/Pb; (B) Au/Bi; (C) Au/Te; (D) Au/Zn; (E) Pb/Zn; (F) Pb/Bi.

To test the hypothesis of internal zonation of Py₂ using LA ICP-MS spot analyses, a c. 1,250 µm transect of a Py₂ mass (sample BC13) comprising six 20 x 20 µm individual ablations (*a-f*) were inspected, with results of 9 analytes compared (Figure 6.20). The region within which spots *a-d* are located is homogenous and lacking in visible inclusions, while the region of the outer two spots (*e-f*) contains inclusions of galena. The centre of Py₂ masses have been classified as a discrete zone designated as Py_{2a}, the earliest recognized phase of pyrite growth within Type II veins. Data show stability in concentrations within the centre of the Py_{2a} mass (spots *a-c*) of Cu (median 102 ppm; IQR = 76 – 133 ppm), Ni (median 5.2 ppm; IQR = 3.91 – 5.3 ppm), As (median 20.8 ppm; IQR = 6.1 – 68 ppm), Ag (median 4.79 ppm; IQR = 4.79 ppm; IQR = 4.14 – 7.02 ppm), Sb (median 2.87 ppm; IQR = 2.27 – 3.77 ppm), Te (median 0.75; IQR = 0.7 – 1.24 ppm), Au (median 0.29; IQR = 0.202 – 0.429 ppm), Pb (median 62.1 ppm; IQR = 60.2 – 89.9 ppm) and Bi (median = 0.56; IQR = 0.374 – 0.886 ppm).

For the outer three spots (*d-f*), deviation from these medians and interquartile ranges is observed, indicating that the central and outer regions of interest belong to geochemically distinctive sub-classifications of Py₂. For spots *d-f*, Cu (median = 14.3 ppm; IQR = 11.1 – 54 ppm), Sb (median 2.55 ppm; IQR = 1.01 – 2.66 ppm) and Pb (median = 8.6 ppm; IQR = 7.5 – 21.1 ppm) show decreased concentrations; As is elevated by two orders of magnitude (median = 10,040 ppm; IQR = 6,890 – 10,120 ppm), while Ni (median = 28.3 ppm; IQR = 4.8 – 54 ppm), Au (median 8.18 ppm; IQR = 3.01 – 8.32 ppm) and Te (median 2.27 ppm; IQR = 0.75 – 3.55 ppm) also show increases. Bi is slightly elevated but remains within the same order of magnitude (median 0.95 ppm; IQR = 0.13 – 1.3 ppm). This geochemical evidence demonstrates that (i) trace element concentrations are not evenly distributed within Py₂, (ii) that zone boundaries associated with masses are cryptic and do not necessarily correspond to petrographically distinctive areas with visual diagnostics (e.g. inclusions), (iii) that the suite Cu, Ni, As, Ag, Sb, Te, Au, Pb and Bi may be used to discriminate sub-phases, (iv) that the tested outer zone in this instance is observed to be particularly enriched in As,

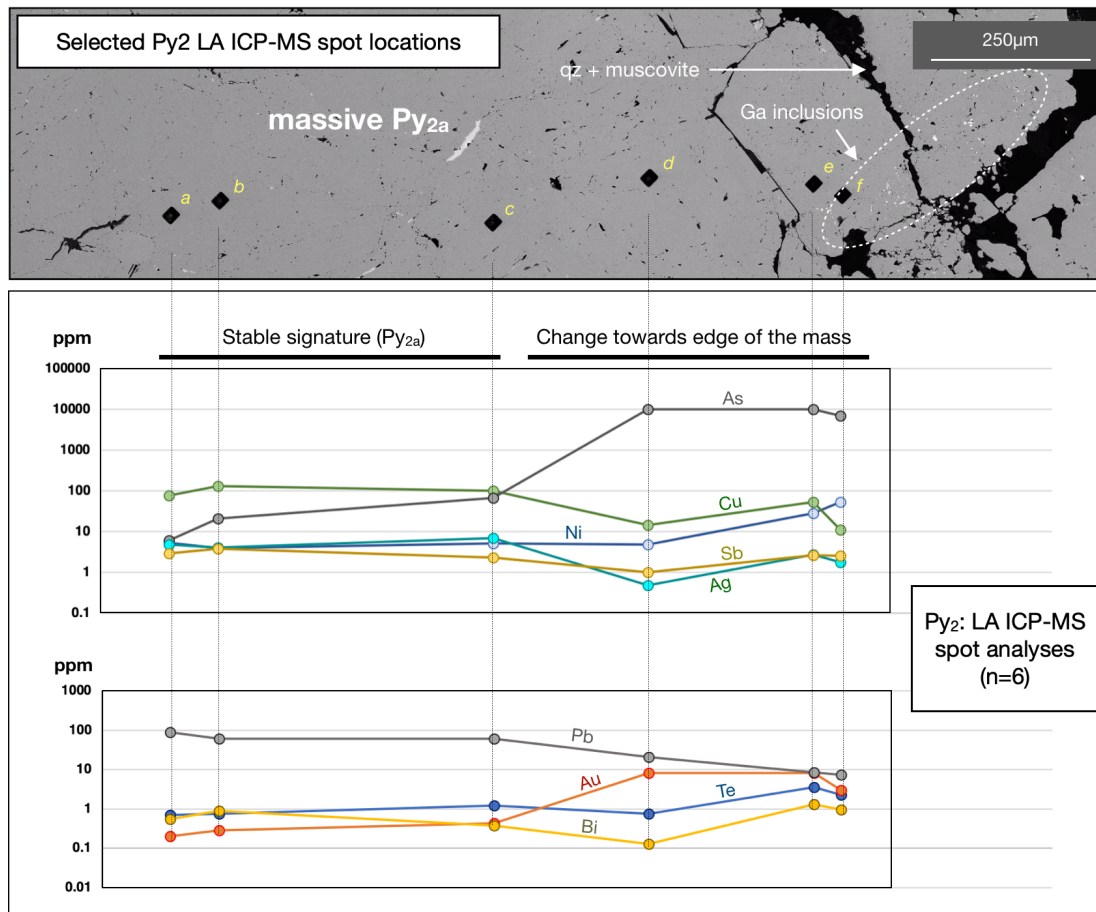


Figure 6.20. Region of interest (shown in a Backscattered Electron SEM image obtained using a voltage of 20 keV at a working distance of 20 mm and a current of 300 pA) toward the boundary of a Py₂ mass within sample BC13 (drill-hole 3382-001), showing the locations of six ablation pits (designated *a-f*) and below, corresponding results for Cu, Ni, As, Ag, Sb, Te, Au, Pb and Ni. A stable signature is observed within the three spots to the left of the image at the centre of the mass (*a-c*), while deviations from these values are recorded in data from the three spots to the right (*d-f*; the outer region of the mass). Pits *e* and *f* are located in a region of abundant galena micro-inclusions, spot data from *d*, *e* and *f* show lower concentrations of Pb are recorded than those obtained from pits *a-c*.

with order-of-magnitude scale variations in other elements, (v) that the broad relationship between Au and As for Py₂ ($\rho = 0.58$; Spearman rank) is reaffirmed, with both showing an outer zone increase, and (vi) that regions of pyrite containing abundant observable inclusions of galena specifically do not necessarily correspond to increased Pb contents within the

crystal itself; the observed inverse relationship suggests that either lattice-bound Pb is concentrated as inclusions, or they are unrelated and a result of metasomatic processes.

6.6.v. Py₃ (within Type II veins)

Py₃, a late overgrowth of Py₂ characterised by diagnostic inclusions of sphalerite, was tested using 5 in-situ analyses. Although analyses are limited, these show comparable enrichments as Py₂ for As (median 4,990 ppm; IQR = 2,780 – 14,010 ppm) and results for Co, Ni and Se (>10ppm) lie within a similar range (Figure 16A). However, Zn, which in Py₂ contains 4,090ppm (median; IQR = 1,746 – 4,830 ppm) records far lower concentrations (median 156.5 ppm; IQR = 104 – 209 ppm). The disconnect between metalliferous inclusions and the lattice-bound signatures observed with respect to Pb and galena in Py₂ is replicated with regards Zn and sphalerite results for Py₃. A mechanism whereby lattice-bound metalloids were transported into aggregated particle clusters may be viable in both cases.

LA ICP-MS spot analyses demonstrate that Py₁, Py₂ and Py₃ represent distinctive phases in the evolution of the system. Evidence suggests that Py₂, which carries inclusions of both Au and Pb, may be an amalgamation of two or more pyrite phases which are linked to specific emplacement events. Neither Au nor Pb enrichments are observed broadly within these two phases, however a disconnect between Pb and the presence of galena is suggested. Late Py₃, which hosts inclusions of sphalerite, shows depletion in Zn.

A Spearman correlation matrix for this generation is presented in Table 6.8 for indicative purposes only due to the low number of analyses (n=5).

All	Spearman Rank Correlation Matrix, n= 96																	
	Co	Ni	Cu	Zn	Ga	As	Se	Mo	Ag	Sn	Sb	Te	W	Au	Hg	Tl	Pb	Bi
Co	1	0.86	0.24	-0.12	0.09	-0.03	-0.21	0.21	0.34	-0.14	0.33	0.39	0.22	-0.09	-0.17	0.07	0.27	0.47
Ni	0.86	1	0.02	-0.45	-0.23	-0.12	-0.22	0.23	0.11	-0.40	0.15	0.26	0.07	-0.23	-0.36	0.06	0.10	0.30
Cu	0.24	0.02	1	0.34	0.28	-0.08	-0.47	0.01	0.78	0.20	0.58	0.40	0.52	0.20	0.34	-0.02	0.61	0.54
Zn	-0.12	-0.45	0.34	1	0.36	-0.22	0.48	0.36	0.17	0.57	-0.02	-0.25	-0.18	-0.18	0.52	0.89	0.24	-0.18
Ga	0.09	-0.23	0.28	0.36	1	0.14	0.11	0.29	0.33	0.24	0.56	0.20	0.30	0.41	0.61	0.73	0.28	0.27
As	-0.03	-0.12	-0.08	-0.22	0.14	1	0.46	0.07	-0.15	-0.23	0.01	0.37	0.18	0.60	0.13	-0.16	-0.15	0.23
Se	-0.21	-0.22	-0.47	0.48	0.11	0.46	1	-0.29	-0.53	0.60	-0.31	-0.31	-0.58	0.41	-0.02	-0.00	-0.36	-0.40
Mo	0.21	0.23	0.01	0.36	0.29	0.07	-0.29	1	0.24	-0.02	0.46	0.24	0.19	-0.04	0.38	0.67	0.36	0.26
Ag	0.34	0.11	0.78	0.17	0.33	-0.15	-0.53	0.24	1	-0.06	0.60	0.56	0.39	0.17	0.28	0.16	0.66	0.66
Sn	-0.14	-0.40	0.20	0.57	0.24	-0.23	0.60	-0.02	-0.06	1	-0.24	-0.39	0.73	-0.38	0.38	0.85	-0.22	-0.46
Sb	0.33	0.15	0.58	-0.02	0.56	0.01	-0.31	0.46	0.60	-0.24	1	0.55	0.55	0.32	0.21	0.43	0.70	0.71
Te	0.39	0.26	0.40	-0.25	0.20	0.37	-0.31	0.24	0.56	-0.39	0.55	1	0.35	0.56	0.06	0.15	0.48	0.71
W	0.22	0.07	0.52	-0.18	0.30	0.18	-0.58	0.19	0.39	0.73	0.55	0.35	1	0.19	0.18	0.15	0.34	0.41
Au	-0.09	-0.23	0.20	-0.18	0.41	0.60	0.41	-0.04	0.17	-0.38	0.32	0.56	0.19	1	0.12	0.03	0.06	0.35
Hg	-0.17	-0.36	0.34	0.52	0.61	0.13	-0.02	0.38	0.28	0.38	0.21	0.06	0.18	0.12	1	0.66	0.16	0.28
Tl	0.07	0.06	-0.02	0.89	0.73	-0.16	-0.00	0.67	0.16	0.85	0.43	0.15	0.15	0.03	0.66	1	0.27	0.15
Pb	0.27	0.10	0.61	0.24	0.28	-0.15	-0.36	0.36	0.66	-0.22	0.70	0.48	0.34	0.06	0.16	0.27	1	0.61
Bi	0.47	0.30	0.54	-0.18	0.27	0.23	-0.40	0.26	0.66	-0.46	0.71	0.71	0.41	0.35	0.28	0.15	0.61	1

Table 6.5. Spearman rank correlation matrix of LA ICP-MS spot analysis results for all pyrite generations, Py₁, Py₂ and Py₃, identified within Cloonacool Type I and Type II veins (n=96 of 107). This table is included to demonstrate that certain correlations are applicable broadly across the entire suite of pyrite generations (e.g. Co, Ni; ρ =0.86).

Py _i	Spearman Rank Correlation Matrix, n= 67																	
	Co	Ni	Cu	Zn	Ga	As	Se	Mo	Ag	Sn	Sb	Te	W	Au	Hg	Tl	Pb	Bi
Co	1	0.79	0.26	0.07	0.16	0.46	0.43	0.16	0.24	-0.12	0.27	0.40	0.21	0.09	0.13	-0.05	0.22	0.48
Ni	0.79	1	0.02	-0.00	-0.12	0.30	0.56	0.17	-0.02	-0.18	-0.00	0.13	0.03	-0.22	0.03	-0.07	0.00	0.21
Cu	0.26	0.02	1	0.06	0.29	0.21	-0.05	-0.01	0.78	0.12	0.54	0.57	0.54	0.42	0.40	-0.15	0.68	0.62
Zn	0.07	-0.00	0.06	1	0.40	0.02	0.41	0.36	0.14	0.95	0.06	-0.00	-0.10	-0.27	0.54	0.89	0.27	0.03
Ga	0.16	-0.12	0.29	0.40	1	0.29	-0.34	0.29	0.37	0.34	0.65	0.39	0.30	0.55	0.79	0.73	0.39	0.44
As	0.46	0.30	0.21	0.02	0.29	1	0.34	0.16	0.16	-0.16	0.28	0.53	0.23	0.57	0.49	-0.06	0.17	0.42
Se	0.43	0.56	-0.05	0.41	-0.34	0.34	1	-0.29	-0.16	0.50	-0.51	-0.14	-0.47	-0.01	1	0.32	-0.44	-0.29
Mo	0.16	0.17	-0.01	0.36	0.29	0.16	-0.29	1	0.19	-0.02	0.44	0.21	0.19	0.06	0.38	0.67	0.36	0.24
Ag	0.24	-0.02	0.78	0.14	0.37	0.16	-0.16	0.19	1	-0.09	0.55	0.70	0.38	0.47	0.46	0.18	0.70	0.74
Sn	-0.12	-0.18	0.12	0.95	0.34	-0.16	0.50	-0.02	-0.09	1	-0.06	-0.27	0.73	-0.32	0.28	0.85	-0.23	-0.27
Sb	0.27	-0.00	0.54	0.06	0.65	0.28	-0.51	0.44	0.55	-0.06	1	0.61	0.59	0.50	0.61	0.43	0.80	0.70
Te	0.40	0.13	0.57	-0.00	0.39	0.53	-0.14	0.21	0.70	-0.27	0.61	1	0.36	0.67	0.53	0.12	0.69	0.81
W	0.21	0.03	0.54	-0.10	0.30	0.23	-0.47	0.19	0.38	0.73	0.59	0.36	1	0.22	0.28	0.15	0.36	0.44
Au	0.09	-0.22	0.42	-0.27	0.55	0.57	-0.01	0.06	0.47	-0.32	0.50	0.67	0.22	1	0.40	0.03	0.35	0.50
Hg	0.13	0.03	0.40	0.54	0.79	0.49	1	0.38	0.46	0.28	0.61	0.53	0.28	0.40	1	0.78	0.54	0.54
Tl	-0.05	-0.07	-0.15	0.89	0.73	-0.06	0.32	0.67	0.18	0.85	0.43	0.12	0.15	0.03	0.78	1	0.17	0.15
Pb	0.22	0.00	0.68	0.27	0.39	0.17	-0.44	0.36	0.70	-0.23	0.80	0.69	0.36	0.35	0.54	0.17	1	0.80
Bi	0.48	0.21	0.62	0.03	0.44	0.42	-0.29	0.24	0.74	-0.27	0.70	0.81	0.44	0.50	0.54	0.15	0.80	1

Table 6.6. Spearman rank correlation matrix of LA ICP-MS spot analysis results for Py₁ observed within early Type I veinlets (n=67 of 72; 95% confidence, r-critical is 0.20).

Py ₂	Spearman Rank Correlation Matrix, n = 24																	
	Co	Ni	Cu	Zn	Ga	As	Se	Mo	Ag	Sn	Sb	Te	W	Au	Hg	Tl	Pb	Bi
Co	1	0.85	0.03	-1	0.50	-0.21	-0.27	-	0.33	1	0.34	0.39	-	0.02	0.01	1	-0.36	0.37
Ni	0.85	1	-0.00	-0.63	0.29	0.00	-0.14	-	-0.05	-0.43	0.27	0.35	-	0.14	-0.06	1	-0.51	0.67
Cu	0.03	-0.00	1	0.68	-0.33	-0.55	-0.84	-	0.86	-0.43	0.74	-0.03	-	-0.22	0.72	1	0.45	0.47
Zn	-1	-0.63	0.68	1	0.57	-0.74	-	-	0.58	-0.07	-0.03	-0.28	-	-0.03	0.15	-	0.37	-0.25
Ga	0.50	0.29	-0.33	0.57	1	0.00	-	-	-0.19	0.14	0.36	0.02	-	0.29	-0.12	-	-0.36	0.31
As	-0.21	0.00	-0.55	-0.74	0.00	1	0.14	-	-0.66	0.26	-0.43	0.34	-	0.58	-0.51	-1	-0.37	-0.28
Se	-0.27	-0.14	-0.84	-	-	0.14	1	-	-0.86	-	-0.50	-0.34	-	0.35	-0.52	-1	-0.42	-0.28
Mo	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ag	0.33	-0.05	0.86	0.58	-0.19	-0.66	-0.86	-	1	0.29	0.71	0.04	-	-0.37	0.70	-	0.44	0.41
Sn	1	-0.43	-0.43	-0.07	0.14	0.26	-	-	0.29	1	-0.50	-0.04	-	-0.04	-0.68	-	-0.14	-0.64
Sb	0.34	0.27	0.74	-0.03	0.36	-0.43	-0.50	-	0.71	-0.50	1	0.30	-	0.00	0.66	-	0.25	0.76
Te	0.39	0.35	-0.03	-0.28	0.02	0.34	-0.34	-	0.04	-0.04	0.30	1	-	0.57	-0.11	1	-0.12	0.39
W	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Au	0.02	0.14	-0.22	-0.03	0.29	0.58	0.35	-	-0.37	-0.04	0.00	0.57	-	1	-0.20	1	-0.23	0.06
Hg	0.01	-0.06	0.72	0.15	-0.12	-0.51	-0.52	-	0.70	-0.68	0.66	-0.11	-	-0.20	1	-1	0.23	0.50
Tl	1	1	1	-	-	-1	-1	-	-	-	-	1	-	1	-1	1	1	-
Pb	-0.36	-0.51	0.45	0.37	-0.36	-0.37	-0.42	-	0.44	-0.14	0.25	-0.12	-	-0.23	0.23	1	1	-0.22
Bi	0.37	0.67	0.47	-0.25	0.31	-0.28	-0.28	-	0.41	-0.64	0.76	0.39	-	0.06	0.50	-	-0.22	1

Table 6.7. Spearman rank correlation matrix of LA ICP-MS spot analysis results for Py₂ observed within early Type II veins (n=24 of 30; 95% confidence, r-critical is 0.34).

Py ₃	Spearman Rank Correlation Matrix, n = 5																	
	Co	Ni	Cu	Zn	Ga	As	Se	Mo	Ag	Sn	Sb	Te	W	Au	Hg	Tl	Pb	Bi
Co	1	0.70	-0.40	1	-	-0.80	1	-	-0.00	-	0.30	-0.30	-	-0.80	-0.36	-	0.60	0.80
Ni	0.70	1	-0.60	1	-	-0.80	1	-	0.20	-	-0.30	-0.50	-	-0.80	-0.56	-	0.60	0.30
Cu	-0.40	-0.60	1	1	-	0.60	1	-	0.60	-	0.50	0.90	-	0.60	0.97	-	0.20	0.10
Zn	1	1	1	1	-	-1	-	-	1	-	1	1	-	-1	1	-	1	1
Ga	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
As	-0.80	-0.80	0.60	-1	-	1	-1	-	0.20	-	0.30	0.70	-	1	0.67	-	-0.60	-0.30
Se	1	1	1	-	-	-1	1	-	1	-	1	1	-	-1	1	-	1	1
Mo	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ag	-0.00	0.20	0.60	1	-	0.20	1	-	1	-	0.30	0.70	-	0.20	0.67	-	0.60	0.30
Sn	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Sb	0.30	-0.30	0.50	1	-	0.30	1	-	0.30	-	1	0.70	-	0.30	0.62	-	0.10	0.80
Te	-0.30	-0.50	0.90	1	-	0.70	1	-	0.70	-	0.70	1	-	0.70	0.97	-	0.10	0.30
W	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Au	-0.80	-0.80	0.60	-1	-	1	-1	-	0.20	-	0.30	0.70	-	1	0.67	-	-0.60	-0.30
Hg	-0.36	-0.56	0.97	1	-	0.67	1	-	0.67	-	0.62	0.97	-	0.67	1	-	0.15	0.21
Tl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Pb	0.60	0.60	0.20	1	-	-0.60	1	-	0.60	-	0.10	0.10	-	-0.60	0.15	-	1	0.50
Bi	0.80	0.30	0.10	1	-	-0.30	1	-	0.30	-	0.80	0.30	-	-0.30	0.21	-	0.50	1

Table 6.8. Spearman rank correlation matrix of LA ICP-MS spot analysis results for Py₃ observed within early Type II veins (n=5 of 5; 95% confidence, r-critical is 0.78: these statistics are included for indicative purposes and are of limited use at 4 degrees of freedom).

6.7. Laser Ablation ICP-MS raster element mapping of pyrite

6.7.i. Experimental approach

LA ICP-MS spot analyses of Py_2 provide evidence of internal compositional zonation. Follow-up LA ICP-MS raster element mapping was conducted on a Type II vein region of interest (sample BC13) measuring approximately $890 \times 530 \mu\text{m}$ (see Figure 6.21 for schematic diagram), with a view to testing this hypothesis, presented in Figure 6.22.

The objectives of this exercise were (i) to determine the internal structure Py_2 subsequent to the precipitation of the initial phase (Py_{2a} ; see Figure 6.20), (ii) to examine the relationship between trace element distribution within the grain and inclusions, (iii) to test the relationship between late micro-fracture infill and inclusions and (iv) to determine the chemical paragenetic sequence of identified internal phases and fracture infill. In order to determine the internal structure and sequence of emplacement events at a targeted region of interest within Py_2 , the suite of elements tested replicated those presented in spot analyses, with ^{55}Mn included along with ^{57}Fe and ^{34}S . Raster element maps were produced semi-quantitatively due to compositional differences between pyrite and adjacent vein host mineralogy (principally quartz). Figure 6.22, within which maps are presented, includes a composite reflected light image of the region of interest, along with a large-scale view which shows the location of the target grain in context of the surrounding grain configuration. The target is located in this image below a homogenous Py_{2a} mass devoid of visible inclusions of galena would be indicative of subsequent phases as established in earlier analytical work using spot analyses. The reasoning behind the selection of this specific area was the abundance of galena inclusions within a region to the left of the grain in the image, the presence of visible Au(-Ag) and the observation of parallel linear structural features (top to bottom), along with perpendicular fractures (left to right) within the right-hand side of the grain as presented. This structural framework along with the aforementioned presence of visible inclusions is

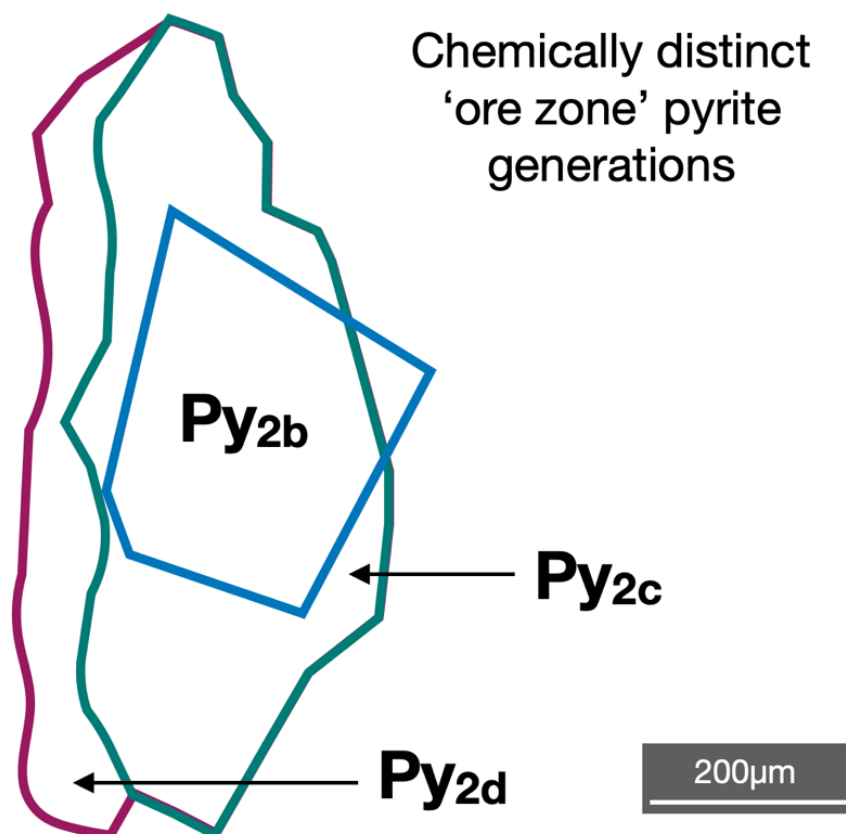
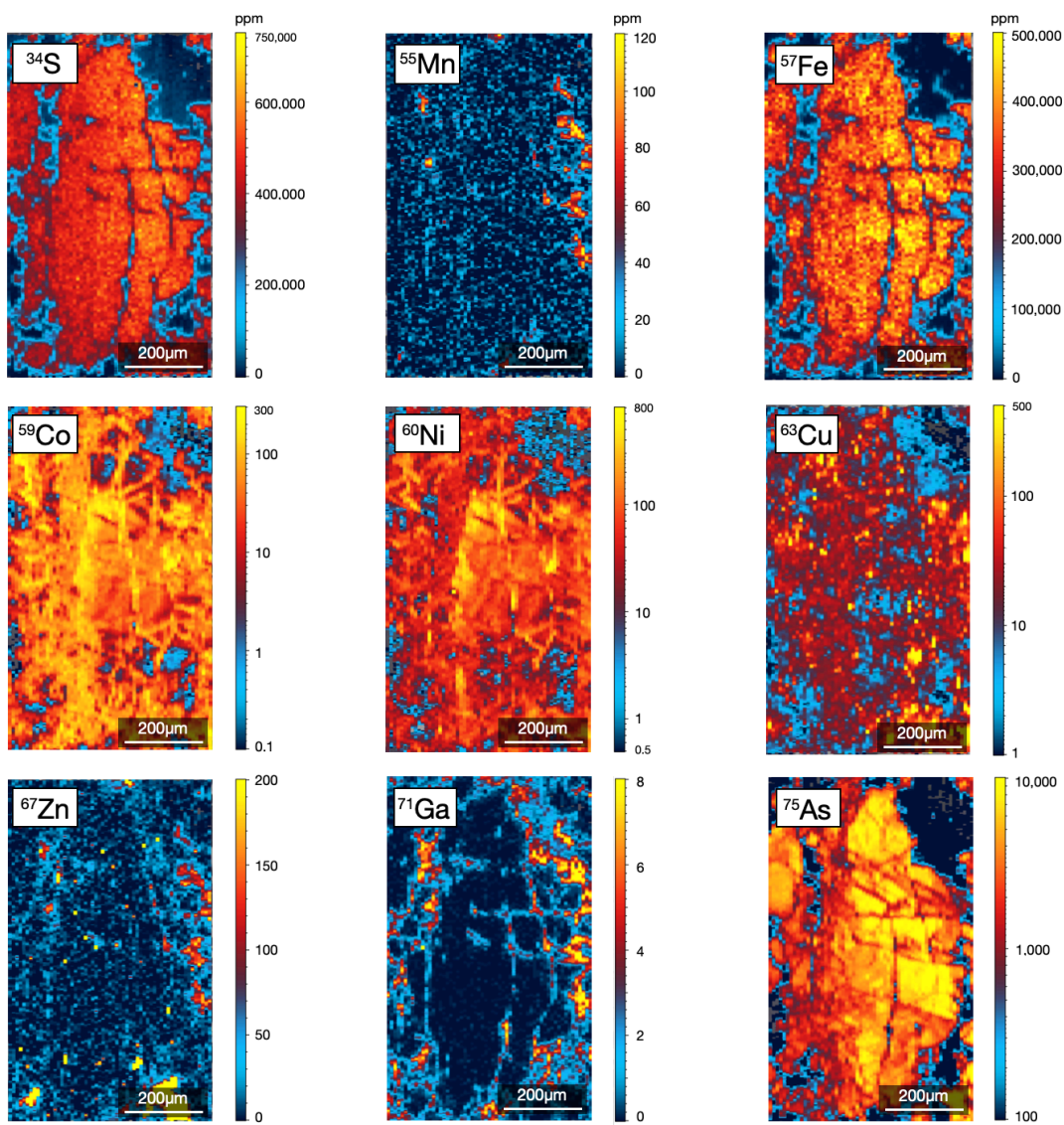
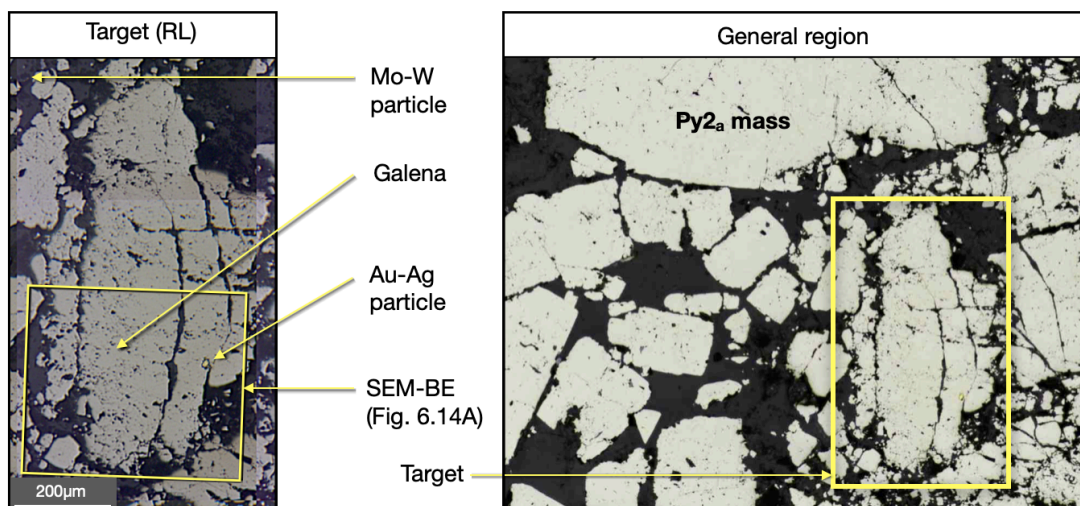
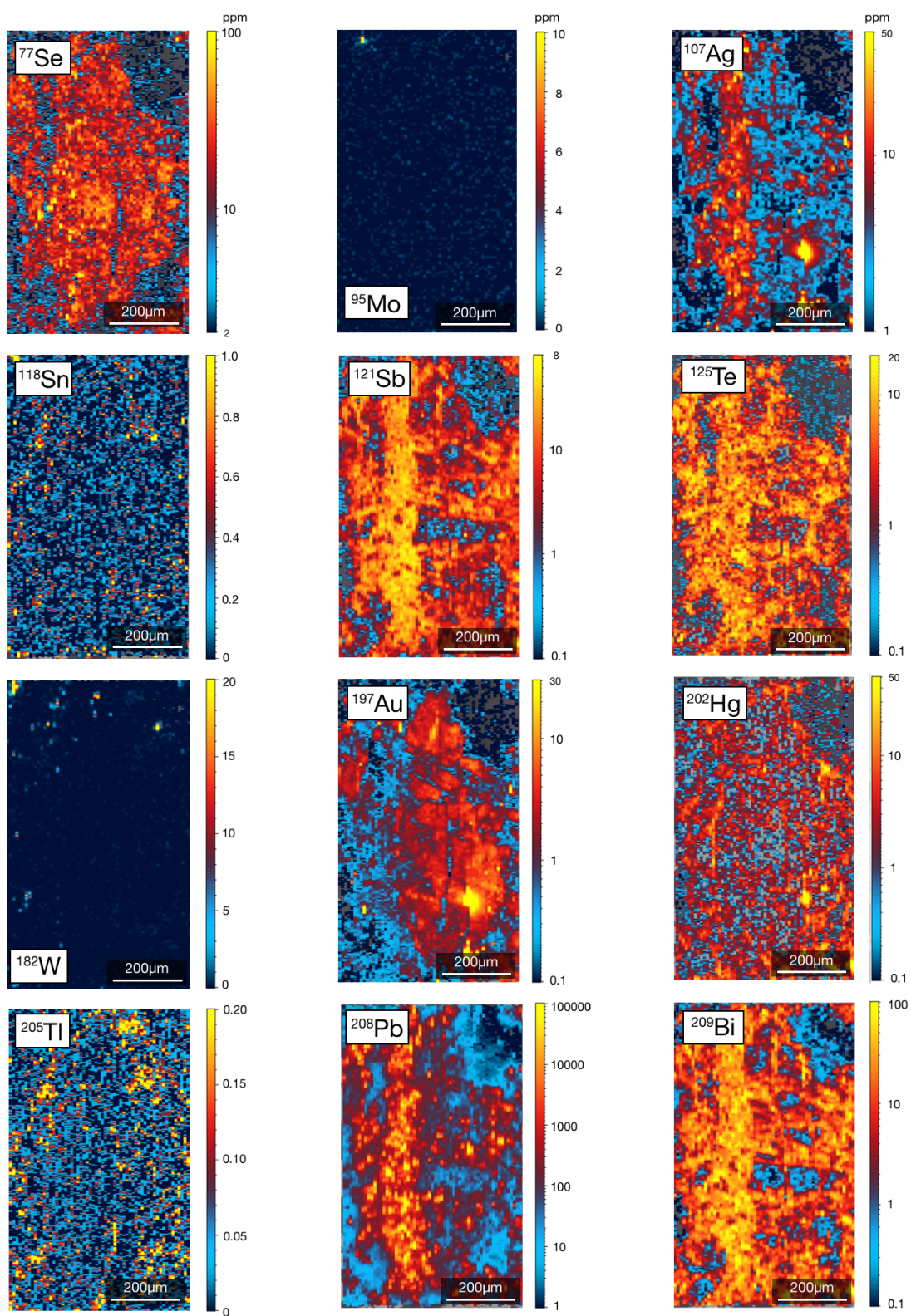


Figure 6.21. Schematic diagram of generations identified within the grain tested using LA ICP-MS raster element mapping (subsequent figure).



Continued overleaf



Caption overleaf

Figure 6.22. A region of interest targeted for LA ICP-MS analysis in two reflected light images, preceding a suite of output of raster element maps corresponding to selected analytes: ^{34}S , ^{55}Mn , ^{57}Fe , ^{59}Co , ^{60}Ni , ^{63}Cu , ^{67}Zn , ^{71}Ga , ^{75}As , ^{77}Se , ^{95}Mo , ^{107}Ag , ^{118}Sn , ^{121}Sb , ^{125}Te , ^{182}W , ^{197}Au , ^{202}Hg , ^{205}Tl , ^{208}Pb and ^{209}Bi . Scales of concentrations are in parts per million (ppm). The lower part of the tested area corresponds to a region examined within the earlier petrographic section (see Figure 6.14A), which provides additional information regarding the distribution of galena and analysis of the observed visible Au inclusion. See previous figure for a schematic diagram of individual generations.

highly indicative of a multi-phase evolution during outward growth in a lateral left-right direction (or vice versa). The tested grain was determined to be a Py_2 generation through petrography: galena inclusions have been identified as diagnostic of this generation, while sphalerite inclusions characteristic of Py_3 are absent. Specific average concentrations were extracted from maps using ‘Monocle’, an add-on for the Iolite processing software (used to reduce acquired time-resolved geochemical data from the ICP-MS), which allows for the extraction of quantitative information from raster element maps (Petrus et al., 2017).

The distribution of Fe and S (>40 wt.%), which form the principle chemical constituents of pyrite, show slight heterogeneity, less pronounced in mapping of S and more so for Fe. Concentrations of Fe show elevated areas to the right of the grain, with uniform top to bottom distribution in alignment with the major axis of the grain. Fe is more patchy, with granular elevated concentrations.

6.7.ii. Euhedral Py_{2b} (Co-Ni-As)

Co and Ni reveal the internal structure of the grain and the sequence of events as fluids transited vein pathways. Both elements reveal the presence of an early morphologically euhedral pyrite phase which acted as the seed for subsequent generations. The earliest recognised phase, named Py_{2b} , is located to the centre-right of the grain as presented in figures (Figure 6.22; a schematic guide is provided below in Figure 6.21). The euhedral crystal

grew outward in two directions, toward the left and top of the current grain; oscillatory zonation within this phase is evident in Co and Ni variations. Average Co contents for this phase are 40.1 ppm ($2\sigma = 3.7$ ppm), while average Ni is 86.1 ppm ($2\sigma = 6.88$ ppm). The rim of Py_{2b} is enriched (>100ppm) in both Co and Ni. Enrichment of As (avg. 4,421 ppm; $2\sigma = 185$ ppm) is also observed within this euhedral phase.

6.7.iii. Auriferous Py_{2c} (Au-As)

Slightly elevated Au (avg. 3.97 ppm; $2\sigma = 0.39$ ppm) and elevated As (avg. 6,608 ppm; $2\sigma = 224$ ppm) concentrations define the second observable internal phase, Py_{2c}, to the right of a chemically distinctive boundary aligned to the major axis, just to the left of the centre of the grain. Later micro-fractures relatively depleted in As are observable cross-cutting Py_{1c} in both top-bottom and left-right orientations. For Au however, variability is observed within those micro-fractures. While Py_{2c} demonstrates a record of Au and As concentration retention, additional tested elements are depleted for this phase.

6.7.iv. Galena-hosting Py_{2d} (Sb-Ag-Te-Bi $\pm$ Pb)

It is observed that Co and Ni are enriched within a zone to the left of the grain (Co >100ppm, Ni c. 10 – 100 ppm) establishing the narrow boundary of a new phase aligned to the major-axis of the grain which formed subsequent to euhedral Py_{2c}. This region, Py_{2d}, corresponds petrographically to the area of observed galena micro-inclusions. Also observed as enrichments within Py_{2d} are relatively elevated in concentrations of Sb (avg. 28.1 ppm; $2\sigma = 1.23$ ppm), Ag (avg. 12.24 ppm; $2\sigma = 1.34$ ppm), Te (avg. 6.68 ppm; $2\sigma = 0.36$ ppm), Pb (2,807 ppm; $2\sigma = 691$ ppm) and Bi (avg. 35.5 ppm; $2\sigma = 2.37$ ppm). Pb is particularly heterogeneous, corresponding to the observation of abundant galena micro-inclusions. Such inclusions are represented by spikes in output data frequently > 1,000 – 10,000 ppm range,

while the signal between inclusions is typically within the 10 - 1,000 ppm range. Evidence confirms Py_{2d} is a discrete paragenetic event resultant of a base- and precious- metal transporting carrier fluid.

6.7.v. Micro-fracture hosted metalliferous emplacement

Py₂ overall exhibits brittle deformation. Within the tested flattened grain in reflected light, micro-fractures are visible in two principle perpendicular orientations, with wider micro-fractures aligned to the major axis than those observable aligned to its minor axis. Minor axis aligned micro-fractures appear to terminate against the Py_{2c}/Py_{2d} boundary suggesting that the event occurred later than Py_{2c}, but earlier than Py_{2d}. Co and Ni concentrations >100 ppm reveal the major-axis aligned network and its relationship to identified Py₂ internal generations (they are depleted in the perpendicular set), cross-cutting both Py_{2b} and Py_{2c}. Micro-fractures in both orientations are enriched in Sb (> 1 ppm, in part > 10 ppm), Te (> 10 ppm), Hg (> 1 ppm), Bi (> 10 ppm) and to a limited extent, Ga (> 1 ppm). A visible auriferous micro-scale particle present at the junction of perpendicular fractures. The relationship of this particle to fracture-infill is ambiguous in raster element mapping, however Au appears to show values > 10 ppm within certain cross-cutting fractures (left-to-right).

6.7.vi. Additional observations

Within outer regions of the overall grain to the right, patches of elevated Mn (>80 ppm), Zn (> 100 ppm), Ga (>6 ppm), Bi (> 10 ppm) and Sb (10 ppm) are observed, which may be attributed to the fluid responsible for sphalerite-rich Py₃. Se shows homogeneous distribution across the tested region > 10 ppm. Mo, W and Tl are broadly unrepresented in analyses, with the exception of a spike corresponding to a likely micro-scale Mo-W bearing

mineral (a possible candidate is molybdenoscheelite) to the top left of the region of interest, and an affinity of Tl > 0.15 ppm to micro-fractures and the overall boundary.

6.7.vii. Overview of findings

LA ICP-MS raster element mapping of a tested region of interest post-dating Py_{2a} masses reveals three subsequent generations (Py_{2b}, Py_{2c} and Py_{2d}). Two generations of micro-fracture infill are also observed, the first timed between Py_{2c} and Py_{2d}, while the second is late. Euhedral Py_{2b} is associated with elevated Co, Ni and As, overgrowth Py_{2c} with Au and As, and subsequent overgrowth Py_{2d} (which carries diagnostic inclusions of galena) with relatively elevated Co, Ni, Ag, Sb, Te, Bi and Pb compared with earlier phases within this framework. Micro-fracture infill is characterised by Sb, Te, Hg, Bi ± Ga (elements associated with phases denote enrichments relative to other tested phases). Mapping reveals concentrations >1 ppm Au within Py_{2c}, and support the earlier observation in petrographic study of visible Au particles associated with fracture-infill.

6.8. Discussion

6.8.i. Petrographic model

This study has determined that two petrographically distinguishable vein types within greenschist to lower amphibolite facies rocks are present at Cloonacool; these are a result of fluid influx exploiting pathways through host semi-pelitic and psammitic rocks in a preferred orientation coincident with deformational fabrics. These are assigned the terms ‘Type I’, the earliest phase, and ‘Type II’, a far more volumetrically significant phase. A cross-cutting relationship is observable which establishes the relative timing (see Figure 6.9D). Early quartz-sulphide veins are characterised by their narrow width averaging 250 µm, and their

	Py_{2b}		Py_{2c}		Py_{2d}	
	Abundance (ppm)	2 σ	Abundance (ppm)	2 σ	Abundance (ppm)	2 σ
Mn	0.77	1.02	0.59	1.12	3.51	0.86
Co	40.9	3.70	27.7	6.02	80.3	3.96
Ni	86.1	6.88	49.1	7.94	119.86	48.5
Cu	29.9	19.0	27.3	8.85	30.72	7.63
Zn	2.36	1.39	18.5	20.6	9.37	7.17
Ga	0.06	0.04	0.10	0.04	0.16	0.05
As	4,421	185	6,608	224	2,332	109
Se	32.5	1.81	21.9	1.37	25.97	1.89
Mo	0.01	0.01	0.02	0.02	0.02	0.01
Ag	3.75	0.55	3.39	0.38	12.24	1.35
Sn	0.02	0.03	0.01	0.04	0.04	0.03
Sb	8.59	2.05	5.56	1.11	28.1	1.23
Te	4.05	0.59	3.46	0.44	6.68	0.36
W	0.01	0.01	0.06	0.10	0.01	0.01
Au	2.05	0.13	3.97	0.39	3.20	3.18
Hg	1.16	0.26	1.53	0.28	2.07	0.24
Tl	0.02	0.01	0.01	0.01	0.03	0.01
Pb	420	206	69.7	44.9	2,807	691
Bi	9.09	1.92	6.70	1.45	35.5	2.37

Table 6.9. Average concentrations (ppm) and internal standard deviation values ($\times 2$, ppm) within regions of interest, extracted from raster element maps using ‘Monocle’, an add-on for the Iolite suite of processing software.

composition, with disseminated Py₁ replacing and overgrowing Ti-oxide phases (ilmenite and rutile). Additional evidence of Mg-Fe oxide growth within these veins is provided. Outer regions demonstrate textural evidence of cyclical zonation. Laser ablation ICP-MS analyses reveal a discrete trace element signature for Py₁, defined by enrichments >100ppm of Co, Ni and As. Metalliferous inclusions are rare, though minor visible Au is encountered; Au phases are most likely related to mineralisation found in Type II veins.

Centimetric Type II veins comprise several discrete metallic emplacement events pertaining to Au, Pb and Zn. Two principle forms are determined, Py₂ and Py₃, the former characterised by angular masses which may be homogenous, and carry inclusions of gold and galena toward its grain boundaries, while Py₃ is an overgrowth containing abundant sphalerite. Examination of coarse Py₂ grains using microscopic techniques reveals discrete textures confirming the presence of internal compositional zonation. Py_{2a} forms the central cores of the masses and contain broadly homogeneous anhedral grains terminating against one another (evidenced by inclusion trails). LA ICP-MS spot analyses have determined that this early phase is relatively depleted (compared with later phases) in As, Ni, Au and Te, while Cu, Sb and Pb show higher concentrations. A lack of visible inclusions, a highly competitive internal crystal framework and As concentrations of < 100ppm may be considered diagnostic of Py_{2a} within Type II veins.

Close inspection of individual spots shows deviations from the stable geochemical signature of Py_{2a} toward the edges of masses and into adjacent recrystallised grains. This study also observes inclusions of galena in abundance within these outer areas. LA ICP-MS element raster mapping was conducted on a Py₂ region of interest which is composed of outer-type grains within which internal zones are microscopically observed, including an area with an abundance of galena inclusions. Using this technique this study observes three geochemically distinct zones which all show an abundance in As > 1,000 ppm, indicating the zones belong to a separate distinct class. Through petrographic and geochemical

constraints these zones are classified as Py_{2b}, Py_{2c} and Py_{2d}. A euhedral Py_{2b} core is observed in analyses of Co and Ni, with oscillatory zones evident and enrichment within its rim. Enrichment (>100 ppm) is observed in As (avg. 4,421 ppm, 2 σ = 185 ppm) and also Pb (avg. 420 ppm, 2 σ = 206 ppm) within this phase, which is not associated with microscopic galena.

6.9. Conclusions

This study represents the first recognition of visible Au within in situ vein material from the Cloonacool prospect, and elucidates its form and relationship with multiple phases of pyrite growth. Overall, results demonstrate that Au-bearing metalliferous fluids were active in the Ox Mountains Inlier coincident with the development of deformation fabrics, supporting prospectivity for Au and potential for further undiscovered resources. The tested Cloonacool prospect shows evidence of a multi-stage fluid and emplacement evolution, evidenced through petrographic and geochemical mapping of pyrite within host veins. Veins demonstrate episodic fluid introduction to favourable pathways (weaknesses) within host semi-pelite and psammite coincident with deformational fabrics, and discrete emplacement phases of Au, Pb and Zn are recognised. It is considered likely that seismic pumping led to episodic injection of orogenic fluids into pathways; and that distortion of host lattices was an important mechanism in creating space for aggregations of particles which may have been emplaced as a result of localised changes in pH and redox conditions. A paragenetic model is presented within this chapter; a key factor for this is a sequence of geochemical events recorded within Py₂ and revealed by LA ICP-MS mapping: early Co-Ni-As enrichment (Py_{2b}) followed by Au-As (likely the ‘ore-stage’ Py_{2c}), which was then followed by emplacement of Ag-Sb-Te-Bi $\pm$ Pb signature (Py_{2d}), preceding a minor late Zn-bearing phase (Py₃). Au preceding the introduction of Bi and Te is also observed within visible phases at Curraghinalt

in *Chapter Five*. This phase of work reveals the potential of integrated optical microscopy, SEM, EDS/EDX and LA ICP-MS methodologies to elucidate complex metalliferous emplacement histories at regional prospects. The integration of these methods into exploration strategies is recommended and discussed further in this thesis in *Chapter Nine*.

Chapter Seven: Appin and Argyll Group shale horizons as potential sources of metals for orogenic gold deposits in north-west Ireland: evidence from pyrite petrography and trace element geochemistry

7.1. Abstract

Carbonaceous shale horizons deposited under anoxic conditions in sedimentary basins provide favourable conditions for the formation of diagenetic and early hydrothermal pyrite. During their growth, abundances of trace elements (e.g. As, Ni, Pb, Zn, Ag, Mo, Te, V and Se) are retained within their crystal structure, acquired from their immediate organic-rich environment aided by the low effective porosity of host shales. Such environments are considered viable source reservoirs for gold, which may be transported by fluids along structural networks and concentrated late in the deformation history of an orogen as deposits. Examination of pyrite and pyrrhotite grains from shale horizons in Dalradian Supergroup strata from County Donegal, Ireland, has revealed petrographic and geochemical insights which provide evidence of trace element mobility synchronous with

the evolution of the Palaeozoic Grampian arc-continent collisional orogen (475-460 Ma). Argyll Group pyrite is anomalous with respect to Au, with grains containing up to 7.5 ppm (median 1.5 ppm; IQR = 0.92 – 2.70 ppm; n=11); coincident Ag is observed for 7 analyses suggesting the presence of Au-Ag particles (Au/Ag avg., 1.22, 2σ = 3.38; n=7). Enrichment (>100 ppm) is observed for Co (median 185 ppm; IQR = 40.4 – 340 ppm; n=109) and Ni (median 420 ppm; IQR = 79.8 – 848 ppm; n=108). Au/As ratios determined using LA ICP-MS spot analyses and raster element mapping techniques demonstrate that retrograde processes drove the liberation of Au nanoparticles which could be mobilised by regional fluids. The occurrence of both pyrite (containing an archive of trace elements within cyclical zones) and xenomorphic pyrrhotite, with a preponderance of the latter in higher grade metamorphic terranes of the Laurentian margin, suggests conditions favourable for devolatilisation mechanisms effecting the mobilisation of Au and trace elements synchronous with deformation of the Grampian Orogen. Tested strata are a feasible source for gold deposits hosted by Dalradian Supergroup stratigraphy, for example those discovered in the Sperrins Inlier of County Tyrone.

7.2. Introduction

Pyrite and pyrrhotite hosted by the Appin and Argyll groups of the Dalradian Supergroup may have contributed Au and associated trace metals to fluids forming orogenic gold deposits in north-west of Ireland; regional thrust and fracture-networks associated with Grampian deformation provide suitable pathways for these fluids. This study tests this hypothesis, through examination of samples from both groups, specifically their morphology, geological setting and in-situ trace element geochemistry.

Four localities of interest were targeted in this phase the study: one in north Donegal (Falcarragh; Appin Group) three of which lie on the Slieve League Peninsula in south-west

Donegal (Glencolumbkille and Derrylahan, Slieve League Formation; Muckros, Termon Pelite; Easdale Subgroup, Argyll Group). The Slieve League Peninsula is a geological area of particular interest, structurally defined by previous workers as an 'orogenic root zone' (Alsop et al., 2001); studies suggest that a complex structural framework is present in the form of a c.120 km W-E oriented shear zone forming contemporaneously with Palaeozoic Grampian orogenesis at the Laurentian continental margin. Such zones present conditions of rock inhomogeneity; pelitic horizons within these strata may be present which would favour enhanced permeability and the migration of Au-bearing hydrothermal fluids. Additionally, formations across the Peninsula are observed to lie at the greenschist-amphibolite metamorphic transition (e.g. Anderson, 1953), where reactions may have taken place liberating metamorphic fluids and mobilising Au and trace elements (e.g. Gregory et al., 2015; Phillips and Powell, 2010).

An integrated approach using traditional microscopy, Scanning Electron Microscopy (SEM) techniques (including Energy Dispersive X-ray Spectroscopy or EDS/EDX) and Laser Ablation Inductively Coupled Plasma - Mass Spectroscopy (LA ICP-MS) has proven effective in elucidating geochemical data at low abundances in the two previous chapters and revealing insights into the evolution of orogeny-associated gold systems, in terms of metalliferous emplacement during prograde deformation and late retrograde conditions. The use and adaptation of such techniques additionally presents an opportunity to test potential sources, and to consider the processes which may have initiated and driven prolonged fluid and metal migration.

A previous study by Parnell et al. (2017) has also considered whether carbonaceous shales stratigraphically below known Dalradian Au deposits in Ireland and Scotland were a viable source for Au and Te. Their work presented petrographic and geochemical data from Argyll Group pyrite at localities over a wide spatial distribution on the two islands including Muckros in County Donegal, a location sampled in this contribution. Parnell et al. (2017)

presented Laser Ablation ICP-MS and S-isotope data as part of their study and concluded that Au and Te were concentrated in early pyrite within an organic-rich marine environment and that these elements were additionally enriched in and reconcentrated in fluids during metamorphism. A Au, Te and Pb association was determined to have an association within tested grain rims, while not necessarily being coeval. They note an absence of Au and Te and trace element abundances within pyrrhotite suggesting liberation during pyrite to pyrrhotite conversion. Variability in S-isotope data is presented by Parnell et al. (2017) from -18.1 to +14.1 ‰ including values between -18.1 and -16.5 ‰ in samples of the Termon Pelite sampled in this study at Muckros. This variability is interpreted by Parnell et al. (2017) as reflecting a depositional origin characterised by microbial sulphate reduction. While this study has also tested the Muckros area as aforementioned, this study has also examined pyrrhotite of the Appin Group (at Falcarragh), and the ‘orogenic root zone’ at Glencolumbkille. Findings of this study are consistent with the hypothesis of pyrite to pyrrhotite conversion and the liberation of trace elements; results show that trace elements (including Co, Ni, Bi, Te) were emplaced within cyclical zones of pyrite synchronous with the development of deformation fabrics in the Argyll Group at the root zone. New information is presented on the solubility of Au and a robust genetic model for early Au mobility.

7.3. Geological background

7.3.i. Stratigraphy

The Appin and Argyll Groups, Dalradian Supergroup

The Appin Group and stratigraphically overlying Argyll Group sit within the Dalradian Supergroup bounded by the older Grampian Group and overlying Southern Highland Group. Overall, these represent a passive margin sequence of Neoproterozoic to Cambrian

age metasedimentary rocks exposed in north-west Ireland and Scotland (Chew et al., 2009b). This sequence was deposited onto the continental margin of Laurentia, and began with emplacement of the Grampian Group which has only limited exposure in Ireland, comprising quartzo-feldspathic meta-arkose formations outcropping in the north-west of County Mayo (Daly et al., 2009).

North Donegal: Falcarragh locality

The earliest formation of interest to this study, the Falcarragh Pelite Formation (Falcarragh locality), belongs to the Blair Atholl Subgroup (Appin Group) and is subdivided into Upper and Lower stratigraphic components. It is considered to be near-shore and remnant of an emergent shelf, the onset of its deposition marking a shift toward marine sedimentation: a shallowing sequence responding to thermal subsidence (Hutton and Alsop, 1996). This formation is described by Long and McConnell (1997) as a uniform sequence of carbonaceous schists, pelitic, with calcareous layers and an abundance of pyrite (of interest to this research). The Falcarragh Pelite Formation lies partially within the Knockateen tectonic slide: above the Creeslough Succession (> 1,100m; pyrite-bearing pelites and the Ards Quartzite) and below the Kilmacrennan Succession (c. 755 m; graphitic pelites, limestone, dolomite, schists and tillite). This slide is a major south-easterly dipping structure, movement along which was aided by evaporitic horizons within the hanging wall and footwall (White and Hutton, 1985).

The Slieve League Peninsula: Glencolumbkille, Derrylahan and Muckros localities

The Slieve League Formation (Glencolumbkille and Derrylahan localities) is part of the Easdale Subgroup (Argyll Group). It is comprised of quartzites, psammites and schists deposited during a deep water event, at the same time as shallower carbonates were being emplaced above quartzite in northern Donegal forming the Cranford Limestone (Hutton

and Alsop, 1996). Muscovite-rich schists of the Termon Pelite at Muckros (also Easdale Subgroup) are considered to be resultant of a basin deepening episode observed across Donegal (Hutton and Alsop, 1996). Pyrite is recognised within metamorphic rocks across the Slieve League Peninsula; an early report by Blake (1862) to the Geological Society of Dublin noted an abundance of pyrite within these formations, described by the author as ‘mica-slates’. Metamorphism of the Slieve League Formation is understood to sit within the biotite zone of the Barrovian classification (Anderson, 1953), with a greenschist-amphibolite transition spatially observed traversing the peninsula [Argyll group rocks between south-west Donegal and west Tyrone are considered by Hutton and Alsop (1996) to be of biotite-kyanite grade, while strata of the Sperrin Mountains are assigned to the lower chlorite-to-biotite category]. Garnetiferous horizons exhibiting chloritic replacement indicative of retrograde metamorphism (Anderson, 1953; Fettes, 1979) are observed to the west of a geographic ‘limit’ which forms an inverted L-shape, traceable north of Muckros Head and east of Glencolumbkille (Anderson, 1953).

Relationship to the Sperrin Mountains gold deposits

Localities of interest on the Slieve League Peninsula (see Figure 7.1) are geologically constrained to the Argyll Group, characterised by renewed rifting and deposition within confined basins. Overlying the Argyll Group is the Southern Highland Group, described by Daly et al. (2009) as consisting of volcanic units and turbidites. Some workers consider the Sperrin Mountains gold deposits to be hosted within the Easdale Subgroup of the Argyll Group (see Long, 1997), while others propose they are hosted by the Southern Highland Group (e.g. Arthurs, 1976),

Group	Subgroup	Relative Position	Host Formation
Southern Highland (Upper Dalradian)		Curraghinalt	Mullaghcarn Fm.
Argyll (Middle Dalradian)	Tayvallich		
	Crinan		
	Easdale	Muckros Glencolumbkille Derrylahan	Termon Pelite Slieve League Fm.
	Islay		
Appin (Lower Dalradian)	Blair Atholl	Falcarragh	Lr. Falcarragh Pelite Fm.
	Ballachulish		
	Lochaber		

Table 7.1. Relative stratigraphic positions within the Dalradian Supergroup of sample locality formations; the position of the host formation of the Curraghinalt Au deposit is shown for reference. Discrepancies in formations between Counties Donegal and Tyrone are not taken into account, and not all formations are included in this table (modified after Alsop and Hutton, 1990).

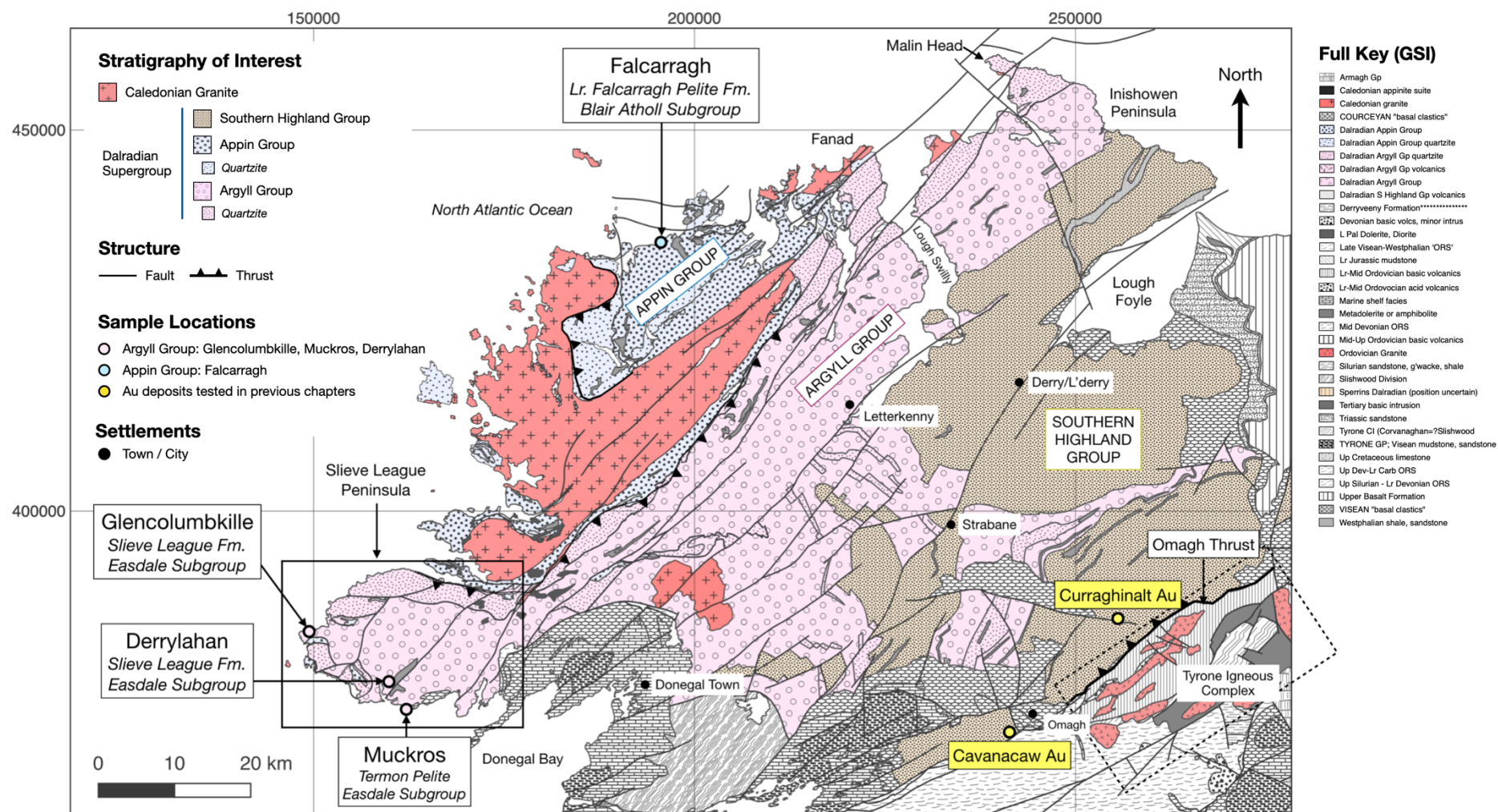


Figure 7.1. Sampling localities (blue, pink dots) in north-west Ireland in relation to Au deposits (yellow) and geological features of interest. Concept adapted from Alsop et al., 2001, generated using datasets available from Geological Survey Ireland using QGIS. The co-ordinate system is TM75 / Irish Grid (metres).

7.3.ii. Structure and deformation

The geometry of Dalradian metasedimentary formations of the Donegal Inlier is characterised by poly-phase deformation associated with collisional orogeny, and complexity defined by thrusts, slides (shear zones) and folding of regional nappes (e.g. Alsop et al., 2001; Hutton and Alsop, 1996; White and Hutton, 1985). There are three deformational phases across the inlier are associated with Grampian orogenesis: F_1 folding, observable on the Inishowen peninsula (NE of the Falcarragh locality); D_2 , associated with NW-directed thrust nappe development and dividing shear zones; and D_3 which is responsible for large recumbent F_3 structures such as the Ballybofey Nappe (Chew et al., 2009b). D_3 was a phase of SE-directed shearing and is generally associated with peak metamorphic conditions across the inlier during the Grampian arc-continent collision geometrically characterised by thrusting of the Dalradian succession over the outboard arc.

North Donegal

Locally in northern Donegal, D_1 is described by White and Hutton (1985) as elusive, resultant in an S_1 cleavage: a preferred orientation of quartz-phylosilicates, muscovite and chlorite, either parallel, or cross-cutting original bedding at a low angle. D_2 , responsible for S_2 fabrics, may be crenulated and cross-cut bedding at low angles. Within the Kilmacrennan Succession, characteristic NW-SE mineral elongation lineation is observed along S_2 cleavage, crenulated by S_3 (resultant of D_3 deformation, locally considered by White and Hutton (1985) to be non-metamorphic).

Two additional late phases of deformation are recognised (D_4 - D_5), described by White and Hutton (1985) with specific reference to formations of the Fanad peninsula (c. 25km to the east of the Falcarragh locality). D_4 is preserved by the Creeslough Succession as the dominant S_4 cleavage, though does not bear a correlative fabric within the Kilmacrennan Succession, providing evidence of a sinistral shear zone which is considered to be

contemporary with the emplacement of the Main Donegal Granite (MDG) at c. 400 Ma. D₄ is described as being associated with a late metamorphic event, present across the region with varied intensity; within tectonic slides (shear zones such as that recorded where stratigraphically the Upper and Lower Falcarragh Pelite Formations are situated), this may occur as an intense and mylonitic S₄ fabric. D₅ manifests as a steep, NNE-SSW trending extensional cleavage (S₅) which cross-cuts S₄. Muscovite porphyroblasts which grew between D₂ and D₃ are considered to represent the peak of regional metamorphism in north Donegal associated with the Grampian collision (MP₂).

Slieve League Peninsula, SW Donegal

The Slieve League Peninsula in south-west Donegal is described by Alsop et al. (2001) as an example of a mid-crustal orogenic root zone (a descriptive term, defined by fold-and-thrust geometries and foliations which dip steeply downwards at the back of a thrust); the zone is structurally characterised as an area of localised complexity, with multiple overprinting composite fabrics resultant from sequential deformation events. Regional foliations on the peninsula have deviated in a strike-swing to W-E orientations from more typical NE-SW trends recorded widely across NW Ireland and Scotland. This strike-swing is considered an original feature of the Laurentian continental margin which was influential on Grampian and broader Caledonian tectonics. Alsop et al. (2001) note that the peninsula records exposure of deep crustal levels, which may be masked elsewhere by the presence of intrusions.

Characteristic of the structural evolution of the peninsula are D₁-D₄ deformation events (as previously described), with the overall geometry controlled by the tectonics linked to late lateral extrusion and shearing. D₁ is associated with the development of tectonic slides, most intensely focused in areas of original basin geometry. North-directed thrusting characterises D₂ deformation; the growth of garnets at Glencolumbkille (as observed by Anderson, 1953) occurred immediately after ductile D₂ thrusting and the development of

MP₂ assemblages. D₃ (a reactivation of D₂ structures) corresponds to a phase of SE-facing fold nappe development, including the F₃ Slieve League Antiform and the Ballybofey Nappe extending into western Tyrone. South-easterly shearing can be traced from the Slieve League Peninsula to the Sperrin Mountains, where Au deposits are hosted proximal to the Fair Head – Clew Bay Line (e.g. Parnell et al., 2000) (see Figure 7.2). SE-directed shearing of the Ballybofey Nappe has been dated at c. 470 Ma by Flowerdew et al. (2000).

Stream sediment gold anomalies and regional structure

The complexity of the structural framework with coincident auriferous anomalies along major structures may be favourable for gold-transporting hydrothermal fluids. Publicly available geochemical and geophysical data acquired as part of the 2011-2013 Tellus Border survey (Geological Survey Ireland, 2020) show a relationship between Au stream sediment anomalies and W-E to SW-NE trending major structures visible in electro-magnetic surveys (Figure 7.3 and Figure 7.4). Au is reported within formations >2.25 µg / kg (units as reported in Tellus study, 1 µg / kg = 1 ppb) in all areas spatially, with the exception of that which includes the Caledonian granite where values are generally below this concentration. Electromagnetic data show the general W-E trend of major structures in the south of Donegal, while north of Slieve League Peninsula (>900,000m using the Irish Transverse Mercator grid), structures have a general SW-NE trend. Specifically focusing on the Slieve League Peninsula in south-west Donegal, Earls (2016) draws attention to elevated concentrations of gold found within stream sediment samples during this study, associated with the Slieve League Formation and Slieve Tooley Quartzite; data show a series of E-W trending anomalies traversing the centre of the peninsula from the Glencolumbkille area, bearing concentrations >7.27 µg / kg (ppb) Au, including zones > 193 µg / kg Au. Placers may be a factor when considering interpretation of stream sediment data.

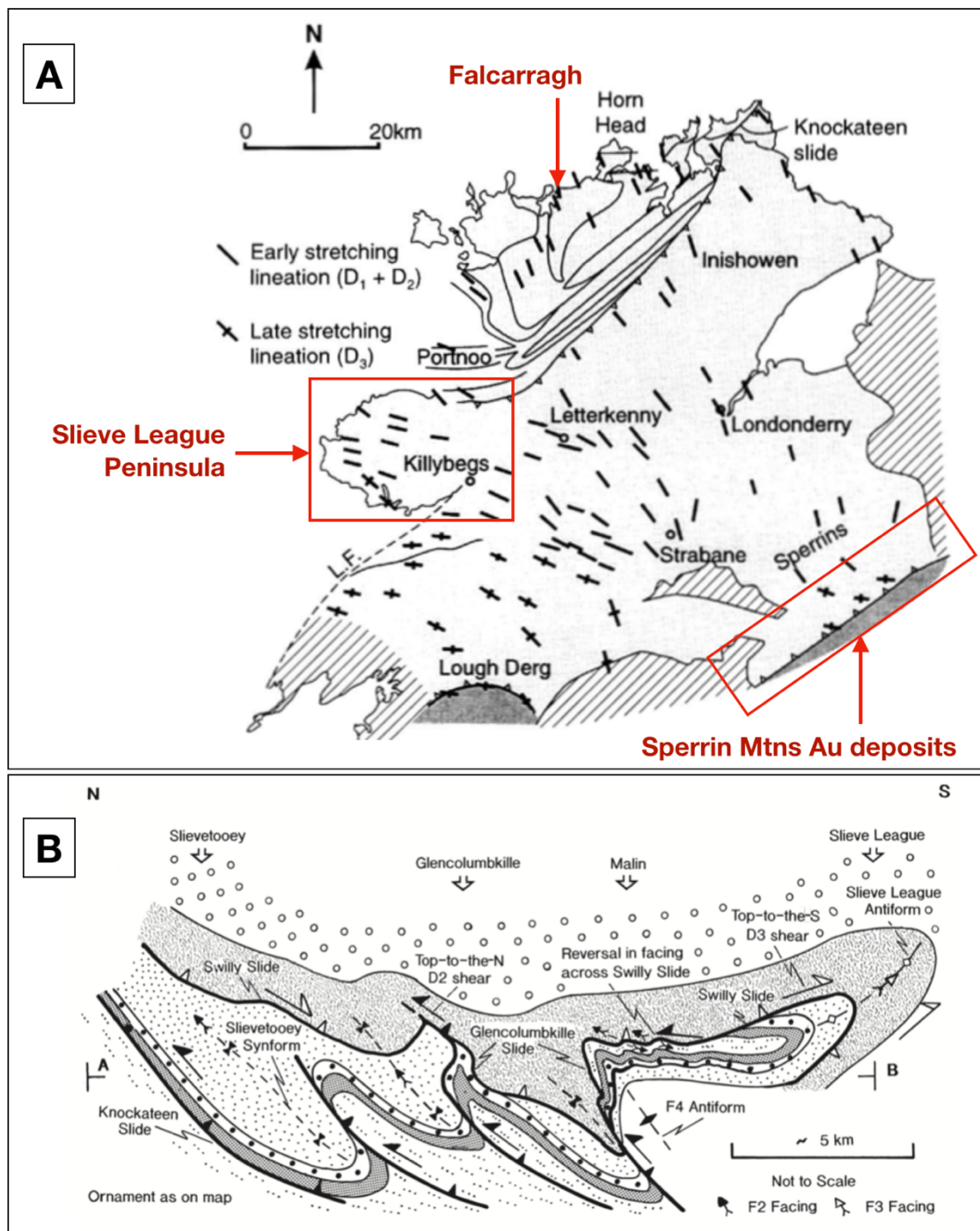


Figure 7.2. (A) Regional lineations in the Donegal and Tyrone (Hutton and Alsop, 1996); (B) local structural complexity, western Slieve League Peninsula (Alsop et al., 2001).

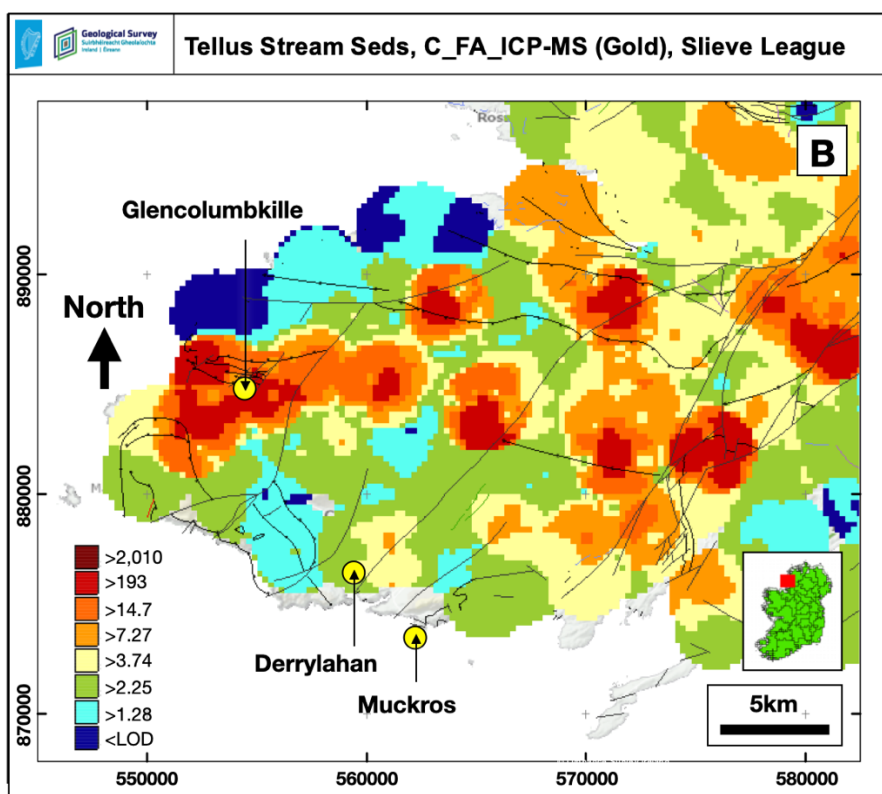
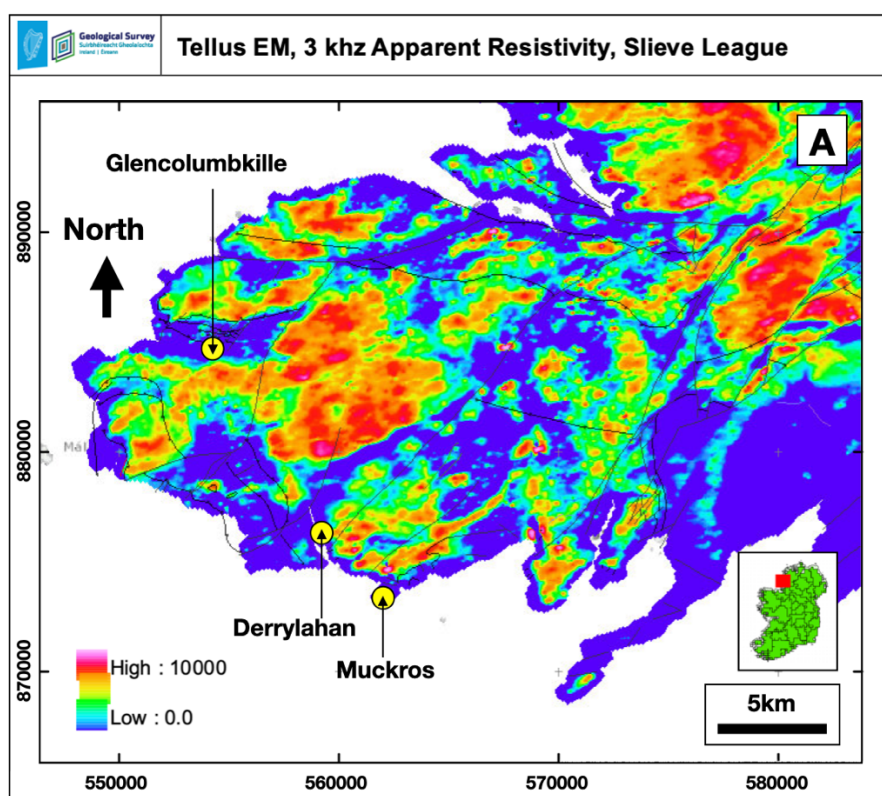


Figure 7.3. (A) 1:600,000 scale map showing results of the Tellus electromagnetic survey (3 kHz apparent resistivity; units in ohm-m) for west Donegal; (B) the results of stream sediment Au analyses for the same region (reported in $\mu\text{g} / \text{kg}$; $1 \mu\text{g} / \text{kg} = 1 \text{ ppb}$). The Falcarragh sample locality in north Donegal is annotated (Geological Survey Ireland, 2020; co-ordinates in metres, ITM grid).

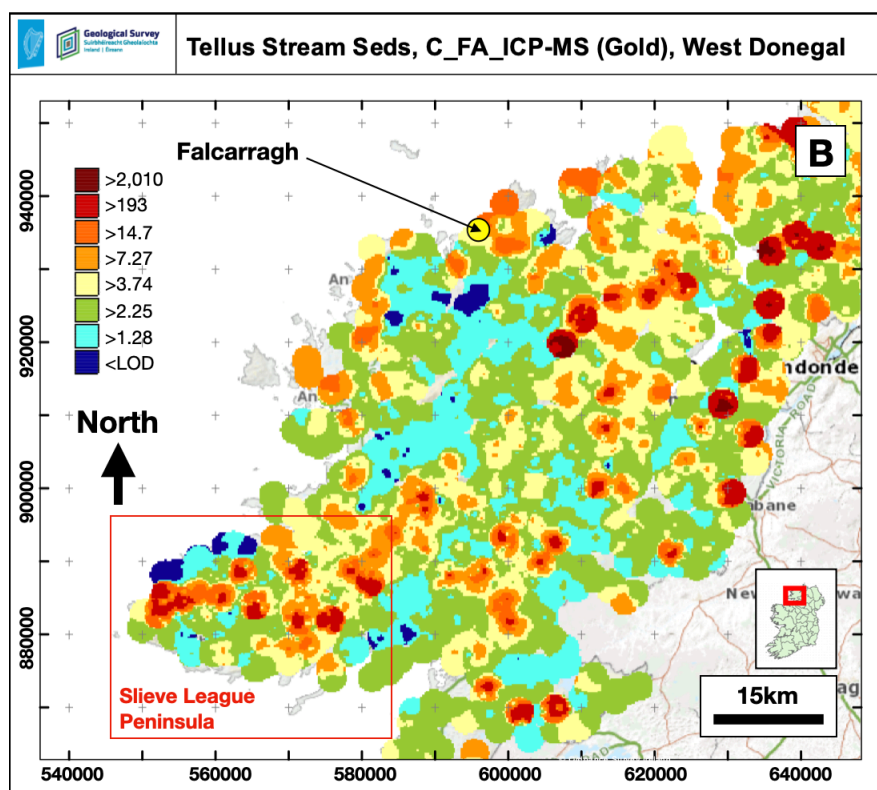
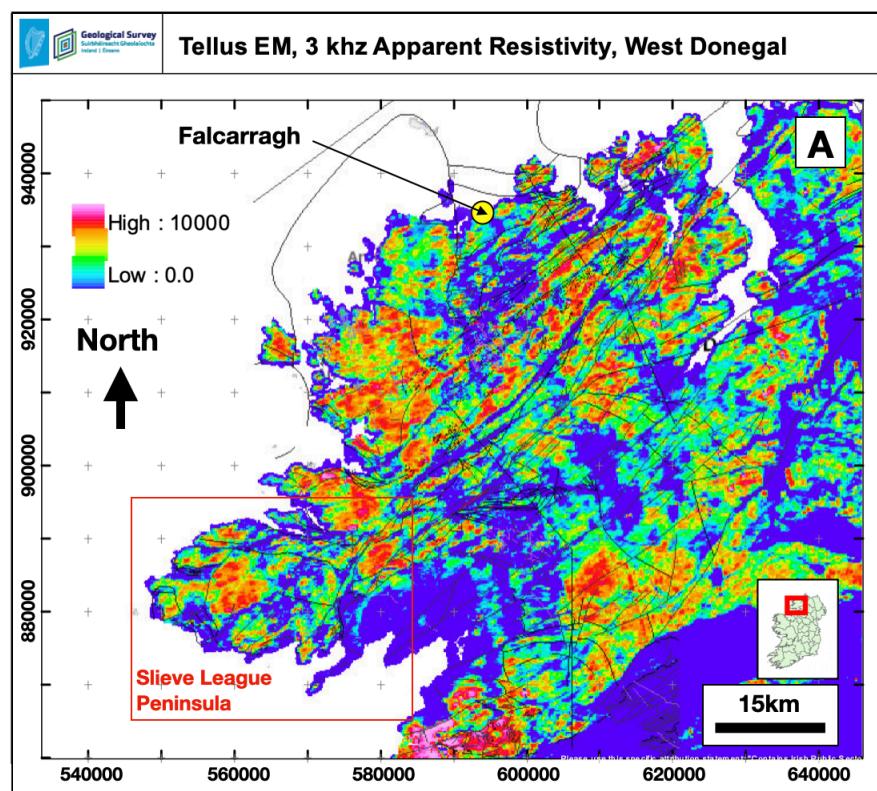


Figure 7.4. (A) 1:200,000 map showing Tellus electromagnetic data (3 kHz apparent resistivity; units in ohm-m) for the Slieve League Peninsula, south-west Donegal; (B) stream sediment sample data (reported in $\mu\text{g} / \text{kg}$; $1 \mu\text{g} / \text{kg} = 1 \text{ ppb}$) for this region. The geographic positions of sample localities are shown in annotations (Geological Survey Ireland, 2020; co-ordinates in metres, ITM grid).

7.4. Sampling and Analytical Methodology

7.4.i. Sampling

Acquisition of carbonaceous shale samples was undertaken in the field, in four localities of north and south-west County Donegal, Ireland, constrained to Dalradian Supergroup formations. Localities, designated Falcarragh (FC; 55° 9' 53.37" N, 8° 3' 59.57" W), Glencolumbkille (GC; 54° 42' 23.79" N, 8° 45' 38.178" W), Derrylahan (DR; 54° 38' 15.252" N, 8° 37' 29.352" W) and Muckros (MK; 54° 37' 3.852" N, 8° 35' 27.3" W) based on the most proximal townlands and villages, were selected in consultation with the literature and Geological Survey Ireland Spatial Resources, an open-source data resource available online. Accessible coastal sections as regions of maximum exposure and inland areas of abundant outcrop were preferred. Falcarragh is located to the north-west of Letterkenny town (following the N56 road), where outcrop at the western end of the beach immediately to the north of the village was sampled, while additional localities are found along the coastline of the Slieve League Peninsula west the fishing port of Killybegs (following the N56 and local roads). Samples were acquired without specialist equipment using a geological hammer with attention paid to minimising environmental and visual disturbance. At Falcarragh (FC), the targeted horizon was the Lower Falcarragh Pelite, within the Blair Atholl Subgroup of the Appin Group. On the Slieve League Peninsula, all targets are attributed to the Easdale Subgroup of the Argyll Group; the Slieve League Formation was sampled at Glencolumbkille (GC) and Derrylahan (DR), while the Termon Pelite was sampled at Muckros (MK). 1-2cm slabs were cut using a manual saw in the Geology Department at Trinity College Dublin, which were further reduced to an appropriate size for thin sections. Slabs were dispatched to Thin Section Lab in Toul, France, who prepared sections approximately 50 mm x 25.4 mm (2" x 1") x 60 µm. This size was selected based on previous experience with the equipment at the geochemistry laboratories, with consideration of the

section holder used for Laser Ablation ICP-MS studies. A 60 μm is appropriate for such work as it maximises the amount of material available while not curtailing the ability to conduct analytical work using optical microscopy. A total of 19 thin sections were acquired from 9 samples in total (9 sections for 4 samples at Falcarragh, 4 sections for 2 samples at Glencolumbkille, 4 sections for 2 samples at Muckros and 2 sections for 1 sample at Derrylahan). Field photographs were taken using an Apple iPhone with GPS capabilities; positions recorded in image metadata were used as a cross-reference with geographic and geological maps.

7.4.ii. Reflected light microscopy

Images and measurements were acquired using a Nikon Eclipse LV100 microscope with reflected and transmitted light capabilities, connected to a Märzhäuser Wetzlar TANGO desktop controller, which enables manual (using a joystick) and automated movement of the stage. High-resolution images of areas of petrographic interest were acquired, while stitched images of selected sections were additionally retrieved using the automated stage movement, fast-focus and Z-stacking capacity of the microscope and movement controlling device. The Nikon NIS-Elements platform and third-party software (e.g. Image-J) were used in data acquisition, the examination of sulphide and host grain morphology, along with post-processing. Stitched images were utilised to target follow-up geochemical work on sulphide grains, in particular in-situ Laser Ablation ICP-MS analyses on target pyrite and pyrrhotite porphyroblasts. All microscopic work of this nature was conducted at iCrag Lab@TCD (also known as the Centre for Microscopy and Analysis) at Trinity College Dublin.

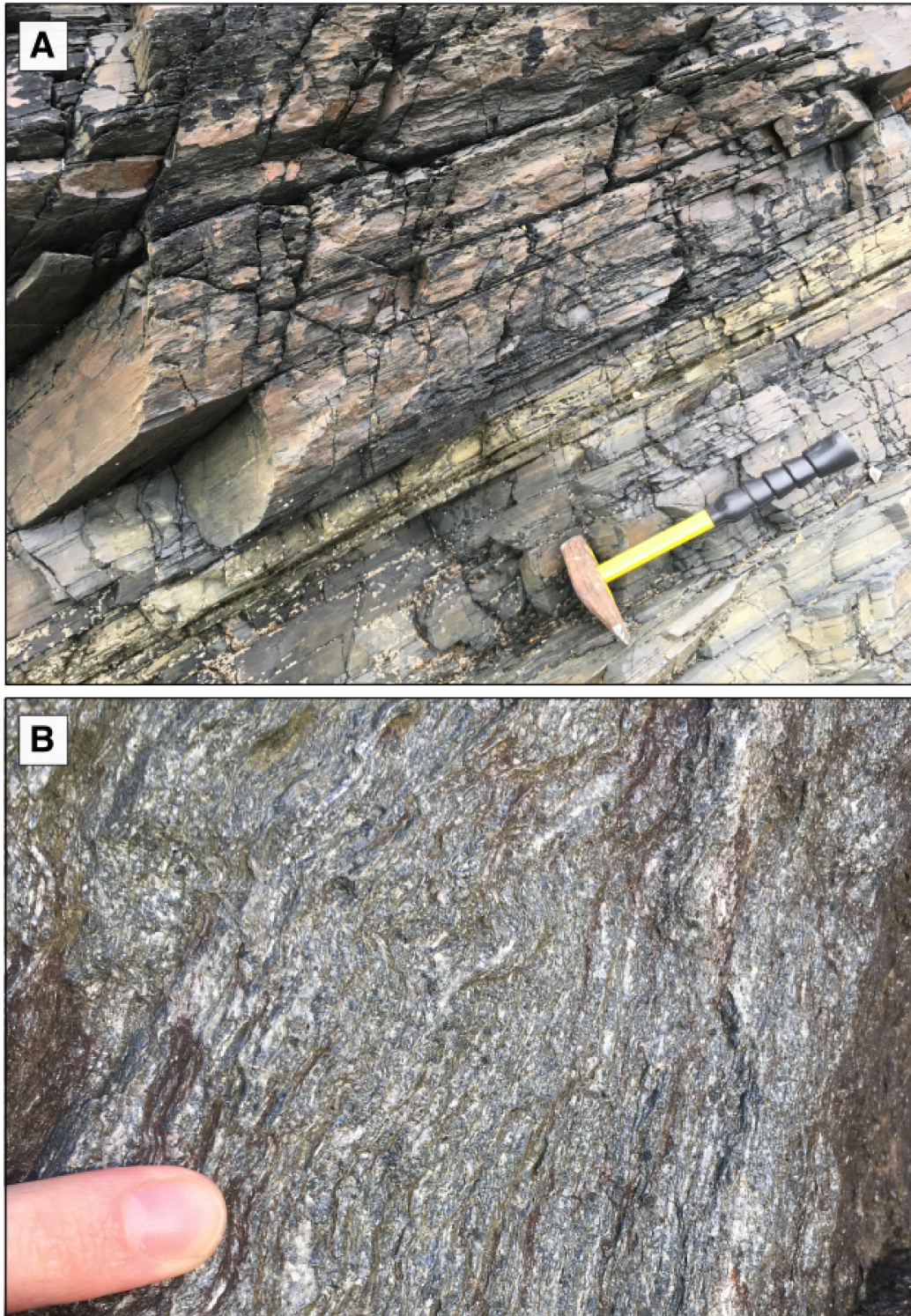


Figure 7.5. (A) Field outcrop of the Lower Falcarragh Pelite Formation (Blair Atholl Subgroup) (FC-locality, see Table 7.2), exhibiting centimetre-scale oxidised horizons (standard geological hammer for scale). (B) micaceous crenulated schistosity within Slieve League Formation (Easdale Subgroup) pelitic rocks of the Argyll Group at Glencolumbkille (GC- locality, see Table 7.1).

Sample	Locality	Lat. (N)	Long. (W)	Formation	Subgroup	Group
D-FC-19/01 D-FC-19/02 D-FC-19/03 D-FC-19/04	Falcarragh	55° 9' 53.37"	8° 3' 59.57"	Lr. Falcarragh Pelite	Blair Atholl *	Appin *
D-GC-19/01 D-GC-19/02	Glencolumbkille	54° 42' 23.79"	8° 45' 38.178"	Slieve League	Easdale †	Argyll †
D-DR-19/01	Derrylahan	54° 38' 15.252"	8° 37' 29.352"	Slieve League	Easdale †	Argyll †
D-MK-19/01 D-MK-19/02	Muckros	54° 37' 3.852"	8° 35' 27.3"	Termon	Easdale †	Argyll †

Table 7.2. Sample locations in County Donegal with co-ordinates in latitude and longitude. Formation names were retrieved in consultation with a Bedrock Geology 1:100,000 scale map accessible via the Geological Survey of Ireland Spatial Resources Public Data Viewer (available online) with reference to literature descriptions in the field. Group classifications: * White and Hutton, 1985; † Alsop and Hutton, 1990.

7.4.iii. Scanning Electron Microscopy

A Tescan MIRA4 XMU Field Emission Scanning Electron Microscope (FE-SEM) with motorised Backscatter Electron (BE) and colour Cathodoluminescence (CL) detectors was used to navigate on sample thin sections and acquire rastered scans, exported as images. The microscope is equipped with an Oxford Instruments X-Max 150mm² detector which was used for Energy-Dispersive X-ray Spectroscopy (EDS/EDX); spectral data are resolved using Oxford Instruments AZtec software which enables the acquisition of point analyses and raster element maps, with semi-quantitative and quantitative options. Performance of the equipment and fluctuations are monitored using a Cobalt pellet standard, constituent of a custom block (#217, Micro-Analysis Consultants Ltd., UK). Quantified results were achieved using measurement of additional pellets within this block of target elements (e.g. Au, Ag, Fe), along with block MINM25-23 (Astimex Standards Ltd., Canada). Point Fe measurements of pyrite and pyrrhotite were acquired to provide a robust internal standard

for subsequent Laser Ablation ICP-MS in-situ quantitative analyses. The Tescan MIRA4 FE-SEM is installed at iCRAG Lab@TCD, Trinity College Dublin.

7.4.iv. Laser Ablation ICP-MS spot analyses and raster mapping

Analyses of pyrite and pyrrhotite grains were conducted using a Teledyne Cetac G2 193 nm Excimer ArF laser with a HelEx 2-volume cell, coupled to a ThermoFisher Scientific Elemental iCAPQs mass spectrometer. A variable volume device developed in-house is retrofitted, linking the ablation cell to the ICP-MS torch; the device enables enhanced sensitivity and smoothing of the signal between the laser and the mass spectrometer, along with a reduction in the formation of oxides through the introduction of a 3-10 ml/min flow of N₂ flow to the sample-gas mixture. A repetition rate of 6-40 Hz and a fluence of 1.0-1.2 J / cm² was deemed optimal, with scan speeds of 16-25 μm / s, determined based on laser tuning conditions and the objectives of experiments. Given the fine grain size encountered (particularly of pyrrhotite), circles rather than squares were deemed appropriate for spot analyses, 10 μm in radius (higher scan speeds were used for larger spots), while 10 μm squares were used for raster element mapping. Data were calibrated using analyses of NIST-610 (National Institute of Standards and Technology, USA), BCR-2G (United States Geological Survey, USA), UQAC-FeS-1 (Université du Québec à Chicoutimi, Canada) standards and a MASS-1 sulphide standard (United States Geological Survey, USA). LA ICP-MS facilities used in this study are located at the Trinity College Dublin Geochemistry Laboratories, Pearse Street, Dublin.

7.4.v. Open-source geophysical and stream-sediment data

Data collected during the Tellus field (geochemical) and airborne geophysical surveys were incorporated into this study in examination of potential fertile structures and local

metalliferous concentrations. The Tellus project is a cross-border (Ireland-Northern Ireland) initiative between the Geological Survey of Ireland, Geological Survey Ireland, Queen's University Belfast and Dundalk Institute of Technology, which provides the results of regional-scale geological, geophysical and geochemical datasets on an open-access platform. The Tellus Border phase of interest to this study, which includes datasets for the County Donegal region, was completed between 2011 and 2013, and was funded by the INTERREG IVA programme of the European Regional Development Fund (ERDF), the Department of Environment, Community and Local Government from Ireland and the Department of the Environment from Northern Ireland. Airborne geophysics included in this study were flown by a DeHavilland DHC-6 Twin Otter plane equipped with instruments for the collection of magnetic, radiometric and conductivity data, flying 60m above the ground at a line spacing of 200m. Soil and stream sediment geochemical samples were collected during this survey by auger and in bottles respectively, which were then analysed for 55 elements and compounds. Further information about the Tellus project and access portals for data are available online at www.tellus.ie.

7.5. Petrography

7.5.i. Glencolumbkille

Hand specimens of samples acquired from Glencolumbkille (D-GC-19/01 and D-GC-19/02), which may be broadly described as graphite-chlorite-muscovite schists, are very finely psammitic and comprise silicate minerals of low hardness. A well-developed fabric is present and < 1 mm scale, evenly-spaced vugs are common. Specimens have an overall smoothness and exhibit slightly oxidised surfaces due to exposure in outcrop. Pyrite is observed in trace abundance, dominantly as disseminated grains with rare clusters present. Thin section optical microscopy reveals a seriate groundmass dominated by fine equigranular

quartz and albite (very fine to medium sand equivalent; avg. 0.18 mm, $2\sigma=0.12$ mm; $n=30$) partially replaced during deformation with acicular muscovite, chlorite and graphite; garnet, ilmenite, rutile and pyrite porphyroblasts observed along with minor accessory zircon. An asymmetric crenulated fabric is indicative of multi-phase deformation.

A characteristic feature observed is an abundance of heterogeneously distributed garnet porphyroblasts (Ca:Mg:Mn = 7:2:1), which have subsequently been partially replaced by chlorite, providing evidence of retrograding metamorphic conditions from amphibolite to greenschist facies. Porphyroblasts have an average 591 μm in diameter ($2\sigma=226$ μm ; $n=62$) and are observed within distinctive regions of tested sections where muscovite appears to replace all previous mineral phases, separated by transitional boundaries from more chloritic areas where aforementioned porphyroblasts are not observed. The observation of garnet partially retrograding to chlorite is consistent with findings by Howarth et al. (1966), and Anderson (1953) who refers to observations within the Glencolumbkille Schists of both partially replaced garnet, and porphyroblasts which have been entirely replaced, as 'chlorite knots'.

Xenomorphic pyrite porphyroblasts exhibiting two distinctive generations are encountered in section D-GC-19/01a, best observed optically in reflected light, with an average axis length of 65 μm ($n=25$; min. 14 μm , max. 182 μm). Grains exhibit an overall porosity. Cores of these grains (Py_1) appear homogeneous, while outer zones (Py_2) contain inclusion trails indicative of oscillatory zonation. Inspection using Field Emission Scanning Electron Microscopy (FE-SEM) reveals that this outer generation contains an entrained schistosity suggesting synchronicity with fabric development. Syn-deformational pyrite is also observed in elongate xenomorphic form in section D-GC-19/01b with an average width of 556 μm (min. 39 μm , max. 1,046 μm $n=26$) and a length of 5,080 μm . Elongate forms exhibit a restricted subhedral Py_1 core (c. 250 μm x 450 μm) overgrown by three

morphologically similar Py_2 bands following the principle deformation fabric. An example of ductile chalcopyrite

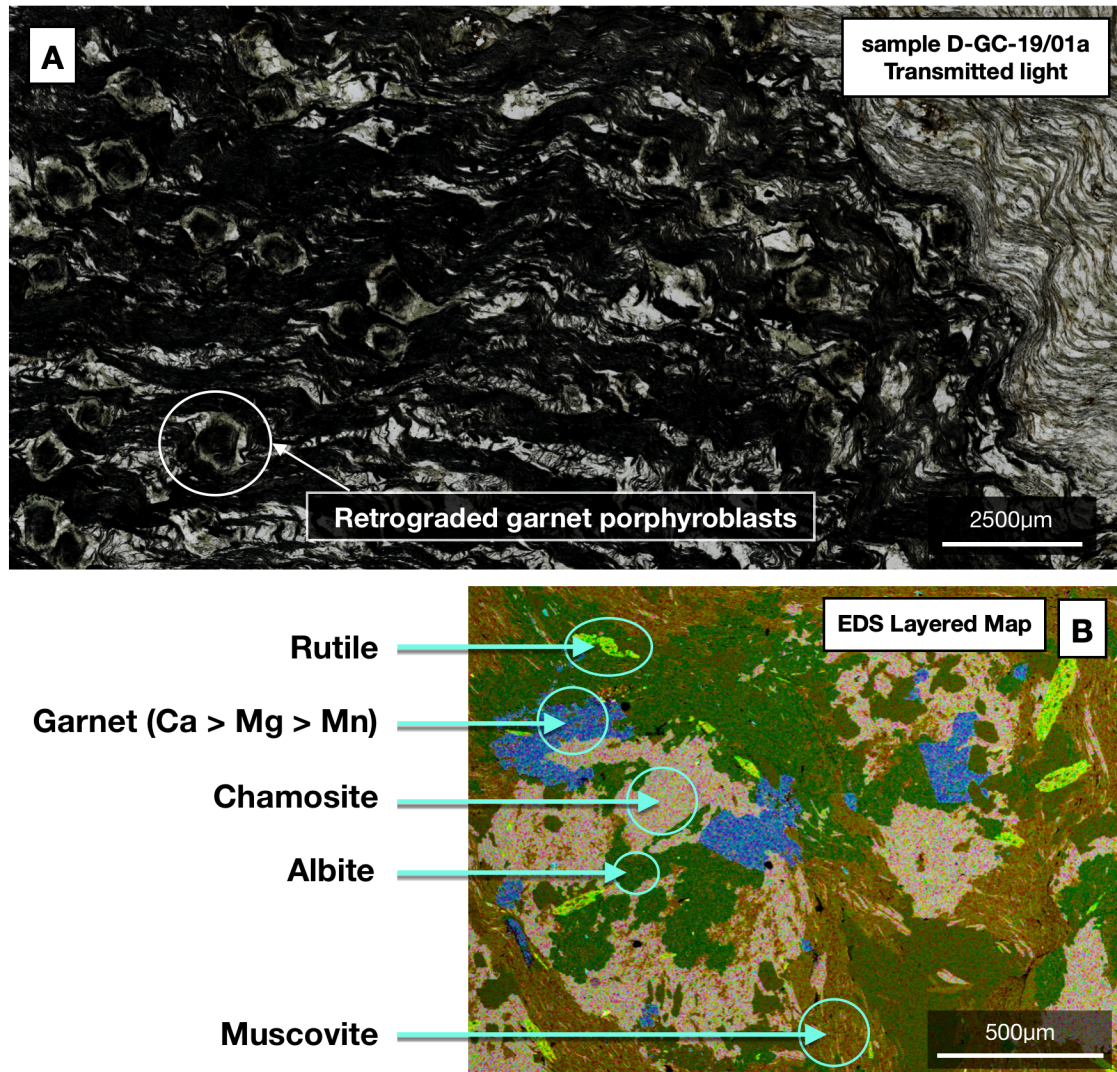


Figure 7.6. Microscopic images from the Glencolumbkille locality, County Donegal (Slieve League Formation, Easdale Subgroup, Argyll Group): (A) Transmitted light image of a region of interest within thin section D-GC-19/01a showing abundant partially-retrograded garnet porphyroblasts within the muscovite-rich area at the centre and left of the image, and their demonstrable absence within an area to the right. A well-developed crenulated fabric is visible through observation of the darker biotite and muscovite minerals throughout the section; (B) a closer false-colour image of a retrograded garnet porphyroblast showing the distribution of minerals of interest. The lime green elongate minerals are slightly ferrous rutile (<5 wt.%), blue represents Ca-rich garnet while the light pink is chamosite. Albite (dark green) and muscovite (brown) envelope the porphyroblast, with minor albite observed within the boundary of the blast.

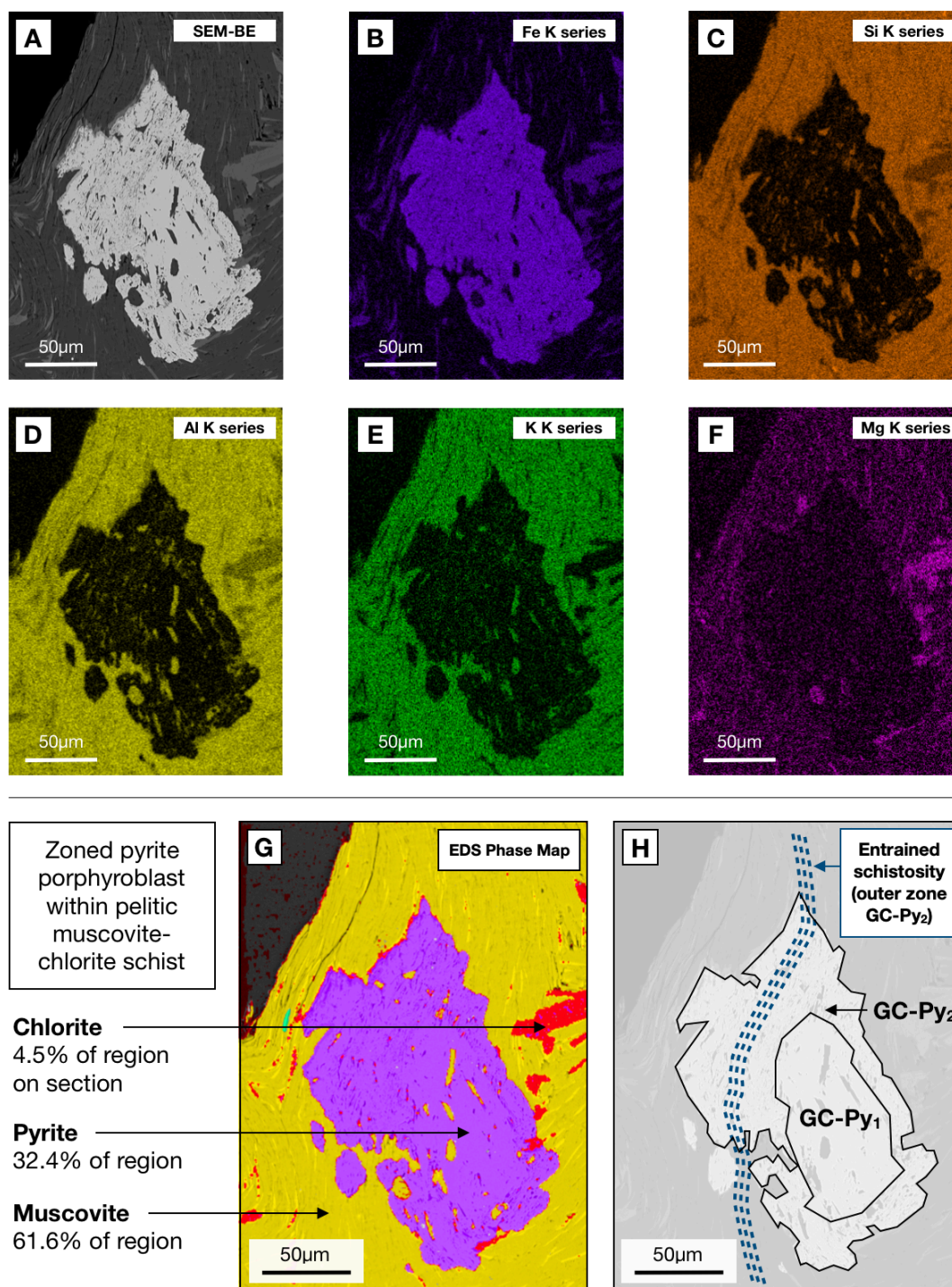


Figure 7.7. Scanning Electron Microscopy (SEM)-acquired images; Glencolumbkille locality, County Donegal (Slieve League Formation, Easdale Subgroup, Argyll Group): (A) A Backscattered Electron raster scan of a pyrite porphyroblast at the edge of section D-GC-19/01a; (B-F) Energy-Dispersive X-ray Spectroscopy (EDS/EDX) maps for Fe, Si, Al, K and Mg respectively; (G) an EDS/EDX false-colour phase discrimination map showing the principle mineral phases of pyrite, chlorite and muscovite; (H) a schematic of the grain showing phases (GC-)Py₁ and (GC-)Py₂, with the entrained schistosity within outer (GC-)Py₂.

Cp₁ (100 µm x 87 µm) which grew synchronously with subhedral Py₁ (60 µm x 68 µm) is observed enveloped by a c. 7.5 µm Si rim within sample D-GC-19/01a. It is considered likely that these rims are composed of andradite (garnet group), based on relatively elevated concentrations of Fe, Ca, Si and O recorded by EDS/EDX mapping, and cross-reference with the literature (e.g. Li, 2012). Partial replacement of ilmenite by pyrite is also observed.

Average concentrations of Fe within tested pyrite using EDS/EDX point analyses were 46.1 wt.% ($2\sigma=1.22$ wt.%; $n=25$), while an average S concentration of 52.1 wt.% ($2\sigma = 3.15$ wt.%) was recorded.

7.5.ii. Muckros

Schistose hand specimens from the Muckros locality are distinctly lustrous, fine grained, and are characterised compositionally by abundant biotite with traces of pyrite. A smooth, evenly spaced symmetrical foliation with localised crenulation at the mm-scale is observable in hand specimens, suggesting heterogeneous deformation intensity. Millimetric vugs are common throughout specimens with their size bearing a relationship with the composition of fabric horizons; the largest are contained within more oxidised brown micaceous bands. Pyrite (<1%) is either finely disseminated or occurring as blebs parallel to the foliation. In thin section, two distinct fabrics are revealed in transmitted light with a secondary foliation at approximately a 55° angle to the first. Samples are principally composed of quartz grains (avg. 0.08 mm, $2\sigma=0.05$ mm; $n=30$). They have been replaced in evenly spaced bands approximately 1-1.5mm apart by strongly micaceous bands which adhere strongly to foliations; an absence of chlorite is also noted.

Average Fe concentrations of pyrite, recorded using EDS/EDX analyses, were 46.1 wt.% ($2\sigma = 0.56$ wt.%; $n=25$), while S reported an average of 52.2 wt.% ($2\sigma = 0.66$ wt.%).

7.5.iii. Derrylahan

Field specimens are pelitic, highly micaceous and exhibit a well-developed folded schistosity; visible blebby sulphide grains appear to be most commonly associated with vuggy biotite-rich horizons. Fracturing is common with rocks, preferentially situated sub-parallel to the main fabric. Transmitted light microscopy reveals an intense mylonitic deformation fabric along which metamorphic muscovite mica (50-60% of observed minerals) and less common biotite (c. 10%) have grown synchronously. The distribution of micas is characterised by asymmetric micro-folding with fold hinge areas demonstrating locally high concentration of muscovite, forming micro-lithons which are themselves folded in subsequent deformation. Within fold flank regions muscovite and biotite appear synchronous, while at fold hinges, muscovite appears to replace earlier biotite. Late deformation is highly ductile and euhedral crystals indicative of recrystallisation are not widely observed. Reflected light microscopy reveals pyrite restricted to thin horizons (avg., 50 to c. 1500 μm in width) forming synchronously with deformation though at a stage prior to the final folding event. These grains are partially dissolved and are heterogeneously distributed, with examples of relatively large, evenly spaced, porous grain clusters >200 μm in width observable separated by trails of fine (<50 μm) disseminated grains.

Pyrite Fe contents averaged 46.4 wt.% ($2\sigma = 0.54$ wt.%; $n=12$) while S is recorded at an average abundance of 52.5 wt.% ($2\sigma = 0.44$ wt.%), using EDS/EDX.

7.5.iv. Falcarragh

Hand specimens from Falcarragh are markedly different to other samples; light grey, uniformly banded pelites exhibiting little deformation, they are highly competent and break brittlely. A penetrative fabric at the scale of hand samples is not visible, nor metamorphic micaceous assemblages with the exception of fine-grained biotite. Visible sulphide is very fine grained and disseminated. Thin section optical microscopy confirms an

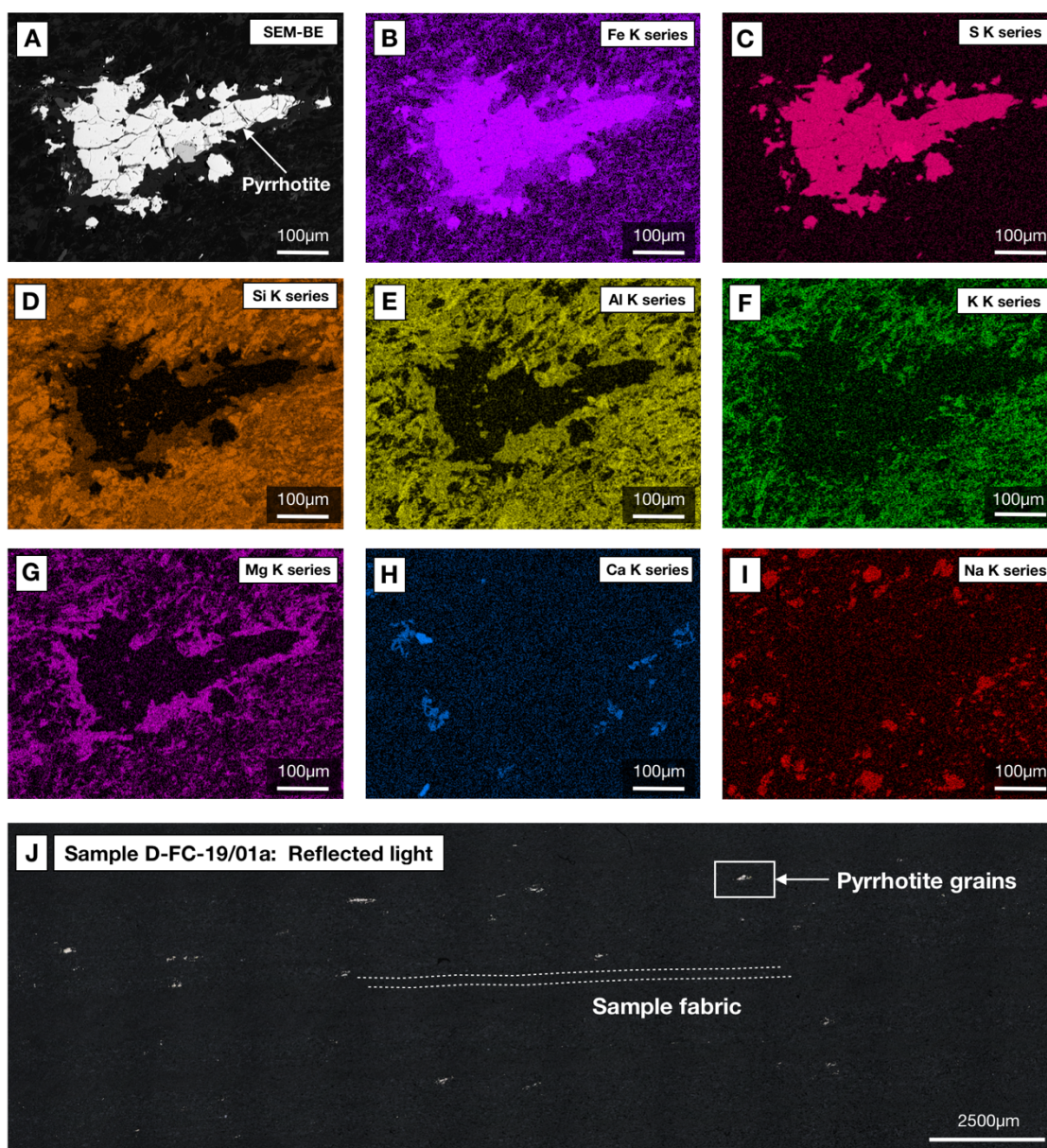


Figure 7.8. (A-I) Analyses of a grain of pyrrhotite from the Falcarragh locality using a Scanning Electron Microscope in Backscattered Electron mode (SEM-BE), including Fe, S, Si, Al, K, Mg, Ca and Na results from Energy Dispersive X-ray Spectroscopy (EDS/EDX) analysis; (J) thin section-scale view of the sample in reflected light showing the sparsity of grains and a lack of deformation of the host fabric. Pyrrhotite is hosted by Al-Mg-K silicates and albite. The area immediately surrounding the grain shows relatively depletion of Fe and enrichment of Mg in comparison with the grain itself, suggesting late reworking and localised alteration. Pyrrhotite grains represent only a small percentage (<5%) of the groundmass and show an alignment with the schistosity which itself shows little evidence of crenulation or distortion.

average host grain size of 30 μm ($2\sigma=18\text{ }\mu\text{m}$; $n=30$). Observed sulphide porphyroblasts are entirely of pyrrhotite, evenly distributed within relatively coarse horizons, bearing a xenomorphic and porous appearance, with an average size of 19 μm ($2\sigma=24\text{ }\mu\text{m}$; $n=30$). Visual inspection in reflected light confirms a relationship with Ti-oxide; pyrrhotite is observed partially entirely replacing earlier Ti-oxide grains, occurring infrequently as elliptical dissolved clusters. Ti-oxide minerals may also occur freely within the matrix without a pyrrhotite association.

The average abundance of Fe within pyrrhotite retrieved using EDS/EDX on analysed samples was 59.2 wt.% ($2\sigma = 1.51\text{ wt.}\%$; $n=15$), while S is present at an average of 39.2 wt.% ($2\sigma = 0.91\text{ wt.}\%$).

7.6. Laser Ablation ICP-MS spot analyses

7.6.i. Approach and limits of detection

A robust dataset of 200 Laser Ablation ICP-MS spot analyses that were conducted on pyrite ($n=150$) and pyrrhotite ($n=50$) grains at the four sampled localities in Donegal. This comprises 50 analyses of Glencolumbkille pyrite (sample D-GC-1901b), 50 analyses of Muckros pyrite (sample D-MK-1902b), 50 analyses of Derrylahan pyrite (sample D-DR-19/01a) and 50 analyses of pyrrhotite from Falcarragh (sample D-FC-19/03b). Circular spots with a diameter of 12 μm were selected based on testing of a range of sizes deemed suitable on adjacent grains; optimal counts recorded by the mass spectrometer while attaining maximum coverage was the determining factor. Full thin section stitched images were used for both targeting and navigation using Chromium software, with MASS-1, UQAC, NIST-610 and BCR used as standards. Once LA ICP-MS experiments were completed, internal Fe standardisation was verified through targeted point analyses on grains using Energy Dispersive X-ray Spectroscopy methods (EDS/EDX) in tandem with the

Scanning Electron Microscope (SEM). Results for UQAC were cross-referenced with known values. Aforementioned Fe standardisation values (reported in the ‘Petrography’ section), retrieved using EDS/EDX, were utilised for data reduction using the ‘Trace Elements’ scheme in Iolite. ^{32}S , ^{55}Mn , ^{57}Fe , ^{59}Co , ^{60}Ni , ^{63}Cu , ^{66}Zn , ^{71}Ga , ^{75}As , ^{78}Se , ^{107}Ag , ^{118}Sn , ^{121}Sb , ^{125}Te , ^{182}W , ^{197}Au , ^{202}Hg , ^{205}Tl , ^{208}Pb and ^{209}Bi were selected as analytes in concert with mapping experiments and based on results from previous experiments that form part of this study. Limits of detection (excluding ^{57}Fe and ^{32}S), unique to individual spots, reported an average for the full dataset of pyrite spots ($n=150$) of 39.8 ppm for ^{55}Mn , 8.66 ppm for ^{59}Co , 23.5 ppm for ^{60}Ni , 5.16 ppm for ^{63}Cu , 108 ppm for ^{66}Zn , 1.1 ppm for ^{71}Ga , 11 ppm for ^{75}As , 102 ppm for ^{78}Se , 0.92 ppm for ^{107}Ag , 2.57 ppm for ^{118}Sn , 1.64 ppm for ^{121}Sb , 4.9 ppm for ^{125}Te , 1.14 ppm for ^{182}W , 1.29 ppm for ^{197}Au (min., 0.33 ppm; max., 3.9 ppm), 3.37 ppm for ^{202}Hg , 0.39 ppm for ^{205}Tl , 1.32 ppm for ^{208}Pb and 0.41 ppm for ^{209}Bi . For Falcarragh pyrrhotite analyses ($n=50$), average detection limits were 435 ppm for ^{55}Mn , 95.5 ppm for ^{59}Co , 290 ppm for ^{60}Ni , 55.4 ppm for ^{63}Cu , 1016 ppm for ^{66}Zn , 13.1 ppm for ^{71}Ga , 149 ppm for ^{75}As , 2,152 ppm for ^{78}Se , 11.2 ppm for ^{107}Ag , 25 ppm for ^{118}Sn , 17.2 ppm for ^{121}Sb , 59.7 ppm for ^{125}Te , 13.9 ppm for ^{182}W , 13.3 ppm for ^{197}Au (min., 3.1 ppm; max., 58 ppm), 37.2 ppm for ^{202}Hg , 3.86 ppm for ^{205}Tl , 10.25 ppm for ^{208}Pb and 4.21 ppm for ^{209}Bi . It was learned that pyrrhotite detection limits are on average an order of magnitude higher than those for pyrite which this study attributes to relative differences in the physical properties of minerals.

7.6.ii. Trace element concentrations and strategy

For tested pyrrhotite at the Falcarragh locality ($n=50$), 3 individual analyses reported an Au concentration above detection with a maximum value of 12.4 ppm. The two lower results were 6.9 ppm and 7.3 ppm. Concentrations of Au are recorded above detection within 11 analyses of pyrite across the three localities ($n=150$), with a maximum of 7.5 ppm recorded in a sample from Derrylahan. The median Au content for analyses within pyrite was 1.5 ppm

(IQR = 0.92 – 2.70 ppm; n=11). Of pyrite analyses where Au is recorded, 4 were from the Derrylahan locality (0.76-7.5 ppm), 6 were from Muckros (1.47-2.7 ppm), and one was from Glencolumbkille (1.4 ppm). Mean elemental abundances for tested analytes indicate relative enrichment in Falcarragh pyrrhotite (n=50) compared to pyrite from the Slieve League Peninsula (n=150), with the exception of Cu, Tl and Pb: following methodology used by Thomas et al. (2011). Median enrichments are observed > 100 ppm for Mn (540 ppm; IQR = 510 – 910 ppm; n=3), Co (549 ppm; IQR = 474 – 606 ppm; n=50), Ni (2,500 ppm; IQR = 1,845 – 2,985 ppm; n=50); IQR = and Zn (12,350, IQR = 1,700 – 23,000 ppm; n=2) for pyrrhotite analyses (n=50), while concentrations > 100 ppm are recorded in pyrite (n=150) for Co (185 ppm; IQR = 40.4 – 340 ppm; n=109), Ni (420 ppm; IQR = 79.8 – 848 ppm; n=108) and Zn (128 ppm; IQR = 100 – 156 ppm; n=16). This information must however be approached with a degree of caution as it is necessary to consider (i) the number of samples reporting above detection for sample populations, (ii) the relatively high detection limits observed for pyrrhotite (an order of magnitude higher than those of pyrite) and (iii) what elevated concentrations with low numbers of samples reporting above detection may represent.

In order to determine which elements are meaningfully enriched and mobile synchronous with the development of phases, and to make determinations with regards to the chemical state and mobility of gold, three methods are used in this study to navigate these issues and provide the practicable information: firstly as demonstrated in Figure 7.10, this study considers the relative mean abundances of elements between pyrrhotite and pyrite (Figure 7.10A), and also the relative proportions of samples reporting above detection ($n > \text{limit of detection} / n$) (Figure 7.10B) which when used cross-referencing with median absolute concentrations may be a more reliable indicator of element mobility. Secondly, the relationship between concentrations of Au, Ag and As can be examined for both pyrrhotite

	Pyrite, Slieve League Peninsula (n=150)				Pyrrhotite, Falcarragh (n=50)			
Analyte	n	median	25th perc.	75th perc.	n	median	25th perc.	75th perc.
Mn	<i>25</i>	<i>51.0</i>	<i>33.5</i>	<i>68.0</i>	<i>3</i>	<i>540</i>	<i>510</i>	<i>910</i>
Co	109	185	40.4	340	50	549	474	606
Ni	108	420	79.8	848	50	2,500	1,845	2,985
Cu	115	17.4	8.50	44.0	<i>2</i>	<i>39.0</i>	<i>36.0</i>	<i>42.0</i>
Zn	<i>16</i>	<i>128</i>	<i>100</i>	<i>156</i>	<i>2</i>	<i>12,350</i>	<i>1,700</i>	<i>23,000</i>
Ga	44	1.28	0.96	2.78	14	8.00	3.85	26.3
As	<i>20</i>	<i>15.8</i>	<i>9.70</i>	<i>47.5</i>	<i>0</i>	<i>-</i>	<i>-</i>	<i>-</i>
Se	49	56.0	33.5	85.0	<i>0</i>	<i>-</i>	<i>-</i>	<i>-</i>
Mo	30	0.64	0.30	1.06	10	1.65	0.51	4.65
Ag	93	1.90	1.28	4.75	11	6.80	5.20	8.10
Sn	35	3.10	2.40	4.00	11	30.0	19.7	39.0
Sb	44	2.60	1.62	4.73	<i>5</i>	<i>12.9</i>	<i>8.30</i>	<i>13.6</i>
Te	35	5.40	4.10	9.00	<i>5</i>	<i>32.0</i>	<i>23.5</i>	<i>73.5</i>
W	32	0.56	0.23	1.55	<i>5</i>	<i>0.39</i>	<i>0.24</i>	<i>7.85</i>
Au	<i>11</i>	<i>1.50</i>	<i>0.92</i>	<i>2.70</i>	<i>3</i>	<i>7.30</i>	<i>6.90</i>	<i>12.4</i>
Hg	<i>17</i>	<i>3.60</i>	<i>3.05</i>	<i>5.60</i>	<i>0</i>	<i>-</i>	<i>-</i>	<i>-</i>
Tl	88	1.05	0.52	4.08	16	2.60	2.33	3.85
Pb	141	54.3	10.4	268	36	30.3	12.9	94.5
Bi	82	1.11	0.56	2.16	34	11.9	5.08	17.93

Table 7.3. Median concentrations of analysed elements for all tested pyrite at the three Slieve League Peninsula localities (Glencolumbkille, Muckros and Derrylahan; n=150) and pyrrhotite at Falcarragh (n=50), with their respective interquartile ranges (shown as 25th and 75th percentile thresholds). The n-value for each analyte describes the number of samples reporting above the limit of detection. Results where <20% of analytes report above detection are shown in italics. Those where >20% of results report above detection are shown in bold type; this is the case in both pyrite and pyrrhotite populations for Co, Ni, Ga, Mo, Ag, Sn, Tl, Pb and Bi.

Analyte	Pyrite, Derrylahan (n=50)				Pyrite, Glencolumbkille (n=50)				Pyrite, Muckros (n=50)			
	n	Median	25th perc.	75th perc.	n	Median	25th perc.	75th perc.	n	Median	25th perc.	75th perc.
Mn	9	42.0	25.0	210	4	66.0	32.3	84.8	12	50.0	34.5	61.8
Co	41	186	111	256	33	500	97.5	2,240	35	45.0	24.1	197
Ni	43	490	349	700	28	3,285	341	4,815	37	69.0	43.5	376
Cu	42	15.8	8.48	42.2	38	28.2	13.8	228	35	12.5	6.30	22
Zn	6	141	111	248	4	105	78.3	148	6	120	95.0	157
Ga	14	1.00	0.76	5.65	14	1.30	1.04	1.86	16	1.50	1.09	2.98
As	3	9.00	6.00	9.40	8	22.5	11.5	202	9	38.0	11.6	47.0
Se	9	36.0	24.5	116	24	42.0	27.8	77.5	16	72.5	58.3	108
Mo	2	0.36	0.35	0.37	15	0.56	0.28	1.80	13	0.79	0.35	1.01
Ag	34	2.55	1.73	4.85	22	1.48	1.06	1.87	37	1.90	1.12	5.70
Sn	4	2.70	1.78	3.55	17	3.60	2.85	4.15	14	2.50	1.95	6.50
Sb	17	3.30	1.34	5.00	20	3.55	2.20	5.48	7	1.40	1.01	1.60
Te	14	5.55	4.40	7.40	5	4.60	4.00	7.85	16	5.85	3.85	9.75
W	14	0.29	0.12	0.65	5	0.36	0.24	1.54	13	1.40	0.78	2.00
Au	4	0.91	0.80	5.86	1	1.40	1.40	1.40	6	1.75	1.49	2.78
Hg	3	3.10	3.00	4.40	7	3.80	3.40	7.30	7	3.60	2.70	6.20
Tl	39	1.10	0.55	1.80	36	3.55	0.75	30.5	13	0.36	0.30	0.59
Pb	49	74.0	37.3	177	50	306	69.3	738	42	5.10	2.48	20.6
Bi	34	1.16	0.60	1.92	22	1.29	0.74	10.6	26	0.72	0.40	1.74

Table 7.4. Median concentrations of selected analytes for individual pyrite populations retrieved on the Slieve League Peninsula at the Derrylahan (n=50), Glencolumbkille (n=50) and Muckros (n=50) localities. Interquartile ranges are reported as 25th and 75th percentile thresholds, while respective n-values denote the number of values reporting above the limit of detection.

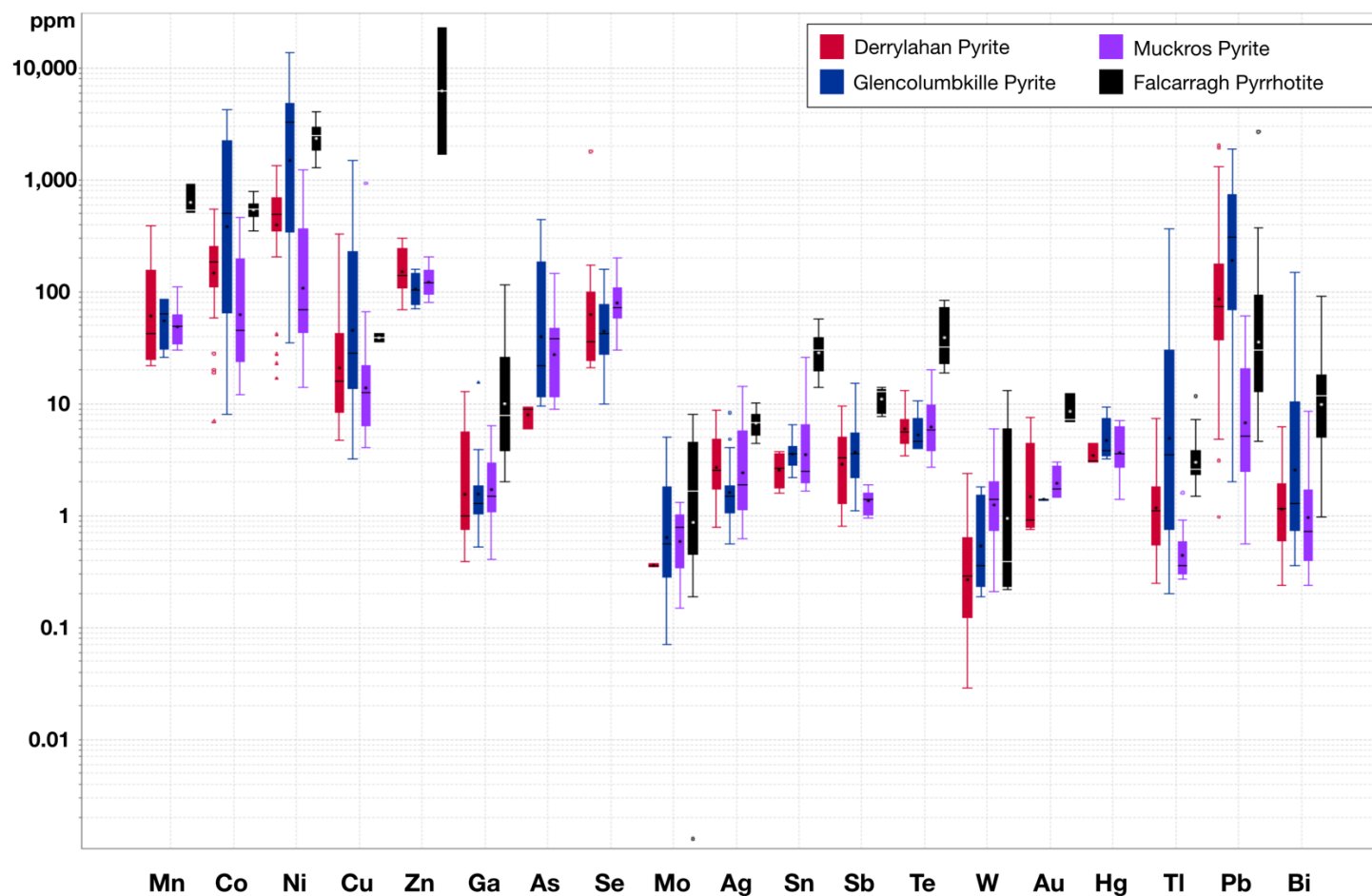


Figure 7.9. Box and whisker diagram showing the distribution of recorded element concentrations using Laser Ablation ICP-MS spot analyses across the four datasets (n=200). Central boxes denote the middle 50% of data within the interquartile range (IQR; Q3-Q1). Outer circles (outliers) $>1.5 \times$ the IQR from the box, while a triangle (far outlier) is $> 3 \times$ IQR from the box. Whiskers are extreme values which are not outliers.

and pyrite, and examining input channels for ICP-MS data retrieved for individual spots in the case of analytes where only a low percentage report concentrations above their respective limit of detection. Third, the ratios of concentrations are examined where a meaningful number of analyses report above detection, and relationships examined between data populations. Lastly in this study, in-situ Laser Ablation ICP-MS element raster mapping is used to record the spatial distribution of element concentrations, as a cross-reference to in-situ spot analyses.

7.6.iii. Comparison of pyrrhotite and pyrite element concentrations

A ratio is calculated where ‘n’ is the total sample population, while ‘(n > LOD)’ is equal to the number of samples reporting above the limit of detection (specific to each individual analysis):

$$[(n > LOD) / n]_{\text{pyrrhotite}} / [(n > LOD) / n]_{\text{pyrite}}$$

The ratio > 1 for Co (1.38), Ni (1.39) and Bi (1.24) demonstrate that these analytes report a higher proportion of results above detection in pyrrhotite than in pyrite (see Figure 7.10B), while for the balance of analytes, more results report above detection in pyrite: Mn (0.36); Cu (0.05); Zn (0.38); Ga (0.95); Ag (0.35); Sn (0.94); Sb (0.34); Te (0.43); Au (0.82); Tl (0.55); Pb (0.77). Mo shows an equal number of analyses reporting above detection in both mineral types (1.00). For As, Se and Hg, no individual results report above detection for pyrrhotite, preventing their inclusion in this figure; the number of analyses reporting above detection for these analytes in pyrite are n = 20 for As (13%), n = 49 for Se (33%) and n = 17 for Hg (11%). >20% of results (an arbitrarily selected threshold) report above detection in samples of both mineral types for Co, Ni, Ga, Mo, Ag, Sn, Tl, Pb and Bi, (this threshold is used as a guide for later scrutiny of element ratios). This methodology

demonstrates that for Co, Ni and Bi, (i) a higher proportion of analyses are recorded above detection in pyrrhotite than in pyrite, (ii) that >20 % of analyses for these elements report above detection, and (iii) that median concentrations are relatively elevated for those elements. It is proposed that Co, Ni and Bi are relatively enriched in Falcarragh pyrrhotite compared to pyrite from the Slieve League Peninsula, with meaningful consideration of the number of individual results acquired. While Mn, Zn, Ga, Mo, Ag, Sn, Sb, Te, W and Au also show relatively higher mean abundances in pyrrhotite in Figure 7.10A, a higher proportion of results was not acquired for these elements in pyrrhotite, and only results for

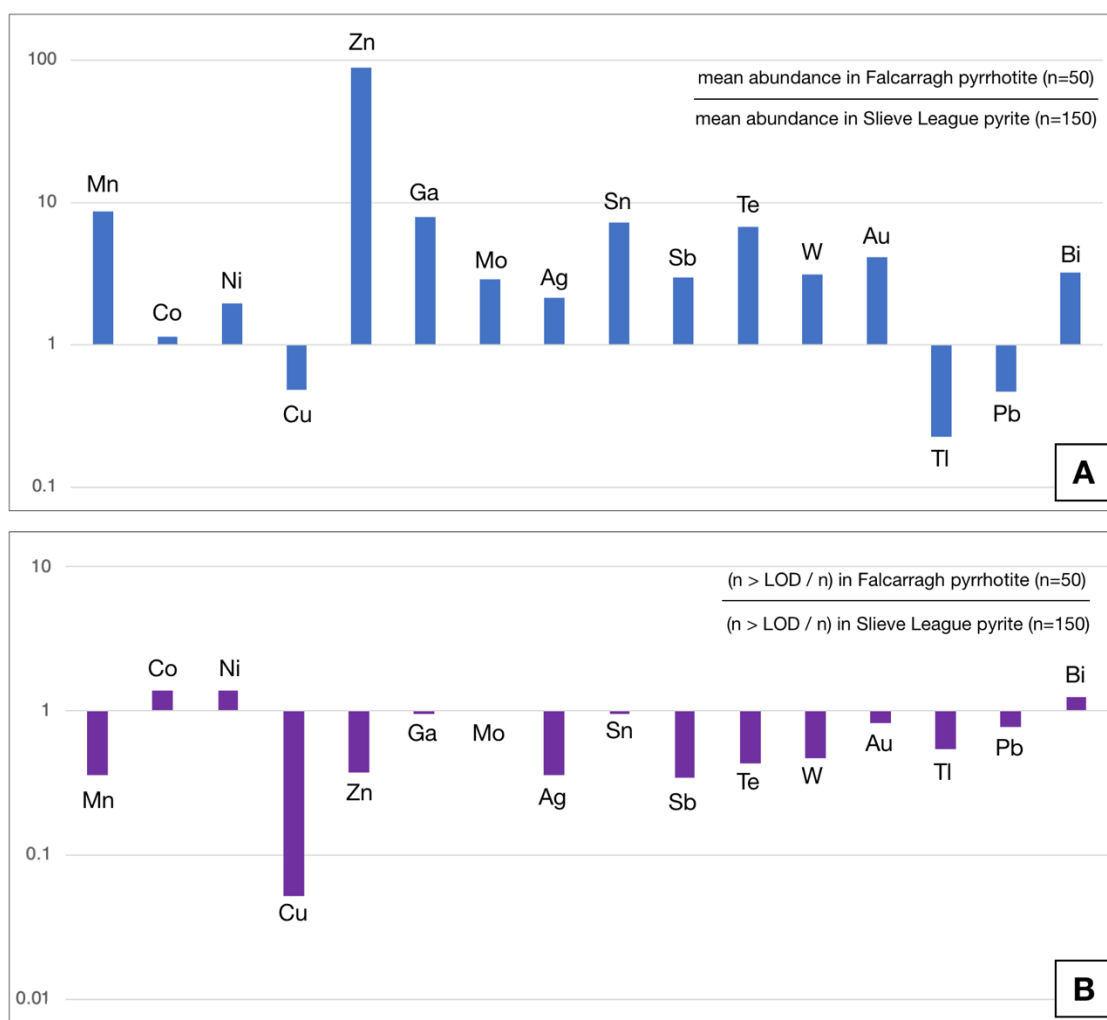


Figure 7.10. (A) Ratio of the mean abundances within pyrrhotite to those in pyrite; (B) ratio of the proportion of analyses reporting above detection (the total number of samples, $n > \text{limit of detection}$, divided by the sample size, n) of pyrrhotite ($n=50$), to that of pyrite ($n=150$).

Ga, Mo, Ag and Sn reported results for both minerals > 20% of the sample size. It is proposed that Ga, Mo, Ag and Sn *may* be relatively enriched, though with a lower overall confidence. For Mn, Zn, Sb, Te, W and Au, the ICP-MS input signal is examined in subsequent sections to determine the reason for elevated absolute abundances.

7.6.iv. Gold-silver and other metalliferous particles

Data acquired during Laser Ablation ICP-MS experiments for Au were inspected to determine whether sharp variability (or ‘spikes’) in recorded input signals may be present (rather than a smooth signal) which may indicate the ablation of micro-inclusions. Au results and input signals were also cross-referenced with those of Ag. For pyrrhotite, Au concentrations above detection occurring in 3 analyses (n=50) were coincident with concentrations of Ag in 2 instances. In the first case (designated ‘FCFr-3’ in Figure 7.11), Au = 12.4 ppm (internal 2σ = 6.2 ppm), coincident with Ag = 7.6 ppm (internal 2σ = 5.4 ppm) (Au/Ag = 1.6), and in the second case (designated ‘FCFr-5’ in Figure 7.11), Au = 7.3 ppm (internal 2σ = 2.8 ppm) while Ag = 6.8 ppm (internal 2σ = 3.6 ppm) (Au/Ag = 1.1). For one of the three analyses where Au was recorded (Au = 6.9 ppm, internal 2σ = 5.6 ppm), coincident Ag was not detected. Examining the input signal for ‘FCFr-3’ and ‘FCFr-5’, multiple deviations from the baseline are observed for the ICP-MS input signal for Au and Ag throughout the ablation cycle; a single sharp increase in one, the other or both is not observed. For the output signal, this is also the case, though there does appear to be a partial match of the elevated signals for Au and Ag for one instance within the ‘FCFr-3’ signal (Au = 161 ppm, Ag = 141 ppm; Au/Ag = 1.14), and one closer to the baseline integration during ‘Analysis 2’ (Au = 46.6 ppm, Ag = 25.3 ppm; Au/Ag = 1.84). The coincident peaks within ‘FCFr-3’ are likely to represent an auriferous micro-inclusion, while this is also possible for coincident peaks within ‘FCFr-5’.

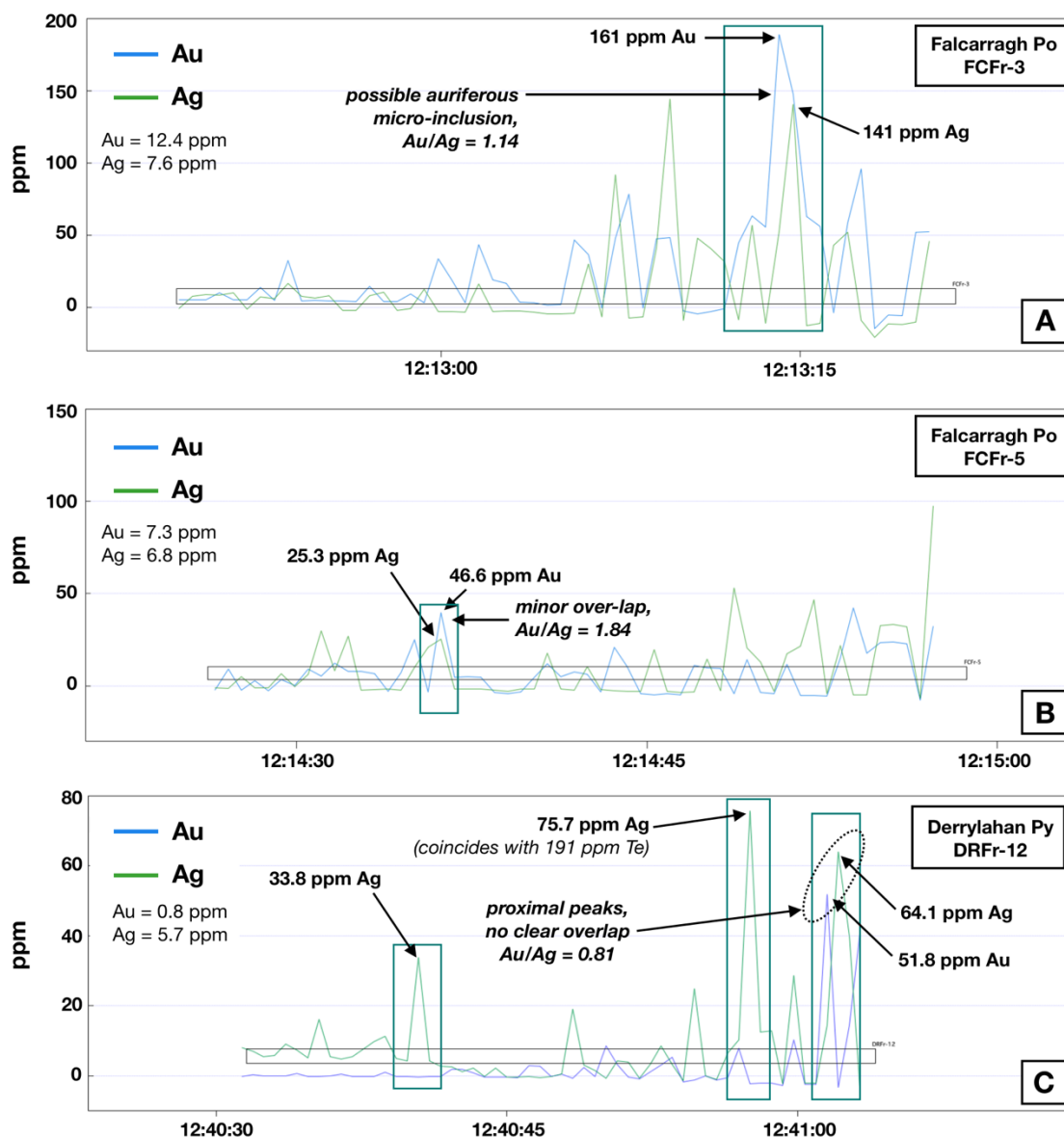


Figure 7.11. (A) and (B): output ICP-MS signals (processed) of Au and Ag for two spot analyses of pyrrhotite from Falcarragh, using the same scale in ppm. For analysis FCFr-3 (A), a likely micro-inclusion gold particle is observed in coincident peaks of Au and Ag ($Au/Ag = 1.14$), while a minor overlap is observed in the record of FCFr-5 (B). (C) shows the ICP-MS results of an ablation pit within Derrylahan pyrite (analysis 'DRFr-12') showing incongruent Ag peaks earlier in the period of ablation, with proximal (but not completely overlapping) Au and Ag peaks after 12:41:00 ($Au/Ag = 0.81$). The second highlighted peak (75.7 ppm Ag) is also coincident with a peak in Te contents of 191 ppm suggesting the presence of a telluride particle. Laser Ablation in all cases took place over a period of 30 seconds. (A) and (B) results are derived from a thin section of sample D-FC-19/03 (section b), while (C) is part of an analyses from an ablated grain on sample D-DR-19/01 (section a).

For individual pyrite results where Au is reporting ($n=11$; see Table 7.5), 7 analyses are coincident with Ag concentrations above limits of detection (a correlation is not observed; $\rho=0.071$, Spearman rank); these are restricted to samples from the Muckros ($\rho=0.4$; $n=5$) and Derrylahan ($n=2$) localities. Au/Ag for analyses where both are present in pyrite ranges from 0.13 to 4.69 (avg., 1.22, $2\sigma = 3.38$; $n=7$). Output peaks in signal may be more argentiferous and show an absence of Au, more suggestive of Ag- inclusions (e.g. proximal peaks in the output signal of Ag with Te indicate the presence of telluride inclusions at Derrylahan).

Within 4 analyses, Au is coincident with As: this includes 3 analyses from the Muckros population and 1 from Glencolumbkille; no coinciding Au and As analyses were recorded above detection for Falcarragh pyrrhotite. Au/As for coinciding analyses range from 0.02 to 0.21 (avg., 0.07, $2\sigma = 0.18$; $n=4$), with a Spearman rank correlation coefficient (ρ) of 0.28. The breadth of the range of Au/Ag values does not immediately suggest the presence of auriferous micro-particles. However, plotting Au/As for analyses (converted to mol %; see Figure 7.12) where both are present and superimposing the solubility limit of Deditius et al. (2014) ($C_{Au} = 0.004.C_{As} + 2 \times 10^{-7}$) applicable to pyrite in orogenic systems (where trace element compositions are modified at temperatures between 300 and 400 °C), it is observed that (i) 4 of the 11 analyses where Au records concentrations plot inside the Au^0 nanoparticle (native metal) field above the solubility curve and (ii) that Au is not present in solution within the crystal lattice [the limit of Reich et al (2005), $C_{Au} = 0.02.C_{As} + 4 \times 10^{-5}$, is shown as a reference: it is appropriate to the solubility of Au in arsenian pyrite at a lower temperature range of 150-250 °C, deduced from samples of Carlin-type and epithermal Au deposits. This curve was re-evaluated for orogenic systems by Deditius et al. (2014)].

Location	Analysis	Au (ppm)	Ag (ppm)	As (ppm)	Au/Ag	Au/As
Derrylahan	Spot2	7.50	1.60	< LOD	4.69	-
Glencolumbkille	Spot32	1.40	< LOD	86.0	-	0.02
Muckros	Spot61	1.50	< LOD	< LOD	-	-
Muckros	Spot76	3.00	10.7	147	0.28	0.02
Muckros	Spot77	2.70	6.70	13.1	0.40	0.21
Muckros	Spot78	1.90	2.60	< LOD	0.73	-
Muckros	Spot84	1.60	11.1	38.0	0.14	0.04
Muckros	Spot137	1.47	0.67	< LOD	2.19	-
Derrylahan	Spot172	0.76	5.70	< LOD	0.13	-
Derrylahan	Spot176	0.92	< LOD	< LOD	-	-
Derrylahan	Spot178	0.90	< LOD	< LOD	4.69	0.02

Table 7.5. Results of individual in-situ Laser Ablation ICP-MS spot analyses of pyrite reporting Au concentrations greater than the limit of detection (LOD) (n=11), corresponding As (n=4) and Ag (n=7) results greater than the LOD where present, and associated ratios. Analyses were conducted on samples D-DR-19/01 (section 'A'), D-GC-19/02 (section 'A') and D-MK-19/02 (section 'B').

Given that retrograde conditions have been observed from amphibolite to greenschist facies synchronous with pyrite growth in petrographic work (see Figure 7.6), it is considered that the higher-temperature curve of Deditius et al. (2014) is appropriate to this study.

Aforementioned ICP-MS output signals agree with the suggestion of gold particles, though these tend to be more erratic than those observed for pyrrhotite and show multiple peaks within single ablation raster maps. Due to the lack of As results reporting above detection for pyrrhotite, it is not possible to use a similar process to that deployed for pyrite (using Au/As ratio and solubility curves) to discriminate micro-inclusions from lattice-bound gold. However, the limited number of Au analyses reporting (n=3 of 50), coupled with evidence of coincident Au and Ag peak concentrations at a ratio of 1.14 – 1.84 from output signals during the ablation of pits suggests that (i) micro-scale gold particles are preserved within grains of pyrrhotite at Falcarragh, and (ii) that gold is not uniformly enriched within the lattice of tested grains.

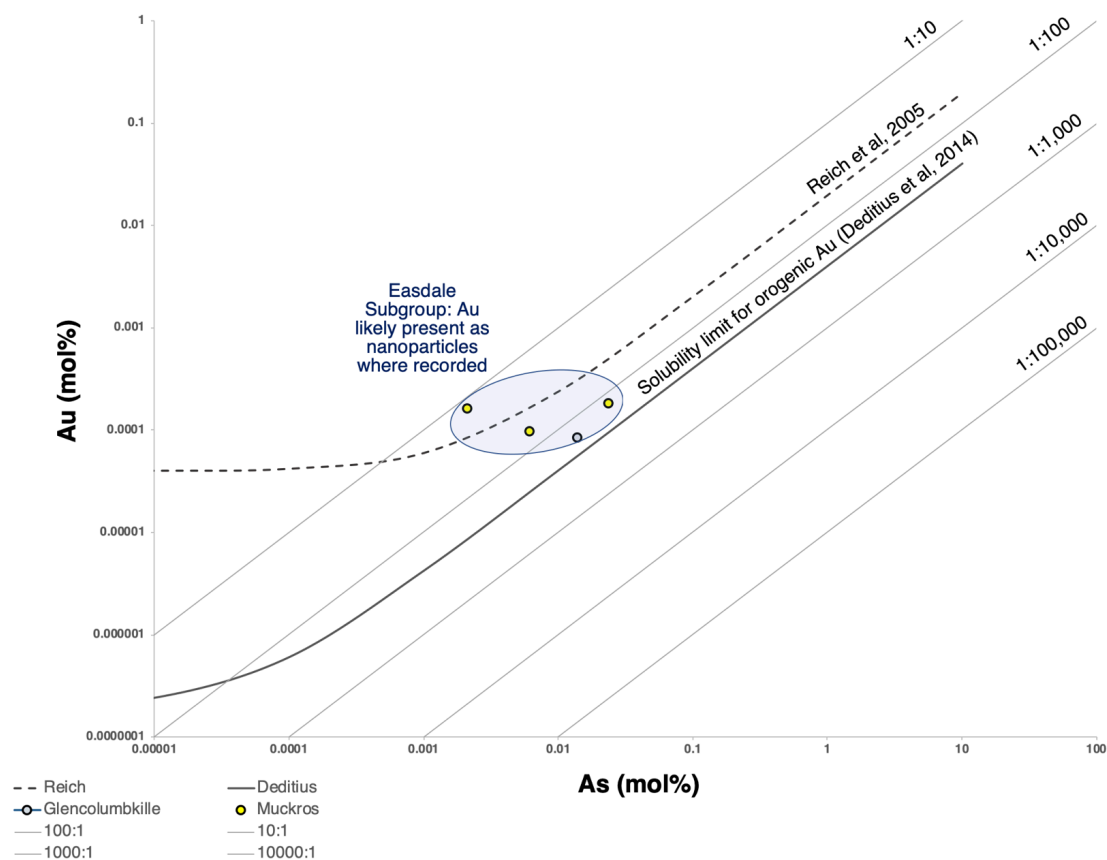


Figure 7.12. As (mol%) vs. Au (mol%) plot showing individual Laser Ablation ICP-MS analyses of pyrite where both report concentrations greater than their respective limit of detection. The Au solubility curve from Deditius et al. (2014) is shown as a solid line, while the curve commonly reported in studies by Reich et al. (2005) is shown as a dashed line. All samples in this plot (n=4) were derived from Easdale Subgroup strata (at Glencolumbkille and Muckros).

Mn and Zn peaks

Elevated concentrations (>100 ppm) are observed where the number of samples is relatively small (< 20% reporting above limits of detection) for Mn and Zn within pyrrhotite samples, and for Zn in pyrite; multiple, erratic Mn peaks are observed within ablation profiles, while single elevated peaks were observed for Zn: these may be attributed to inclusions of sphalerite.

7.6.v. Trace element correlation and ratios

For samples of pyrite (n=150), Au (n=11) demonstrates a positive correlation with Ga ($\rho=0.89$, Spearman rank), Bi ($\rho=0.68$) and Te ($\rho=0.5$); a negative correlation is observed with Ni ($\rho=-0.52$). Ag (n=93) shows an affinity for Hg ($\rho=0.88$) and As ($\rho=0.5$). A limited number of samples reporting above detection prohibits the extraction of robust additional correlations, however geochemical ‘signatures’ from pyrite (all of which are hosted within the Easdale Subgroup of the Argyll Group) may be interpreted broadly as Au-Ga-Bi(-Te) and As-Hg-Te-Ag-Sn(-W-Sb).

For Falcarragh pyrrhotite samples (n=50; Blair Atholl Subgroup, Appin Group), Co correlates positively with Mo ($\rho=0.67$) and negatively with Au ($\rho=-0.5$), Ag ($\rho=-0.46$) and Te ($\rho=-0.4$). Ni shows a positive correlation with Sn ($\rho=0.65$) and Mn ($\rho=0.5$), and a negative correlation with Mo ($\rho=-0.78$). Bi (n=34) is positively correlated with Mo ($\rho=0.89$), Pb ($\rho=0.77$) and negatively correlated with W ($\rho=-0.7$).

The average Co/Ni ratio for tested pyrite is 0.54 (n=96), with a positive correlation observed between the two elements ($\rho=0.83$, Spearman rank); individual Co/Ni ratios for pyrite at targeted localities is 0.39 for Derrylahan ($\rho=0.61$; n=39), 0.63 for Glencolumbkille ($\rho=0.73$; n=26) and 0.64 for Muckros ($\rho=0.8$; n=31) (see Figure 7.13). The Co/Ni ratio for Falcarragh pyrrhotite is 0.25 (n=50), recording a negative relationship in Spearman rank pairing ($\rho=-0.38$). Pyrrhotite values cluster in Co-Ni space while pyrite values show dispersal proximal, but principally below, the Co/Ni = 1 line. No results report >1 for pyrrhotite, while for pyrite, 1 from Derrylahan (3%), 6 from Glencolumbkille (23%) and 5 from Muckros (16%) have Co/Ni >1. Results from the Glencolumbkille locality show a separation in Co-Ni space between those broadly >1,000 ppm and <1,000 ppm Ni. This may be attributed to grain zonation between Py₁ and Py₂ observed during petrographic phase of this study (see Figure 7.7).

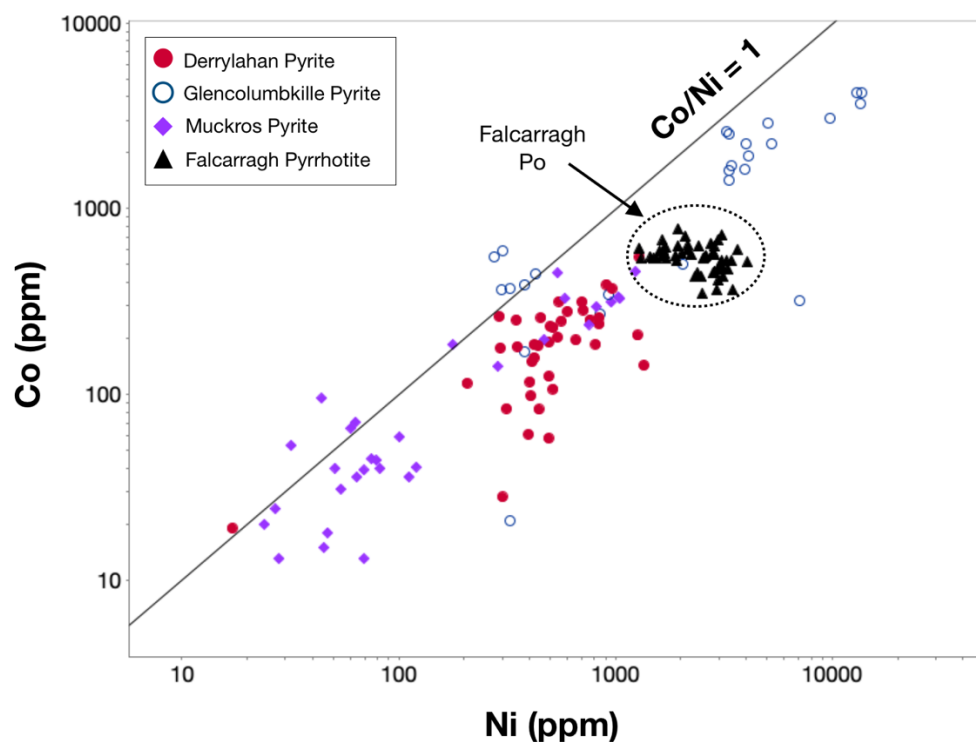


Figure 7.13. Plot of Co vs Ni for tested sample populations of pyrite and pyrrhotite ($\rho = 0.87$, Spearman rank; $n=146$ where a value reports above detection for both analytes). Two populations are inferred from data from Muckros and Glencolumbkille pyrite (Slieve League Formation; Easdale Subgroup), while tight clustering is observed for Derrylahan pyrite (Termon Pelite; Easdale Subgroup) and Falcarragh pyrrhotite (Blair Atholl Subgroup). It is proposed that Co/Ni ratios may be used as a discriminator for regional sulphide signatures.

For selected trace element ratios (see Figure 7.14), abundances of trace elements recorded from samples of pyrrhotite are demonstrably elevated, with the exception of Co/Ni, Co/Bi and Pb/Bi, where pyrite from Glencolumbkille exhibits higher abundances. Average ratios are Co/Ni = 0.25 ($n=50$), Co/Bi = 83.8 ($n=34$), Pb/Bi = 7.61 ($n=31$); additional ratios using limited results greater than detection include Au/Ag = 1.35 ($n=2$), Au/Te = 0.18 ($n=2$).

7.6.vi. Summary

Au results suggest the presence of Au^0 nanoparticles which may cluster to form micro-scale particles observed within output signals, while trace element associations are

recorded as correlative geochemical signatures. Data suggest that trace elements were mobile synchronous with deformation of the orogen.

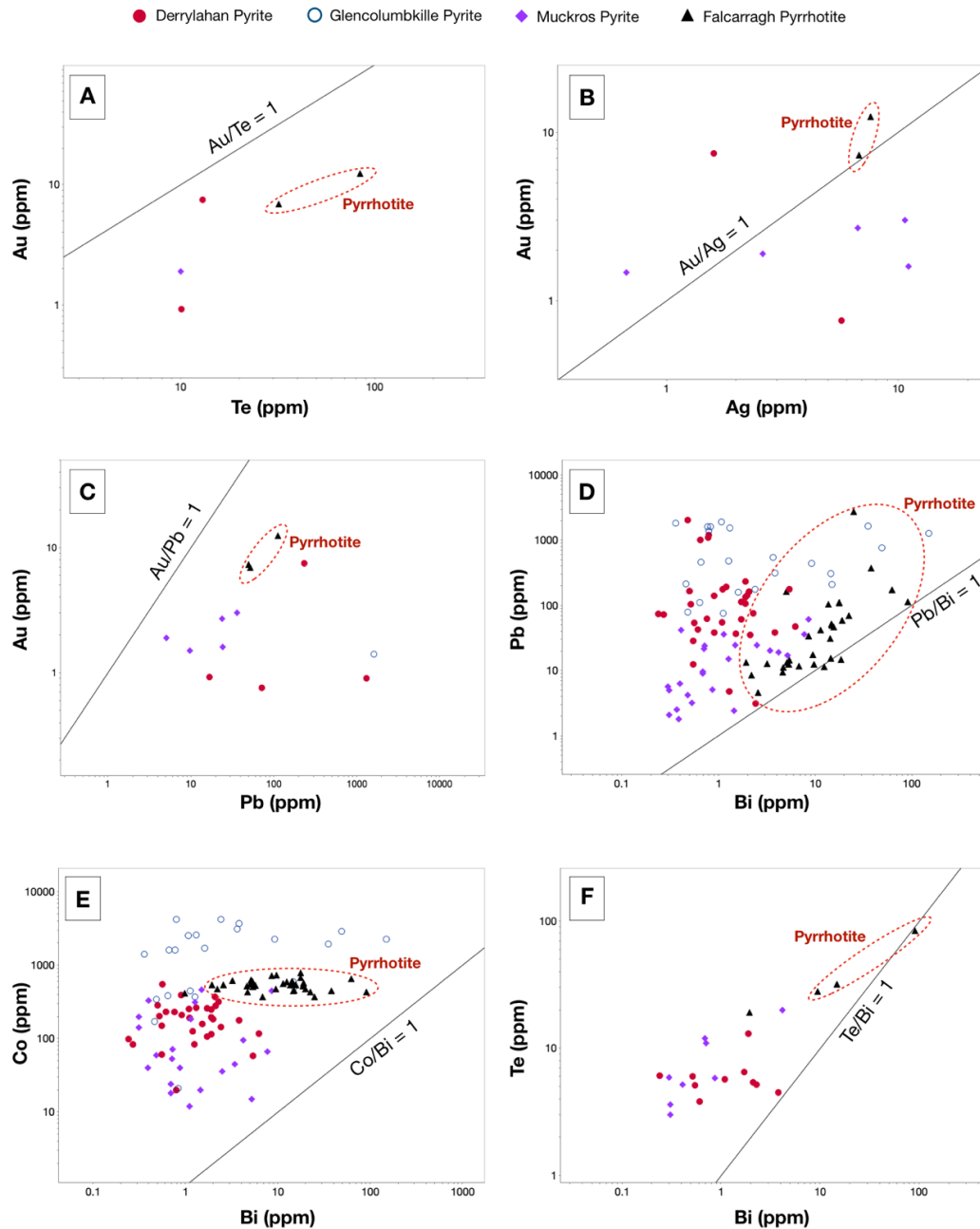


Figure 7.14. Trace element ratios: (A) Au/Te ($\rho = 0.8$, Spearman rank; $n=5$); (B) Au/Ag ($\rho = 0.23$; $n=9$); (C) Au/Pb ($\rho = 0.049$; $n=13$); (D) Pb/Bi ($\rho = 0.12$; $n=110$); (E) Co/Bi ($\rho = 0.47$; $n=108$); (F) Te/Bi ($\rho = 0.56$; $n=22$). Pyrrhotite result fields are shown using dashed ellipses.

7.7. Laser Ablation ICP-MS element raster mapping

Semi-quantitative raster element mapping was conducted on two grains of pyrite using Laser Ablation ICP-MS, to elucidate the distribution of elements of interest within and between sulphide generations. Py(x-) designations hitherto provided are chosen based on petrographic and geochemical interpretations. The analyte suite selected was determined based on consultation with the literature, synchronicity with geochemical work in this and previous chapters of this thesis, and avoidance of possible interference with carrier gasses, particularly O, Ar and He; analytes chosen and presented are ^{55}Mn , ^{57}Fe , ^{59}Co , ^{60}Ni , ^{63}Cu , ^{67}Zn , ^{71}Ga , ^{75}As , ^{77}Se , ^{107}Ag , ^{118}Sn , ^{121}Sb , ^{125}Te , ^{182}W , ^{197}Au , ^{202}Hg , ^{205}Tl , ^{208}Pb and ^{209}Bi . It was decided to focus on samples from the Glencolumbkille locality as host to pyrite-bearing rocks at the greenschist-amphibolite boundary (e.g. Anderson, 1953) acquired on the Slieve League Peninsula, hypothesised by previous workers as a mid-crustal ‘root zone’ at the core of the Grampian orogen itself (Alsop et al., 2001) and hence a feasible metal source region for orogenic systems. These samples belong stratigraphically to the Slieve League Formation of the Easdale Subgroup, constituent of the Argyll Group (Dalradian Supergroup).

The two targeted grains of pyrite exhibited different morphologies in earlier petrographic work. The first presented, ‘Target 1’ (see Figure 7.15), is porous, and contains a central core area which has a trapezoidal shape (designated Py₁), overgrown by a pyrite phase characterised by oscillatory zonation (Py₂), revealed by inclusion trails aligned to the overall schistosity, and dissolution textures which may be attributed to fluid interactions. This grain was examined using optical microscopy and EDS/EDX analyses, presented in Figure 7.7. A second grain, ‘Target 2’ (see Figure 7.17), was selected as its morphology is strikingly different; a comparable core region to the first tested porphyroblast is visible (Py₃), however the euhedral overgrowth (Py₄) lacks any visible evidence of syn-deformational structural deformity, indicating that it is relatively the latest observed phase. Comparing the overall results of Laser Ablation ICP-MS analyses on both target porphyroblasts, they both broadly show core regions depleted

in analysed trace elements, while outer regions (overgrowth phases) demonstrate relative enrichments.

For Target 1 (Figure 7.15), the core, defined as Py_1 is characterised by relatively elevated As and Se (when compared with outer zone, Py_2) and a heterogeneous distribution defining two internal zones. Py_1 overall shows a median As enrichment of 219 ppm ($2\sigma = 23$ ppm), and of 46.7 ppm ($2\sigma = 3$ ppm) for Se. A central zone within this core, is revealed which records a relatively elevated As abundance of 508 ppm ($2\sigma = 52$ ppm), while an outer zone registers an As median value of 130 ppm ($2\sigma = 9$ ppm). Py_1 overall is mostly devoid of trace element enrichment, with the exception of As (>100 ppm) and Se (>50 ppm); the rim of Py_1 is enriched in Co ($>1,000$ ppm), Ni (>100 ppm), Zn (>10 ppm), Ga (>5 ppm) and Bi (>100 ppm). The overgrowth exhibiting deformation textures, Py_2 , is characterised by relatively elevated concentrations of Co ($>1,000$ ppm), Ni (>100 ppm), Cu (>10 ppm), Zn (>10 ppm), Ga (>3 ppm), As (>10 ppm), Se (>30 ppm), Ag (>1.5 ppm), Sn (>1 ppm), Sb (>10 ppm), Te (>6 ppm) and W (>0.1 ppm) in specific internal sub-zones, Tl (>1 ppm), Pb (>100 ppm) and Bi (>100 ppm). Co, Ni, Zn, Se, Sb and Bi concentrations are clearly observed to oscillate cyclically with progressive growth. The outer rim of the porphyroblast itself (of Py_2) is characterised by elevated Co, Ni, Zn, Ga, with relatively depleted As, Ag, Sb and Te. Au is depleted across the entire porphyroblast, with highly localised concentrations >0.2 ppm providing only sparse evidence of gold particles: where identifiable, Au is coincident with the rims of Py_1 and of internal zones within Py_2 , areas most identifiable by Te and Ag enrichment. This supports findings in LA ICP-MS spot analyses where one Au analyses reported above the limit of detection (1.40 ppm; Table 7.5). Hg also shows minor relative enrichments, with values >1 ppm observed to have a spatial relationship with the boundaries of the two principle generations Py_1 and Py_2 . The heterogeneous distribution of trace elements within Py_2 (e.g. Co, Ni, Bi) suggesting cyclical zonation is supported by examination of transect output signals (Figure 7.16) and may be interpreted as episodic enrichment coincident with development of the entrained schistosity.

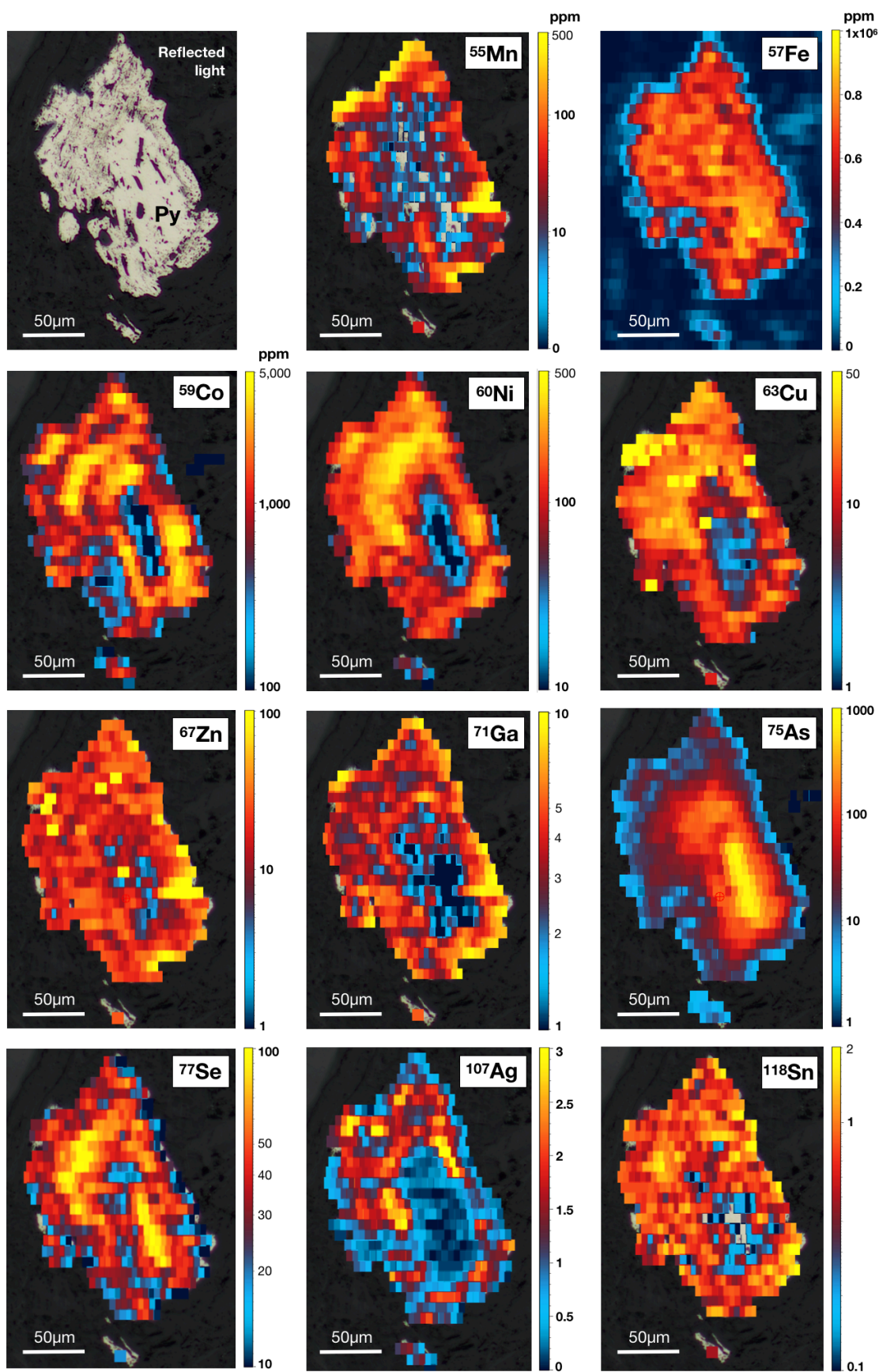


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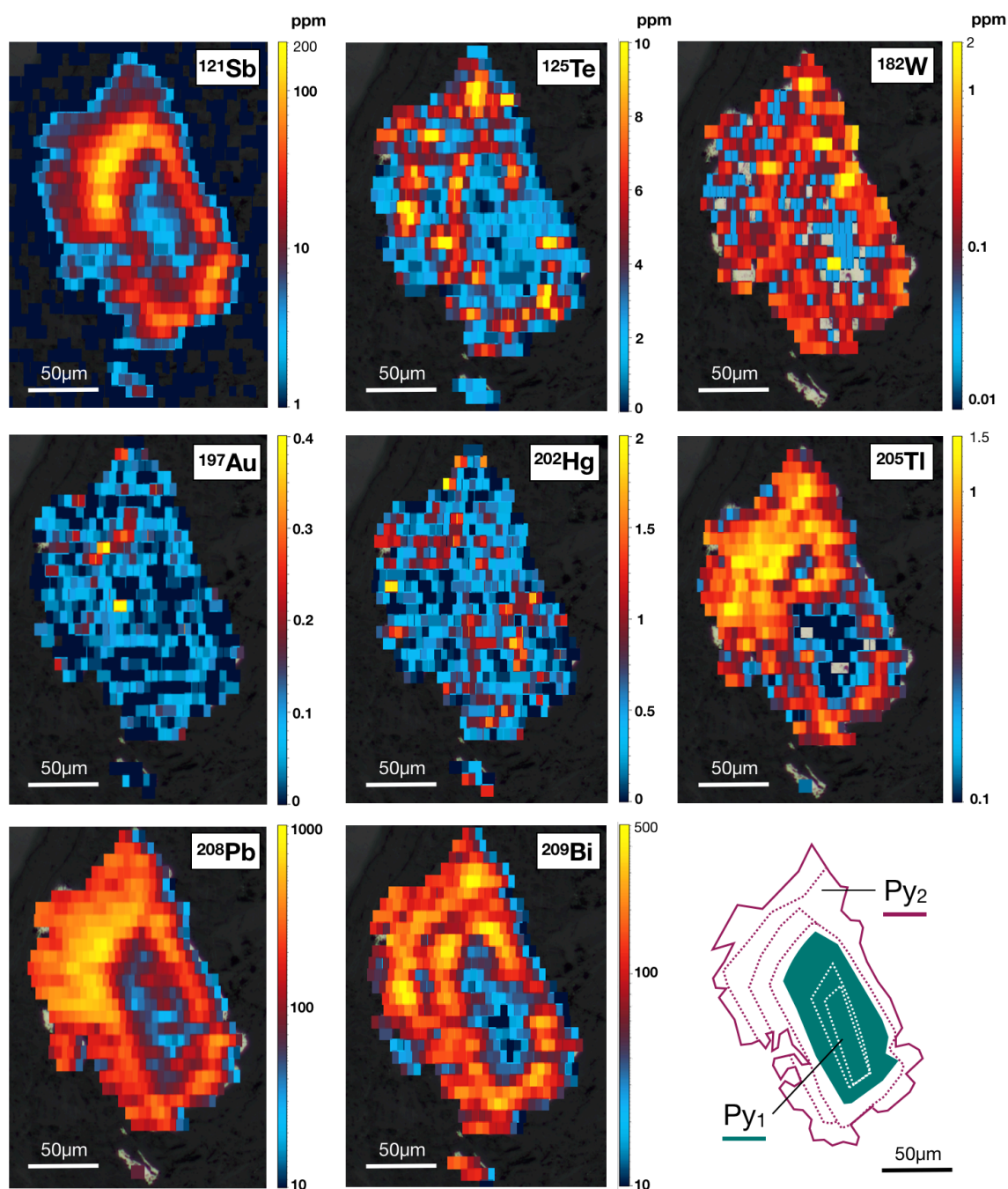


Figure 7.15. Laser Ablation ICP-MS raster element maps with concentrations reported in parts per million (ppm) for an identified pyrite porphyroblast (“Target 1”) hosted by the Slieve League Formation (Easdale Subgroup) within sample D-GC-19/01. A schematic of identified growth zones is presented for reader navigation: Py_1 (green), Py_2 (white), internal cyclical zones (dashes), grain rim (purple line).

For Target 2 (Figure 7.17), the core (Py_3), identifiable by its porosity in microscope imaging, is depleted in trace elements with the exception of Tl which shows elevated concentrations >10 ppm, and As >1 ppm (this is a difference with the core (Py_1) of “Target 1” where Tl values are < 0.35 ppm). The outer euhedral overgrowth of the grain, designated Py_4 (as it is the last phase)

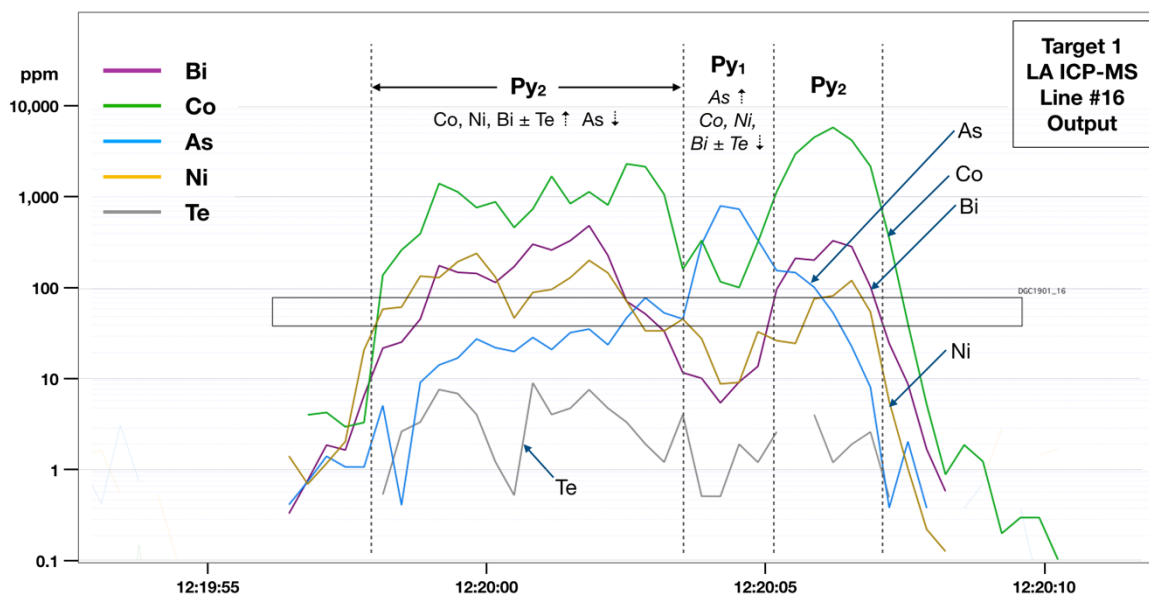


Figure 7.16. Output ICP-MS signals following data reduction using Iolite for Target 1 pyrite grain (Glencolumbkille locality; Easdale Subgroup; sample D-FC-19/01). Relatively elevated of As at concentrations >100 ppm within Py₁, while trace elements are generally depleted. Overgrowth Py₂ is relatively enriched in trace elements (Co, Ni, Bi and Te are shown in this selection) with lower As concentrations. Zonation of Co is evidenced from oscillations in the Py₂ output signal, suggesting episodic fluid interaction synchronous with fabric development.

has an overall homogenous appearance and shows neither cyclical zonation nor internal chemical inhomogeneity. This overgrowth is relatively enriched in Co (>4,000 ppm), Ni (>1.5 wt.%), Cu (>100 ppm), Se (>150 ppm), Sb (>1 ppm) and Pb (>1,000 ppm). The outer rim of the porphyroblast is relatively depleted in Co, Ni, Sb, Tl and Pb, while enriched in Mn, Zn, Ga, As and Bi, which itself is also observed along the outer rim of internal Py₃. Minor localised enrichments are observed within the grain overall for Zn, Sn, Te and Hg. Te is enriched along one crystal face of the overall porphyroblast at concentrations >2 ppm. Au is depleted across the entire porphyroblast with the exception of pixel-scale observable high values >0.15 ppm confined to the boundary of the grain.

Within previous Laser Ablation ICP-MS spot analyses, the limit of detection for Au was determined to be 1.29 ppm for ¹⁹⁷Au (min., 0.33 ppm; max., 3.9 ppm), while for LA ICP-MS raster element mapping using line transects, the limit of detection was 0.76 ppm (min. 0.036

ppm; max., 16 ppm) for the two experiments. This difference is a potentially useful observation when considering the distribution of low Au results as indicative of the presence of particles.

While results using LA ICP-MS methods do not support Glencolumbkille specifically as a likely source area for Au, LA ICP-MS spot analyses provide a useful indicator of trace element mobility broadly for syn-deformational pyrite, and raster element mapping reveals a distinction between early trace-element poor pyrite and later phases of enrichment synchronous with development of fabrics, indicating a relationship between fabric development and trace element mobility.

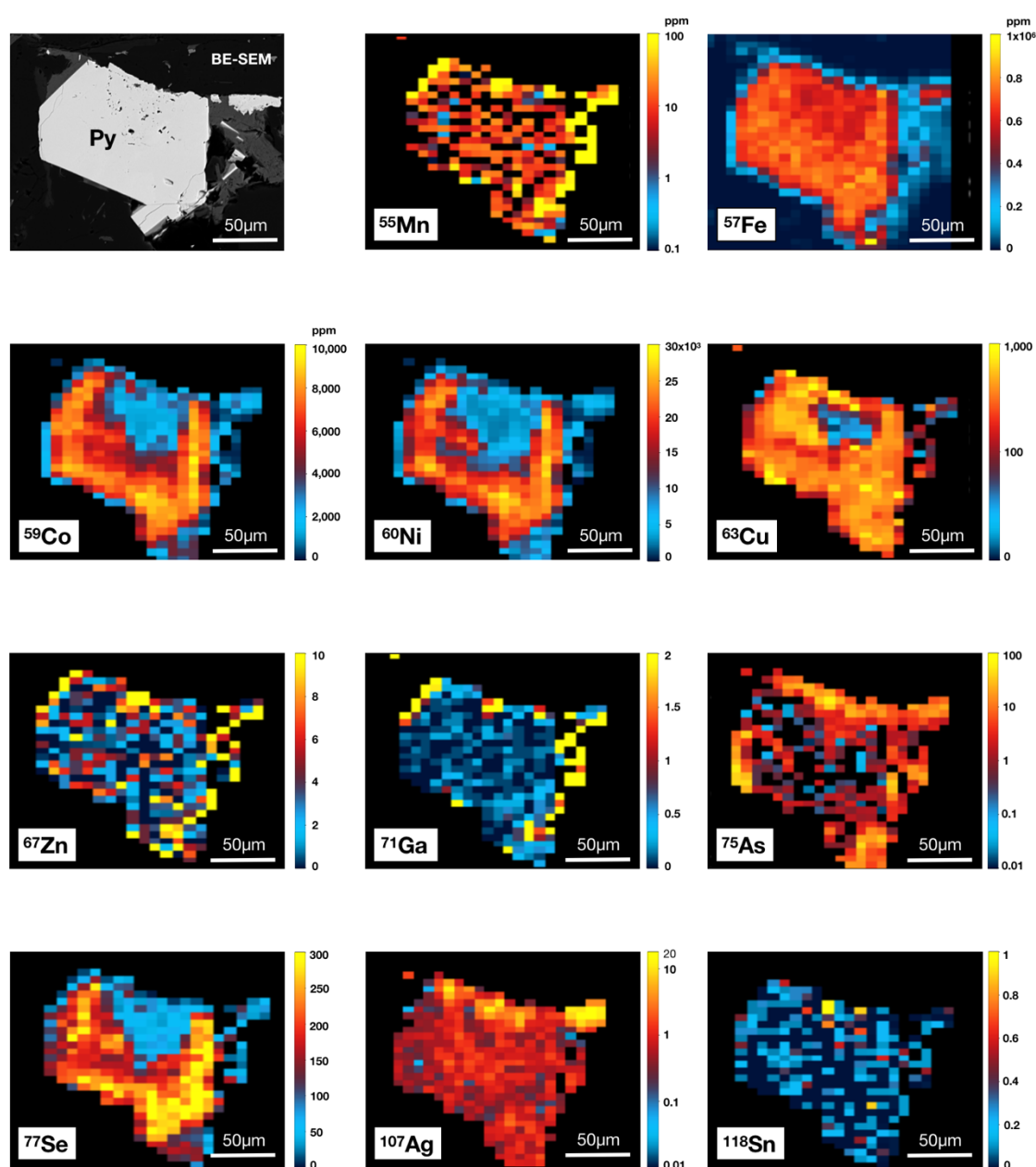


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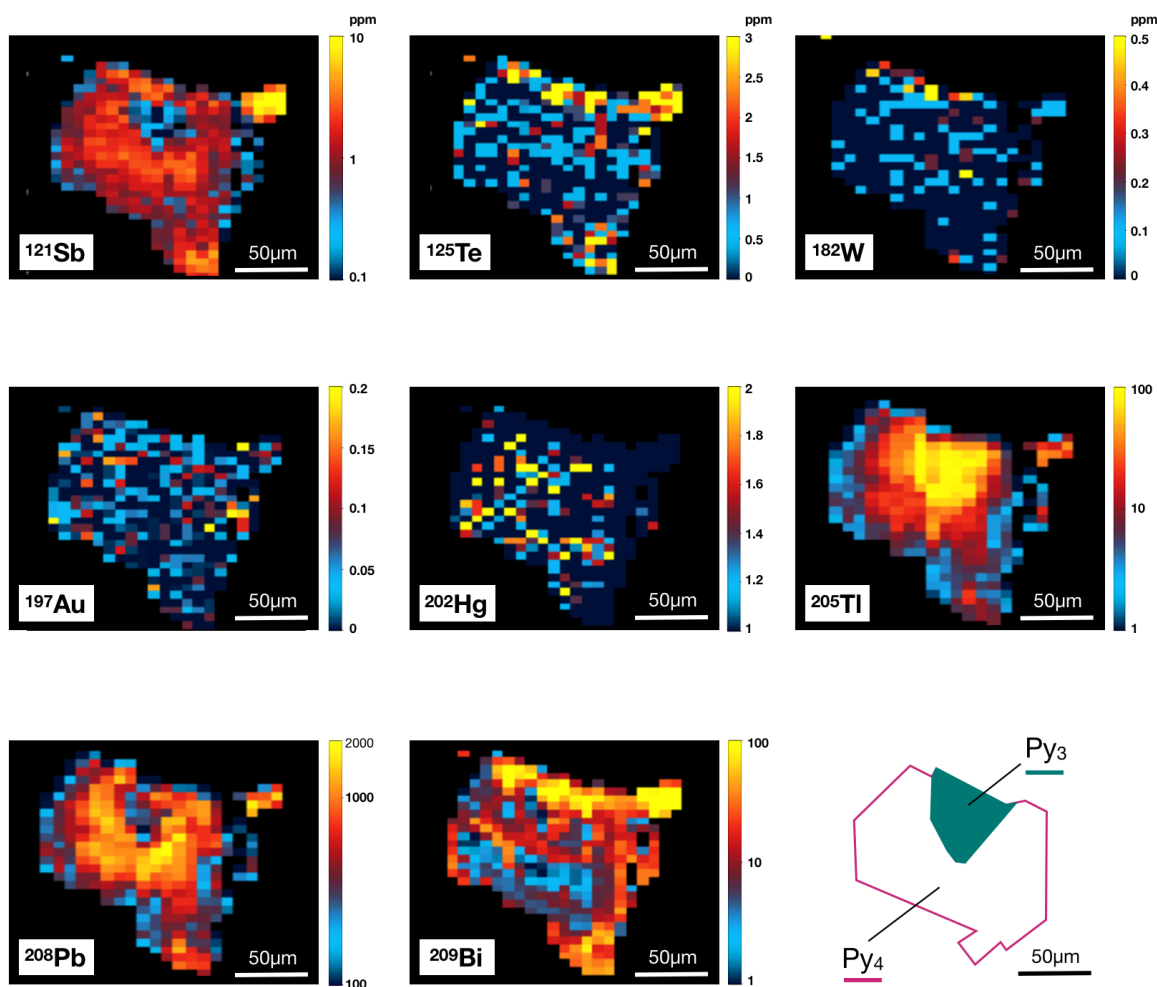


Figure 7.17. Laser Ablation ICP-MS raster element maps of a euhedral porphyroblast from the Glencolumbkille locality (Target 2; sample D-GC-19/02a).

7.8. Discussion

7.8.i. Overview

Work presented in this chapter was planned to test possible sources of Au in the north-west of Ireland which this study hypothesises were mobilised contemporaneously with the Ordovician Grampian arc-continent collision (e.g. Rice et al., 2016), forming deposits at localities including Curraghinalt in County Tyrone, and others along a SW-NE trend that continues into Scotland. The Grampian event comprised multiple phases of deformation of the margin of the Laurentian palaeocontinent, recognisable in formations in north-west Europe and the east of North

America (e.g. Kennedy, 1979; Kennedy, 1975). Metamorphism in active orogens during such episodes of deformation can drive the mobility of metals and associated elements in fluids: for example, mobile Au has been observed to have an association with As, Hg and Sb in active orogens such as the Southern Alps of New Zealand (Pitcairn et al., 2014).

Gregory et al. (2015) have revealed that within orogenic terranes, As, Ni, Pb, Cu and Co have the highest median abundances in sedimentary pyrite (100-1,000 ppm), followed by Mo, Sb, Zn and Se at abundances of 10-100 ppm, while Ag, Bi, Te, Au (and Cd) tend to lie in the 0.01 – 10 ppm range. As, Ni, Co, Sb, Se and Mo ('Group 1' elements) tend to be incorporated within the structure of pyrite or are present as nano-inclusions; Bi, Pb, Ag, Au, Te and Cu ('Group 2') show high variability and may occur as micro-inclusions, while Zn and Cd ('Group 3') are almost entirely present as micro-inclusions of sphalerite. Examining the contents of metals and trace elements hosted by pyrite in such settings may provide insight into the availability of those elements for remobilisation in metamorphically driven fluids.

The objectives of this work have been firstly to test pyrite and pyrrhotite within horizons of the Appin and Argyll Group of the Dalradian Supergroup as a potential source of Au and associated elements through microanalytical study of grains (using techniques such as Laser Ablation ICP-MS), and secondly to consider processes which may have been active during orogenesis which may have driven the mobilisation and subsequent transport of metals. Geochemical results have included 150 in-situ analyses of pyrite from the Argyll Group, and 50 analyses of pyrrhotite from the Appin Group, both within the Dalradian Supergroup and at localities in County Donegal to the north-west of known Au occurrences and at deeper stratigraphic levels.

7.8.ii. Appin Group pyrrhotite

Results suggest that the Appin Group was a likely source of metals for orogenic gold deposits, for two reasons: (i) the presence and morphology of pyrrhotite within the carbonaceous shales is indicative of pyrite to pyrrhotite conversion reactions, such reactions will have released significant trace metals in fluids; and (ii) geochemical findings demonstrate retention of certain elements (e.g. Co, Ni and Bi), mobilisation of others into inclusions (e.g. Zn) and depletion in other elements relative to expected abundances that may be anticipated in precursor diagenetic pyrite (e.g. Gregory et al., 2015).

Pyrrhotite is observed in pelitic samples of the Lower Falcarragh Pelite Formation, belonging to the Appin Group (lower-to-mid Dalradian Supergroup), while no pyrite was encountered locally. Grains are xenomorphic and display evidence of recrystallisation of rims exhibiting coincident Mg, Si and Fe (see Figure 7.8). This evidence suggests porphyroblasts pre-date a later phase of silicification which may be linked to metamorphism associated with the development of Grampian fabrics. Porphyroblasts are irregularly shaped and aligned to a weak fabric; Hutton and Alsop (1995) suggest that this fabric likely corresponds to a regional foliation S_2 . In Laser Ablation ICP-MS spot analyses of pyrrhotite, only 3 of 50 analyses reported above detection for Au, which itself was an average of 13.9 ppm. This limit sets a high threshold for reporting of concentrations; however, results do indicate that a modest amount of Au was mobile contemporary with their development or transformation from pyrite to pyrrhotite at the greenschist-amphibolite facies transition. That Au results are rare but elevated upon detection (median = 7.30 ppm; IQR 6.90 – 12.4 ppm; $n=3$) suggests that Au is present as Au^0 nanoparticles rather than as a refractory Au^{1+} phase within the crystal lattice. This was tested through examination of output signals, which show that Au presents as peaks (with coincident Ag) rather than continuous smooth profiles (see Figure 7.11). While the average concentrations of most elements were higher in samples of pyrrhotite than those in pyrite, this study has ascertained Co (median = 549 ppm; IQR = 474-606 ppm; $n=50$), Ni (median = 2,500 ppm; IQR = 1,845 – 2,985 ppm) and Bi (median = 11.9 ppm; IQR = 5.08 – 17.9 ppm; $n=34$) as the only analytes

demonstrating meaningful relative enrichment, through comparison with pyrite analyses of the proportion of results above respective limits of detection (see Figure 7.10 and Table 7.3). A key observation from this phase of work is that Co, Ni and Bi are retained within the crystal structure of pyrrhotite (following hypothesised pyrite to pyrrhotite conversion), certain trace elements are depleted (Cu, Tl, Pb), while others form discrete sulphide phases (e.g. Zn in sphalerite). No individual results of As, Se or Hg reported above detection for pyrrhotite; according to Gregory et al. (2015), arsenic would lie in the 100-1,000 ppm range in precursor diagenetic pyrite, Se would be expected in the 10-100 ppm range. It is therefore suggested that these have been liberated into metamorphic fluids during conversion, along with Au and other trace elements, e.g. Te which is not present as abundant inclusions or lattice-bound concentrations within pyrrhotite.

7.8.iii. Argyll Group pyrite

At Glencolumbkille on the Slieve League Peninsula, within a structurally defined ‘orogenic root zone’ (Alsop et al., 2001) proximal to the greenschist-amphibolite transition, mapped by Anderson (1953) and confirmed in petrographic work in this study, this research finds porphyroblasts of pyrite which exhibit simple and oscillatory chemical zonation. The first recognised generations belong to a relatively homogeneous internal core (Py₁) and an outer zone (Py₂) recording an entrained schistosity, confirming synchronous growth with a significant phase of deformation. Internal cores are shown using Laser Ablation ICP-MS raster element mapping to be relatively depleted in trace elements, only recording elevated concentrations of As (>100ppm) and Se (>50 ppm). The balance of trace elements tested, with the exception of Au and Hg, show relative enrichment with Py₂ and oscillatory zonation, particularly of Co and Ni. Chlorite alteration of garnet observed within the matrix of samples (supported by the euhedral morphology of Py₄ at Glencolumbkille) confirms that these formations were subject to retrograde conditions subsequent to a period of intense deformation forming multiple fabrics.

The lack of deformation textures entrained within Py₁ suggests that this phase was early, and not associated within the main schistosity.

Average abundances were extracted from regions of interest corresponding to phases Py₁, Py₂, Py₃ and Py₄ using Monocle, an add-on script for the Iolite data reduction software (Petrus et al., 2017). Plotting this data in logarithmic space (Figure 7.18) along with mean and median abundances of spot data acquired for Glencolumbkille pyrite in the previous section (n=50).

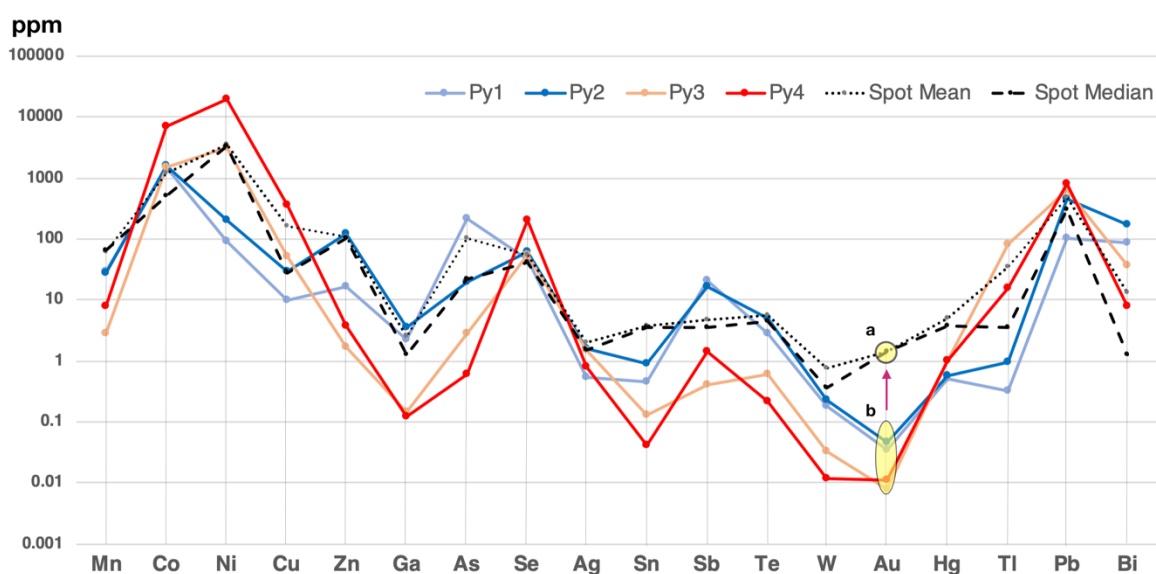


Figure 7.18. Plotted mean abundances for pyrite phases Py₁-Py₄ extracted from spatially defined regions of interest using the Monocle add-on script for Iolite (Petrus et al., 2017), shown alongside mean and median abundances for analytes within Glencolumbkille pyrite acquired using Laser Ablation ICP-MS spot analyses (n=50).

Two key observations are made: (i) that largely undeformed Py₃-Py₄ porphyroblasts demonstrate generally lower overall trace element concentrations than earlier Py₁-Py₂ porphyroblasts, and (ii) that abundance of Au acquired during Laser Ablation ICP-MS spot analyses (c. 1 ppm) lies one to two orders of magnitude higher than all concentrations observed within mapped regions of interest (c. 0.1 ppm for Py₁-Py₂ porphyroblasts and 0.01 ppm for Py₃-Py₄ porphyroblasts). This

second observation possibly provides evidence that Au is dominantly present within Glencolumbkille pyrite as Au^0 nanoparticles, skewing the overall recorded abundance, rather than being more uniformly distributed as refractory Au^{1+} within the mineral lattice of pyrite. A ‘trend’ toward the solubility limit in Au-As space (see Figure 7.19) is revealed through the extraction of quantitative information from LA ICP-MS raster element maps; this information supports the hypothesis of Au^0 nanoparticle liberation with the precipitation of successive pyrite generations (Py_1 to Py_4). The euhedral morphology of Py_4 (see Figure 7.17) suggests that it is retrograde, the average ratio of Au/As for this phase plots above the solubility curve Figure 7.19), supporting this hypothesis.

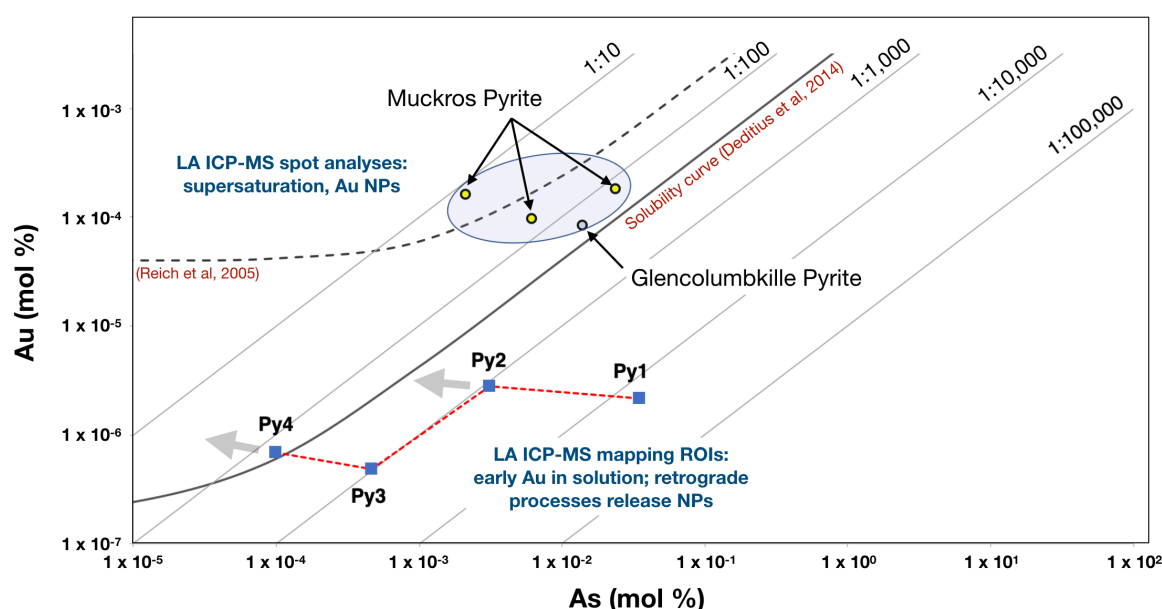


Figure 7.19. Au (mol%) / As (mol %) plot showing individual Laser Ablation ICP-MS spot analyses of Easdale Subgroup pyrite from Muckros ($n=3$) and Glencolumbkille ($n=1$) (circles) plotting above the Au solubility curve of Deditius et al. (2014), and average abundances of Au and As from regions of interest retrieved from Laser Ablation ICP-MS element raster mapping of pyrite grains at Glencolumbkille using Monocle; average values for Py_1 , Py_2 and Py_3 plot below the solubility curve, while Py_4 plots above it. Applying trajectory arrows between Py_1 and Py_2 (characterised by entrained deformation fabrics), and between Py_3 and Py_4 , trends are observed towards the solubility curve and supersaturation, consistent with retrograde metamorphism. While Laser Ablation ICP-MS spot analyses report individual analyses in the Au^0 nanoparticle field, the use of Monocle allows this study to account for distribution across a larger spatially defined region than single ablation pits, limiting the effect of individual particles and revealing (i) low levels of Au^{1+} in solution, (ii) relatively elevated Au within Py_1 - Py_2 porphyroblasts compared with Py_3 - Py_4 porphyroblasts and (ii) retrograde trends toward a supersaturation scenario.

7.8.iv. Genetic model for Au and trace element mobility

The proposed model for Au and trace element mobilisation from carbonaceous shale horizons within the Appin and Argyll Groups draws on observations within this study, research of shale hosted pyrite geochemistry by Thomas et al. (2011), Large et al. (2012) and Gregory et al. (2015), of gold particles and transport complexes by Deditius et al. (2014) and Pokrovski et al. (2014), of the role of metamorphism by workers including Pitcairn et al. (2014), and regional geological insights into stratigraphy, structure and deformation by Alsop et al. (2001), Chew et al. (2009b) and Rooney et al. (2011) among others referenced.

Early syn-sedimentary pyrite formed progressively during basin development and deposition of shallow to deep marine turbidite sequences which form Appin and Argyll Group carbonaceous shales. Thick sedimentary successions were deposited between the Neoproterozoic and the early Cambrian, and are principally exposed in Caledonian terranes from western Ireland to the Shetland Islands (Rooney et al., 2011). While diagenetic pyrite forms within the Appin Group are not directly observed, tested grains record high contents of Co and Ni, with a Co/Ni ratio of 0.29 (using a ratio of median values) which if recorded within precursor pyrite would be suggestive of a diagenetic sedimentary signature (Loftus-Hills and Solomon, 1967); this may be reconciled with the seafloor sedimentation models of Thomas et al. (2011) and Large et al. (2012). Mobile Au⁰ nanoparticles and associated trace elements are concentrated within these pyrites during diagenesis. During the Grampian collision of the outboard island arc with the eastern margin of Laurentia, these formations were deformed and uplifted, with resultant metamorphism reaching upper-greenschist facies conditions. At the greenschist-amphibolite transition, pyrite-pyrrhotite conversion reactions may take place as evidenced in thin sections from the Appin Group. This would be facilitated by high fluid-rock ratios, with fluids permeating brittle fractures within the Appin, Argyll and overlaying Southern Highland Group, including regional scale D₂ thrust and nappe structures. During this period, outer pyrite rims form on early forms within tested formations of the Argyll Group (evidenced in Py₂ at Glencolumbkille) which record relative enrichments of trace elements; an entrained

schistosity in Py₂ growths confirm element mobility synchronous with prograde deformation. Extensive quartz vein networks across the Appin and Argyll Groups are evidence of extensive fluid flux within fracture pathways related to rock inhomogeneity and rheological differences. D₁-D₃ NNW-SSE oriented lineations between Falcarragh and the Sperrin Mountains and synchronous E-W lineations from the Slieve League Peninsula toward this region could act as a pathway network which suggests that these localities are potential metal sources for orogenic gold deposits of the Sperrins Inlier.

7.8.v. Trace element incorporation into sedimentary pyrite

The process of Au concentration in north-west Ireland is likely to begin during the Neoproterozoic with an initial concentration of trace elements within diagenetic pyrite in a marine environment associated with turbiditic sedimentation within the Dalradian basin, predating the Grampian arc-continent collisional orogeny by >100 Myr. As described in *Chapter Three*, the Appin and Argyll Groups represent shallow-to-deep marine turbiditic environments, and in such a context the crystallisation of pyrite is likely to have occurred. Large et al. (2009), citing previous workers (Folk, 2005; Schieber, 2002; Scholz and Neumann, 2007) describe a process by which trace elements (Zn, Cu, Cd, V, Cr, Co and As) are incorporated into pyrite forming within a few millimetres of the seafloor surface as a result of depletion of oxygen and biogenic activity and sulphate-reducing bacterial activity. These elements are released from sedimentary clasts before and during reduction. Within orogenic and Carlin type sediment-hosted deposits, their own research found that diagenetic pyrite (which may form the cores of compositionally zoned porphyroblasts) records elevated Au along with As, Ni, Pb, Zn, Mo, Te, V and Se. Fine-grained framboidal forms have an association principally with low-temperature pyrite forming <150°C, while such morphologies are less common in hydrothermal and metamorphic fluids >200°C.

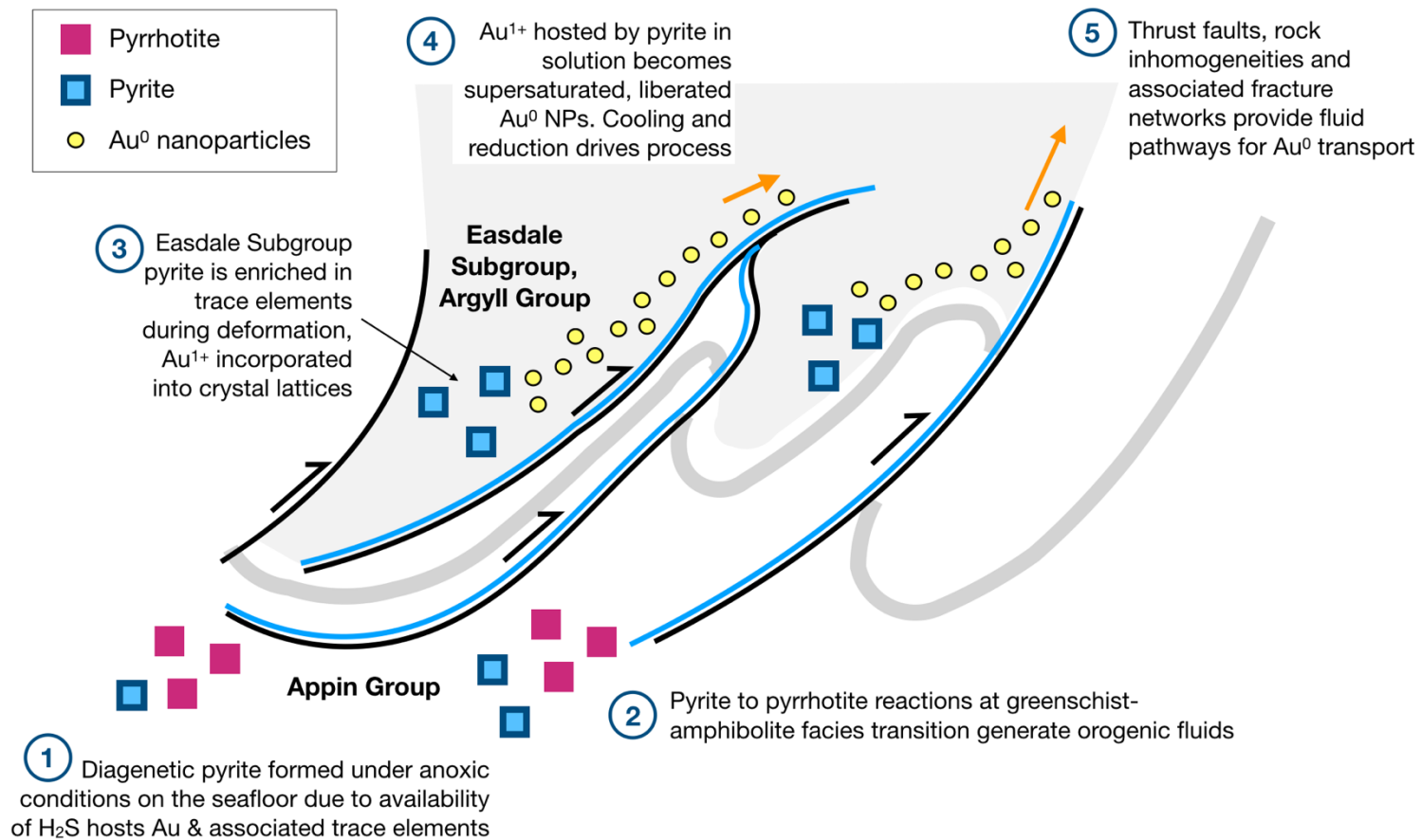


Figure 7.20. Model of Au and trace element mobilisation at the transition from greenschist to amphibolite facies in Appin & Argyll Group strata

Framboidal pyrite was not encountered in this study within tested samples of the Appin and Argyll Groups. Within Appin Group samples (the oldest tested strata), xenomorphic pyrrhotite showing evidence of recrystallised rims is encountered likely converted from earlier pyrite that may have included framboidal morphologies. LA ICP-MS analyses (n=50) of pyrrhotite grains record elevated concentrations (>100 ppm) of Mn and Zn, while a higher proportion of Co, Ni and Bi results reported above detection than in tested samples of pyrite from the Argyll Group, providing an indication of their relative abundance in the former unit. While not strictly applicable to pyrrhotite, a Co/Ni ratio of 0.29 (as aforementioned) may be an indicator of a diagenetic origin assuming retention of element abundances within the crystal lattice. 150 LA ICP-MS spot analyses of pyrite (without regard to individual zonation) from the Argyll Group demonstrate elevated contents of Co, Ni (>100 ppm) and Pb (>150 ppm), with pyrite recording an average Co/Ni signature of 0.54 (n=96) which may be considered demonstrative of a diagenetic component (Co/Ni <1; Large et al, 2009).

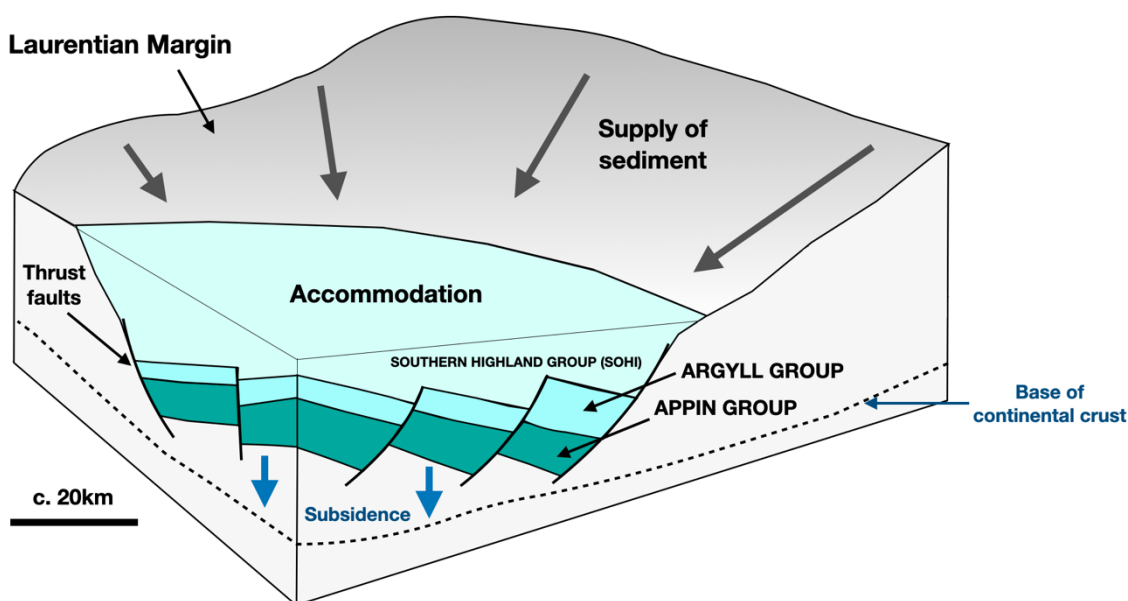


Figure 7.21. Schematic model for Neoproterozoic-Cambrian Dalradian basin sedimentation. The Laurentian margin acts as a source of sediment for the basin which records thrust faulting and subsidence.

It may be suggested based on the above data, that of trace elements which may have been concentrated into the earliest pyrite in the Appin Group based on the observations of Large et al (2009), only Co (median 549 ppm; n=50), Ni (median 2,500 ppm; n=50) and arguably Pb (median 30.3 ppm; n=36) are retained within pyrrhotite (n=50) and that concentrations of other elements which may have been incorporated into precursor pyrite (Au, As, Ni, Pb, Zn, Mo, Te, Se, Cu) were liberated into metamorphic fluids following conversion reactions at the greenschist-amphibolite boundary. Liberation of trace elements from pyrite (n=150) within the Argyll Group, also recording elevated Co (median 185 ppm; n=109), Ni (median 420 ppm; n=108) and to an extent, Pb (median 54.3 ppm; n=141) may also be inferred.

While conversion to pyrrhotite is not directly observed, evidence that these formations traversed the greenschist-amphibolite transition and subsequently retrograded to greenschist conditions is confirmed through the observation of chloritic alteration of garnet within the host formation at Glencolumbkille (the Slieve League Formation). LA ICP-MS element raster mapping has been demonstrably useful in discerning the evolution of pyrite with deformation; relatively homogeneous Py₁ at Glencolumbkille is largely depleted in tested trace elements (with the exception of As, >100ppm) relative to overgrowth Py₂ which retains an entrained schistosity observable traversing the grain and into the host rock. This observation demonstrates that synchronous with a phase of deformation, trace elements were mobile, including Co (>1,000 ppm), Ni, Sb, Pb, Bi (>100 ppm), Se (>50 ppm), Cu and Zn (>10 ppm). Great care must be exercised in the interpretations of Au signatures given the limited number of results reporting above detection in LA ICP-MS spot analyses for both Appin Group pyrrhotite (n=3 of 50) and Argyll Group pyrite (n=11 of 150), nevertheless, examination of output signals strongly suggests the presence of auriferous particles through confirmed elevated peaks coincident with Ag for both sets of analyses.

7.8.vi. Processes which mobilise Au

Pokrovski et al. (2014) note that natural processes which mobilise and concentrate Au are complex, and that they remain contentious. They observe the importance of temperature, pressure, salinity, pH and redox conditions as the key parameters controlling Au transport in solution and precipitation in hydrothermal fluids, though caution that quantitative information is largely only available for aqueous and dense ($>0.3 - 0.4 \text{ g/cm}^3$) supercritical phases. While fluids are mobile in the crust, Au redistribution and deposition is controlled by cooling, decompression, phase separation, interactions with rocks and mixing with external waters. These factors may be considered in the context of acquired qualitative observations and data.

Temperature and Au complexing

Petrographic evidence from the Appin and Argyll Group is indicative of a prograde (Appin Group) and retrograde (Argyll Group) traverse of the greenschist-amphibolite transition: (i) the presence of xenomorphic pyrrhotite in Appin Group samples which may have undergone pyrite-pyrrhotite conversion reactions and (ii) retrograding garnet within Argyll Group samples exhibiting chloritic alteration. In terms of temperature, this transition occurs at c. 500°C confirming that these conditions were attained during deformation. Peak metamorphic conditions associated with the Grampian orogenic event are recorded across the Dalradian Supergroup in Ireland and Scotland. In County Mayo, peak temperatures are considered unlikely to have exceeded 450°C (460 Ma; Rb-Sr dating of muscovite; Chew et al., 2003), while metamorphism is understood to have reached the garnet zone across the Donegal Inlier (Pitcher and Berger (1972) in Chew and Strachan (2014)). Amphibolite facies conditions are confirmed on the Slieve League Peninsula at Glencolumbkille (tested Argyll Group within Chapter 4), where garnet zone metamorphism is recorded, immediately following regional D_2 metamorphism associated with N-directed thrusting (Alsop et al., 2001). While specific peak metamorphic conditions could not be found in the literature for formations hosting tested samples of the Falcarragh locality (Lower Falcarragh Pelite Formation), information is available

from the Creeslough Succession (of which this formation lies within a tectonic slide above it) from White and Hutton (1985), who observe muscovite porphyroblasts representing this peak, also attributed to D₂. Such porphyroblasts indicate greenschist to amphibolite facies transition (Da Mommio, 2018) and therefore minimum temperatures of c. 300 °C. Contemporary theory of orogenic gold systems attributes the release of metamorphic fluids (H₂O-CO₂-H₂S) with $X(\text{CO}_2)$ close to 0.25 and the potential to carry Au and trace elements to devolatilisation reactions at the ‘critical’ greenschist-amphibolite facies transition, e.g. Phillips and Powell (2010). The solubility of Au and temperature are proportional in aqueous fluids where oxygen fugacity ($f\text{O}_2$) and sulphur are buffered by sulphide mineral assemblages including pyrite-pyrrhotite-magnetite, of which pyrite and pyrrhotite are directly observed in this study in samples of the Appin and Argyll Group; increasing temperature which would have coincided with fluid release results in changes in the dominant complex species from AuHS^- at temperatures < 200 °C to $\text{AuHS}^0 + \text{Au}(\text{HS})_2^-$ between 200 and 450 °C (to upper greenschist facies), and to AuCl^- at temperatures exceeding 500 °C, coinciding with increased Au concentrations in hydrothermal fluids from 0.001 ppm at 200 °C to >10 ppm above 500 °C (Pokrovski et al., 2014). Given that devolatilisation reactions liberating fluid occur between 420 and 520 °C (Phillips and Powell, 2010) and the aforementioned peak metamorphic conditions likely to be associated with the Appin and Argyll Groups during the Grampian collision, it is therefore conceivable that based on temperature considerations: Au was likely to have been predominantly transported by $\text{AuHS}_0 + \text{Au}(\text{HS})_2^-$ under retrograding conditions within the lower-to-mid Dalradian Supergroup as temperatures cooled (at temperatures > 400 °C and under oxidising conditions, it has been demonstrated by Zotov et al. (2018) that AuCl_2^- can account for the efficient transport of Au; while this study does not favour prodigious Cl-complexing in the tested Grampian system of north-west Ireland, it acknowledges that they may have aided Au transport at high temperatures during specific intervals where oxidising conditions may have been present).

Pressure

While pressure is not considered to be a major factor in the solubility of Au, Pokrovski et al. (2014) note that an inverse proportionality is observed, whereby increased solubility may be associated with decreasing pressure, under conditions whereby H₂S is increasingly dissolved in a fluid. Fluids generated at the greenschist-amphibolite facies transition were likely to have been of a H₂O-CO₂-H₂S composition and temperature considerations determine that HS-species was likely dominant under retrograding conditions (confirmed petrographically within Argyll Group samples at Glencolumbkille). Exhumation under retrograding greenschist facies conditions would be accompanied by depressurisation. Pressures of 9 – 11 kbar, at the high end of the scale within the greenschist and amphibolite fields, are associated with peak metamorphism in contiguous Dalradian Supergroup rocks of the SW Highlands of Scotland (Kleine et al., 2015), which may have rapidly depressurised, synchronous with rapid cooling of the orogen interpreted by Chew and Strachan (2014). H₂S-bearing metamorphic fluids, a likelihood of AuHS₀ + Au(HS)₂⁻ complexing, accompanied by rapid exhumation and depressurisation provided conditions which favoured increased Au solubility.

Redox conditions

The Neoproterozoic-Cambrian interval (800-515 Ma) within which Dalradian Supergroup basin sediments were first deposited lies within a time period (c. 800 and 400 Ma) which was characterised overall by rising atmospheric O₂ levels, the oxygenation of deep marine environments and increases in marine sulphate concentrations (Stolper and Bucholz, 2019) [it is also speculated that these conditions led to an increase in *f*O₂ levels of sources of island arc magmas]. It is proposed that Fe-rich conditions were pervasive during the Neoproterozoic, characterised by the breakup of super-continent, extensive glaciation and a ‘drawdown’ of marine sulphate following the extensive marine euxinia and the burial of pyrite during the previous billion years, when a ‘global reservoir’ of hydrogen sulphide (H₂S) was present in the deep mid-Proterozoic (1.8-1.0 Ga) ocean (Canfield, 1998; Canfield et al., 2008; Fralick and

Canfield, 2004; Johnston et al., 2010; Lyons et al., 2009; Swanson-Hysell et al., 2010 cited in Planavsky et al., 2011). Evidence is presented from the Chuar Group (>742 Ma) in Arizona (USA) by Johnston et al. (2010) of high pyrite abundances associated with dominant anoxic and ferruginous conditions, supporting a 'return' of ferruginous subsurface waters, replacing euxinia.

The growth of early pyrite in such anoxic and sulphidic conditions (e.g. during the Neoproterozoic-Cambrian Dalradian Supergroup basin sedimentation) is described by Sholtz and Neuman, 2007 (in Large et al., 2009) who refer to biogenic activity resulting in depleted oxygen in basins and uptake of trace metals into sulphide phases. It is proposed that Au was incorporated during basin sedimentation, and later remobilised during the Grampian Orogeny (Ordovician). This study suggests that this early pyrite has been converted to pyrrhotite during the Grampian event (interpreted for Falcarragh pyrrhotite examined in this study, Appin Group), with contemporary metamorphic conditions at the greenschist-amphibolite facies transition driving the release of fluids and trace metals; trace element signatures recorded in later pyrite (e.g. Py₂ at Glencolumbkille, Argyll Group) demonstrate mobility of those trace elements derived from those liberated fluids.

Environmental conditions determined by previous workers in the literature and trace element abundances in tested samples were favourable for pyrite growth, while the retention of trace elements within growth zones determined by this study (e.g. of Co, Ni and Pb, along with trace Au likely to be preserved as Au₀ nanoparticles) agrees with findings for anoxic basins by previous workers (e.g. Large et al, 2009; Thomas et al, 2011).

Anoxic conditions determined by previous workers (e.g. Dahl et al., 2013) provides supporting evidence for early mobility of Au as HS-complexes associated with deformed sediment accumulations of the Laurentian margin.

7.9. Conclusions

Petrographic and geochemical examination of pyrrhotite (Falcarragh, County Donegal; Blair Atholl Subgroup, Appin Group) and pyrite (Glencolumbkille, Muckros and Derrylahan, Slieve League Peninsula, County Donegal; Easdale Subgroup, Argyll Group) from carbonaceous shales within lower-to-mid strata of the Dalradian Supergroup, using traditional microscopy, Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS/EDX) and Laser Ablation ICP-MS techniques, reveal evidence of mobilisation of trace elements synchronous with deformation during the Grampian arc-continent collision. LA ICP-MS results presented in this chapter are considered speculative given the number of analyses reporting above limits of detection, and further analyses are recommended to fully discern trends. Nevertheless, anomalous Au values encountered in grains of pyrite in the Argyll Group indicate a significant reservoir of Au within deep sediments in lower stratigraphy of the Dalradian Supergroup: prolific quartz veining across the sequence suggests that this presents a viable source for orogenic gold deposits of north-west Ireland. Mobilisation was driven by orogenic processes and metamorphism at the greenschist-amphibolite transition; large-scale fluid release is supported by evidence of low Au contents within pyrrhotite. The observation of pyrrhotite within the Appin Group and its absence within tested samples from the Argyll Group supports a metamorphic gradient. Fluids exploited complex structural networks along orogeny-associated D₁-D₃ lineations, D₂ nappe structures and major thrusts. Bi-sulphide (HS⁻) complexes were viable carriers of Au due to the presence of anoxic conditions (leading to depleted O₂, an increase in free sulphide: S₂⁻, HS⁻ and H₂S) pervasive during Neoproterozoic-Cambrian marine sedimentation and during the early Ordovician along the Laurentian margin.

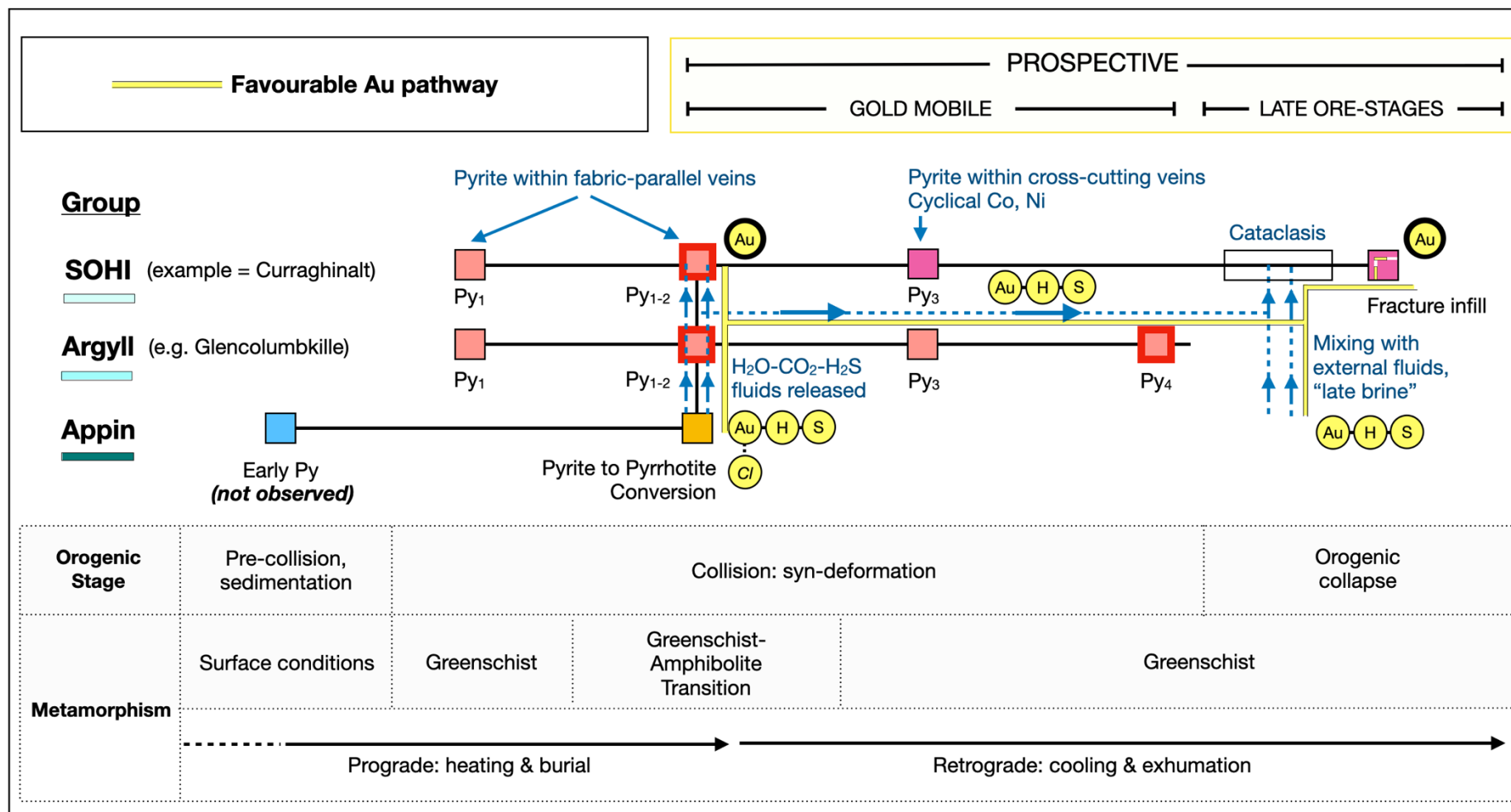


Figure 7.22. Model of theoretical ‘pathways’ for fluids and Au-complexes, in the context of tested pyrite generations, Grampian orogenic stages, metamorphism and tested Dalradian Supergroup stratigraphy. The model predicts Au prospectivity within pyrite generations synchronous with peak orogenic conditions initiated metamorphic fluid flow and the mobility of Au in HS-complexes, while late enrichments are associated with fluid mixing and the input of Au from secondary sources carried by late fluids.

Chapter Eight: Geochemical signatures and emplacement at Cavanacaw, Northern Ireland and Cononish, SW Scotland.

8.1. Abstract

Cavanacaw and Cononish are two economically important late-orogenic vein-hosted Au deposits situated within the Grampian Terrane and of regional interest to this study. Cavanacaw, while also located within the Sperrins Inlier, exhibits distinctive physical and mineralogical differences to Curraghinalt (see *Chapter Five*), while at the regional scale of the orogen, the Cononish deposit in Scotland is considered to have been emplaced later in the evolution of the orogen (c. 50 Myr following the peak of Grampian deformation), and has a noted association with Te. This chapter considers local and regional scale differences and possible relationships through a petrographic appraisal of both deposits and a limited suite of Laser Ablation ICP-MS spot analyses (n=56) on samples of Au-associated pyrite from the two deposits. Paragenetic analyses indicates that Au-associated pyrite at Cavanacaw proceeds the paragenetically subsequent to the precipitation of galena and arsenopyrite, and carries elevated Pb (median = 907 ppm; IQR = 71 – 17,875 ppm; n=6) and As (median = 1,325 ppm; IQR = 285 – 8,398 ppm; n=6). Au within this phase is present at an abundance of 3 ppm (IQR = 1.28 – 9.30 ppm; n=6); ratios of Au/As (avg., 0.009) plot dominantly below the solubility curve for orogenic systems indicating that Au is principally lattice-bound. Geochemically Cavanacaw auriferous

pyrite is statistically similar to ore-hosting pyrite from Curraghinalt (Py₃, see *Chapter Five*) for Te, Zn, Bi, Mn, Se, Sn, Ni, W, Co and Mo, while dissimilar for Ag, Tl, Ga, Cu, As, Sb, Au and Pb, suggesting there is some similarity in source reservoir.

Analyses from Cononish show that Au is present within micro-fracture infill and has a chalcopyrite association, similar to that observed at Curraghinalt (Py₃). LA ICP-MS spot analyses reveal enrichment in Cononish pyrite (Py₁) solely for Se (median = 600 ppm; IQR = 410 – 1,075 ppm; n=35), while Au is present at concentrations comparable to Cavanacaw with a median of 2.8 ppm (IQR = 1 – 45 ppm), correlating positively with ($\rho \geq 0.5$, Spearman rank) with Ag, W, Te, Hg, Sb, Pb and Cu. Au/As (avg., 17.7; n=14) ratios plot above the solubility curve: this is indicative of the formation of Au⁰ nanoparticles due to retrograde conditions. LA ICP-MS raster element mapping of a tested region of interest demonstrates that (as observed at Curraghinalt in *Chapter Five*) micro-fracture networks carrying Au are complex, and trace element enriched. Au along with Te, Co, Ni, Cu, As, Ag, Sb, Hg, Pb and Bi are observed at elevated concentrations within this network: it is proposed that two distinct enrichment events are recognised within micro-fractures: event I (Py₂; Co-Ni-As-Ag-Sb-Te-Pb-Bi) and event II (Au-Hg-Ag; synchronous with the emplacement of Cu and Sb). An association between Au, Hg and Sb at Cavanacaw could be indicative of an epizonal formation depths (greenschist facies; < 6 km), while an Au-Hg(-Sb-Te) signature at Cononish suggests that it may have formed at deeper levels (epizonal to mesozonal; < 6 – 12 km) in the crust (greenschist to amphibolite facies). Analyses by previous workers have suggested that late fluids at Cononish may be metamorphic; it is hypothesised by this study that while other types of fluids may have had a role in initial emplacement of pyrite, late fluids were an important carrier of Au, and trace elements including Te. Such late fluids are unlikely to be derived from Grampian deformation (peak c. 468 Ma) given the possible late timing of emplacement suggested by previous workers (428-425 Ma), suggesting a possible external component to the system. The Au/As trend derived from LA ICP-MS spot analyses is highly distinctive from other tested deposits in this study, supporting a late timing and a geochemically distinctive source.

8.2. Introduction

Cavanacaw is an active mine located approximately 5 km SW of Omagh in County Tyrone, Northern Ireland (Earls et al., 2003; Phelps and Mawson, 2013) and c. 21 km SW of the Curraghinalt Au deposit examined earlier in this thesis in *Chapter Five*. This deposit is considered in the literature in studies of regional fluid flow, geochemical comparison in terms of bulk geochemistry of veins and gold-bearing particles (e.g. Earls et al., 2003; Parnell et al., 2000). Cononish is a vein-hosted Au deposit in Scotland, located approximately 70km north of Glasgow near Tyndrum (Lyell et al., 2019; Pitcairn et al., 2015; Spence-Jones et al., 2018). Located c. 250 km to the NE of the Sperrin Mountains deposits of Northern Ireland, the Scottish Cononish deposit is of interest in terms of regional prospectivity within the Dalradian Supergroup. This chapter presents the results of a limited set of Laser Ablation ICP-MS analyses conducted on samples of pyrite within late orogenic veins hosting visible Au from the two deposits. It (i) considers the question of the relationship between Curraghinalt and Cavanacaw from the perspective of trace element mobility and (ii) the previously recorded association of Au at Cavanacaw with Pb, and at Cononish with Te, through examination of host pyrite as a geochemical archive of hydrothermal events. This chapter also presents evidence of late introduction of trace elements including Au into late micro-fractures at Cononish comparable to that observed at Curraghinalt, and considers emplacement processes active late orogenic deposits suggested as being separated in time by tens of millions of years (c. 24-37 Myr; Rice et al., 2016; Tanner, 2012).

Cavanacaw is described by Birtel et al. (2013) as hydrothermal, structurally controlled and hosted by meta-sediments of the Dalradian Supergroup. The principle resource and focus of economic activity is the Kearney vein swarm, an array of sub-parallel veins, hosted by the Lack Inlier. Research conducted since 2000 has focused on structural controls (Shaw et al., 2019), the examination of gold-bearing grains (e.g. Birtel et al., 2013; Chapman et al., 2000), technical studies associated with the mineral resource (Phelps and Mawson, 2013), local and

regional prospectivity through interpretations of Tellus-survey multi-disciplinary data acquisition (Lusty et al., 2009) along with reinterpretations of lithostratigraphy (McFarlane et al., 2009). Wide-ranging studies which included regional and deposit-specific information on mineralogy, sulphide paragenesis, geochemistry, sulphur isotopes, fluid inclusion work and structural geology have been presented by Parnell et al. (2000) and Earls et al. (2003). Most recent estimated resources at the Cavanacaw deposit include 77,919 t at 5.87 g/t for 20,772 oz contained Au in the measured category, 651,582 t at 5.85 g/t for 121,761 oz contained Au in the indicated category, and 1,403,746 t at 6.54 g/t for 295,599 oz contained Au in the inferred category; reported resource estimation parameters included the capping of Au grade at 75 g/t, a cut-off grade of 2.5 g/t Au and a diluted minimum vein width of 0.9m (Galantas Gold Corporation, 2013). The Kearney vein swarm was discovered during the mid-1980s by RioFinex North Ltd., during a regional survey conducted following the discovery of the Curraghinalt deposit within similar host stratigraphy (Phelps and Mawson, 2013). Veining was delineated and Au confirmed during exploration work which included the soil and deep overburden sampling (Parnell et al., 2000), stripping of overburden and trenching guided by Induced Polarisation (IP) surveying (Earls et al., 2003), channel sampling and diamond drilling. The vein has been exposed by exploration activity for 300m along strike (Earls et al., 2003). Mining commenced in 2006 as an open pit operation (Phelps and Mawson, 2013).

The Cononish system is described as a near-vertical Au and base-metal-bearing complex of quartz-carbonate veins (Lyell et al., 2019) and is hosted by deformed Dalradian Supergroup metasedimentary rocks which attained amphibolite facies metamorphic conditions (Spence-Jones et al., 2018). Veining is hosted within the Cononish Fault: a riedel structure, associated with the Tyndrum Fault which cross-cuts the Grampian and Appin Groups (Earls et al., 1992 cited in Lyell et al., 2019) The timing of mineralisation at Cononish has been placed by at between 428 and 425 Ma using U-Pb (zircon) and Re-Os (molybdenite) dating of plutons and lavas in the in the Tyndrum-Dalmally area; faulting associated with quartz and breccias has been interpreted as synchronous with sills and lamprophyre bodies (Tanner, 2012) [this approach is

seen by this study as potentially problematic, see *Discussion*]. Si-rich fluids were injected into propagating major fractures, forming km-scale quartz-breccia veins. This timing (mid- to late-Silurian) significantly post-dates the peak of metamorphism associated with the Grampian arc-continent collisional event (c. 468 Ma). Initially discovered in 1984 by Ennex who constructed a preliminary adit in 1986 (Tanner, 2012), work at the deposit is in mine development phase. Cononish will be the first modern commercial gold mine in Scotland (Lyell et al., 2019). Measured and indicated resources of 541,000 tonnes at 14.3g/t for 248,000 oz contained Au (and 59.9g/t Ag for 1,043,000 oz contained Ag), and inferred resources of 75,000 tonnes at 7.4g/t Au for 18,000 oz contained Au (and 21.9 g/t Ag for 53,000 oz contained Ag) have been estimated within a single vein at Cononish; operators plan to extract ore using a selected method of retreat, sublevel open stoping involving the mining of horizontal drives at 15m vertical intervals (Scotgold Resources Limited, 2020a).

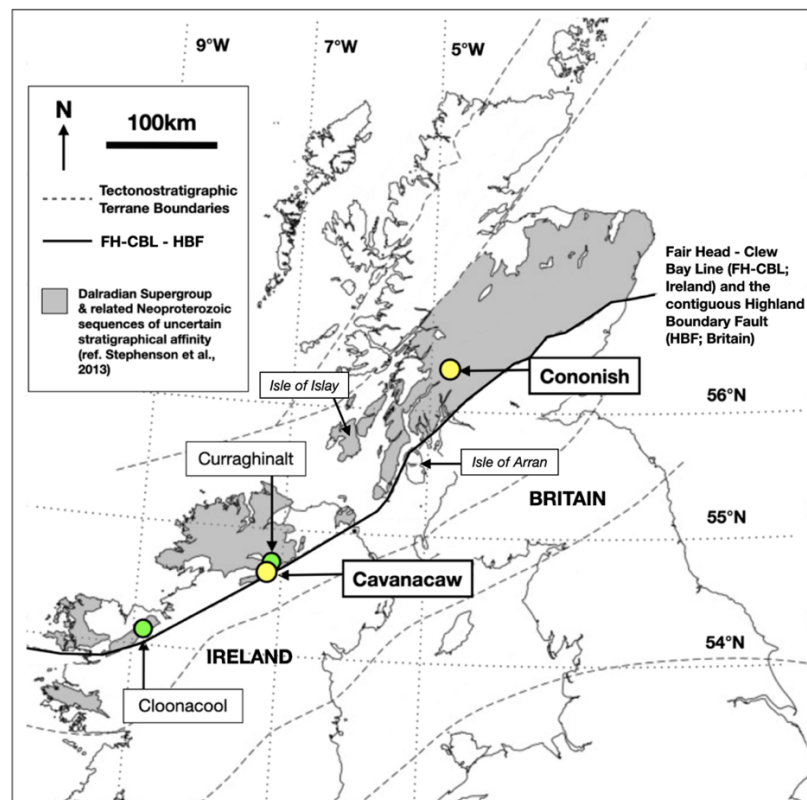


Figure 8.1. Location map of the Cavanacaw Au deposit, County Tyrone, Northern Ireland, and the Cononish Au deposit in SW Scotland (in yellow), their relative location to previously considered Au-bearing localities of this thesis (Curraghinalt and Cloonacool; in green); and the location Dalradian Supergroup formations on the islands of Ireland and Britain. The Isles of Islay and Arran mentioned in this thesis are attributed as a reference. Information included from Stephenson et al. (2013).

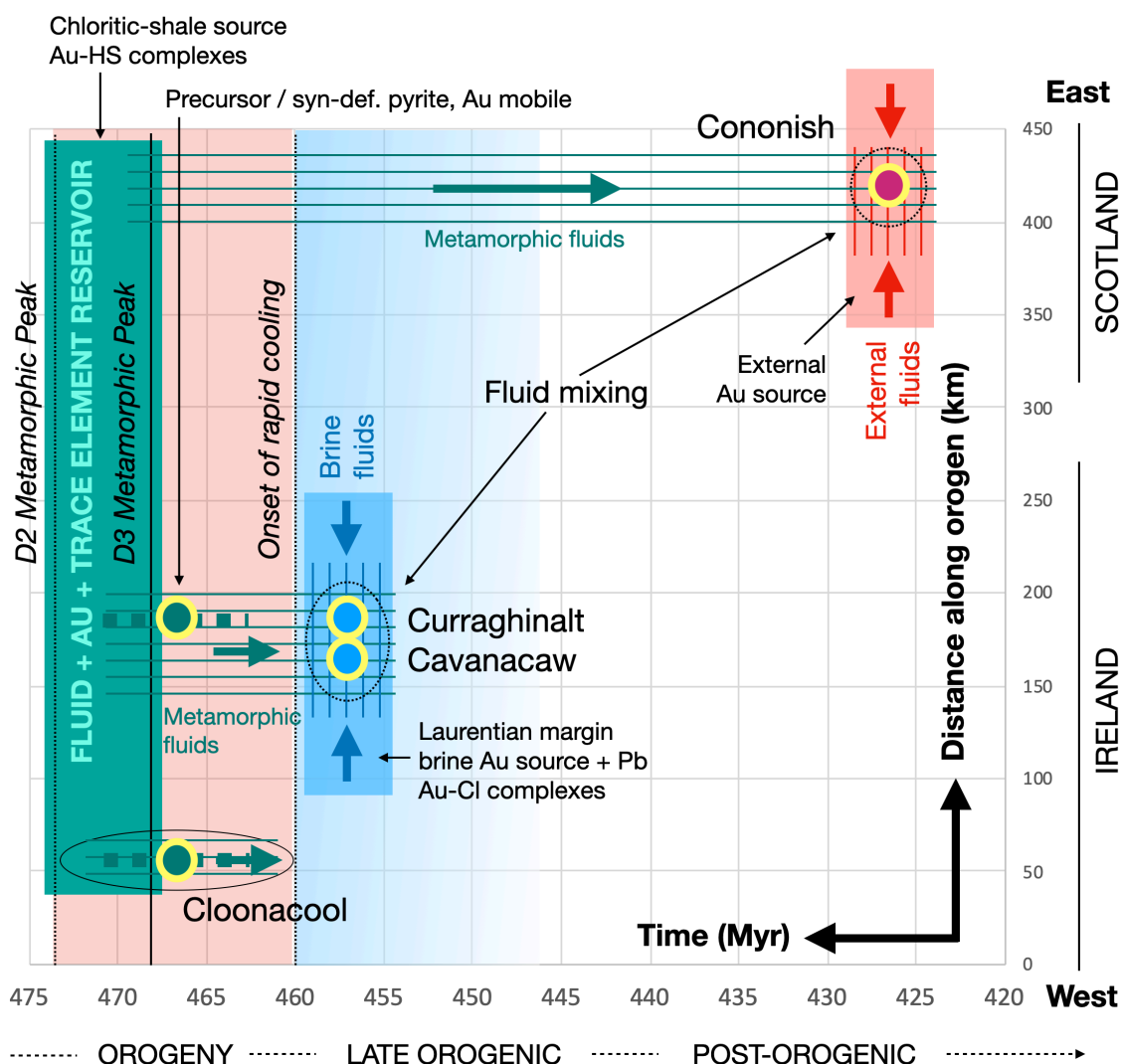


Figure 8.2. Hypotheses tested in this chapter: (i) localised discrete geochemical signatures recorded by pyrite will support the input of fluid and trace elements from discrete sources; late pyrite at Cavanacaw is broadly similar to Curraghinalt and is likely to record broadly similar geochemistry, while late pyrite at Cononish records a unique signature which supports the introduction of fluid and metals from an (e.g. magmatic) source; (ii) trace element signatures within pyrite will elucidate likely emplacement processes. This model shows time on the X-axis in millions of years, and on the Y-axis, relative distance along the orogen in km, normalised to a straight line linking Westport, County Mayo (0 km), to Stonehaven, Aberdeenshire (the approximate end points on land of the FHCBL-HBF). The approximated positions of deposits and prospects are located on the chart: for Curraghinalt and Cononish, mid-points of mineralisation intervals retrieved from Rice et al. (2016) and Tanner (2013) are shown, while all others are estimated based on petrographic work in this study and the genetic association of Cavanacaw and Curraghinalt suggested in work on regional fluid flow in the Sperrin Mountains by workers including Parnell et al. (2000). While ‘brine fluids’ are separated out in this schematic, they may also be considered metamorphic fluids. Regional event information is interpreted from Chew et al (2009).

8.3. Geological background

8.3.i. The Cavanacaw Au(-Ag) deposit, Northern Ireland

The host Lack Inlier is a package bounded by faults and overlain by sedimentary rocks of Upper Palaeozoic age (McFarlane et al., 2009). Work by Cliff and Wolfenden (1992, cited in Earls et al., 2003) indicates that the Cavanacaw deposit may be hosted by the Mullaghcarn and Glengawna Formations, which also host the Curraghinalt deposit to the NE (see *Chapter Five*). The approximately N-S trending Kearney swarm hosting mineralisation is comprised of 16 vein structures (with individually attributed names, using a similar approach to Curraghinalt; these include Kearney, Joshua's, Kerr, Gormley Main, Elkin's, Gormley West 2, Princes, Garry, Kearney North, Sammy's, Peter's, Brendan, Gormley West 1, Discovery, Black and Sharkey), identified within an area of c. 6 km². The largest of these is Kearney, which has a strike length of 850m which may extend to 100 m taking into account its Induced Polarisation (IP; geophysical) response (see Figure 8.3), steeply dipping approximately 70 degrees to the east with widths exceeding 6.6m (Phelps and Mawson, 2013). The vein is intercepted by a 100-200m wide shear zone (Cliff and Wolfenden, 1992, cited in Earls et al, 2003; Phelps and Mawson, 2013) and is cross-cut by NW-SE trending joints and faults. ENE-NNW trending shear zones (e.g. Luis Shear Zone, see Figure 8.3) which may be thrusts are also recognised in the area, these may have undergone relatively late movement (Earls et al, 2003). The Cavanacaw orebody is described by Birtel et al. (2013) as heterogeneous in terms of its mineralogy and proximal gangue. Veins themselves are comprised of sulphides (mainly pyrite, arsenopyrite, galena, chalcopyrite and tennantite) within a matrix of quartz, albite and K-feldspar; host mineralogy includes muscovite, biotite and chamosite (chlorite). Au is described as being hosted within grains of electrum, which are observed by Parnell et al. (2000) associated with grains of pyrite and galena. Birtel et al. (2013) observe that electrum may occur as inclusions, in veinlets within larger quartz veins, and in 'sulphide patches' in complex micro-structures.

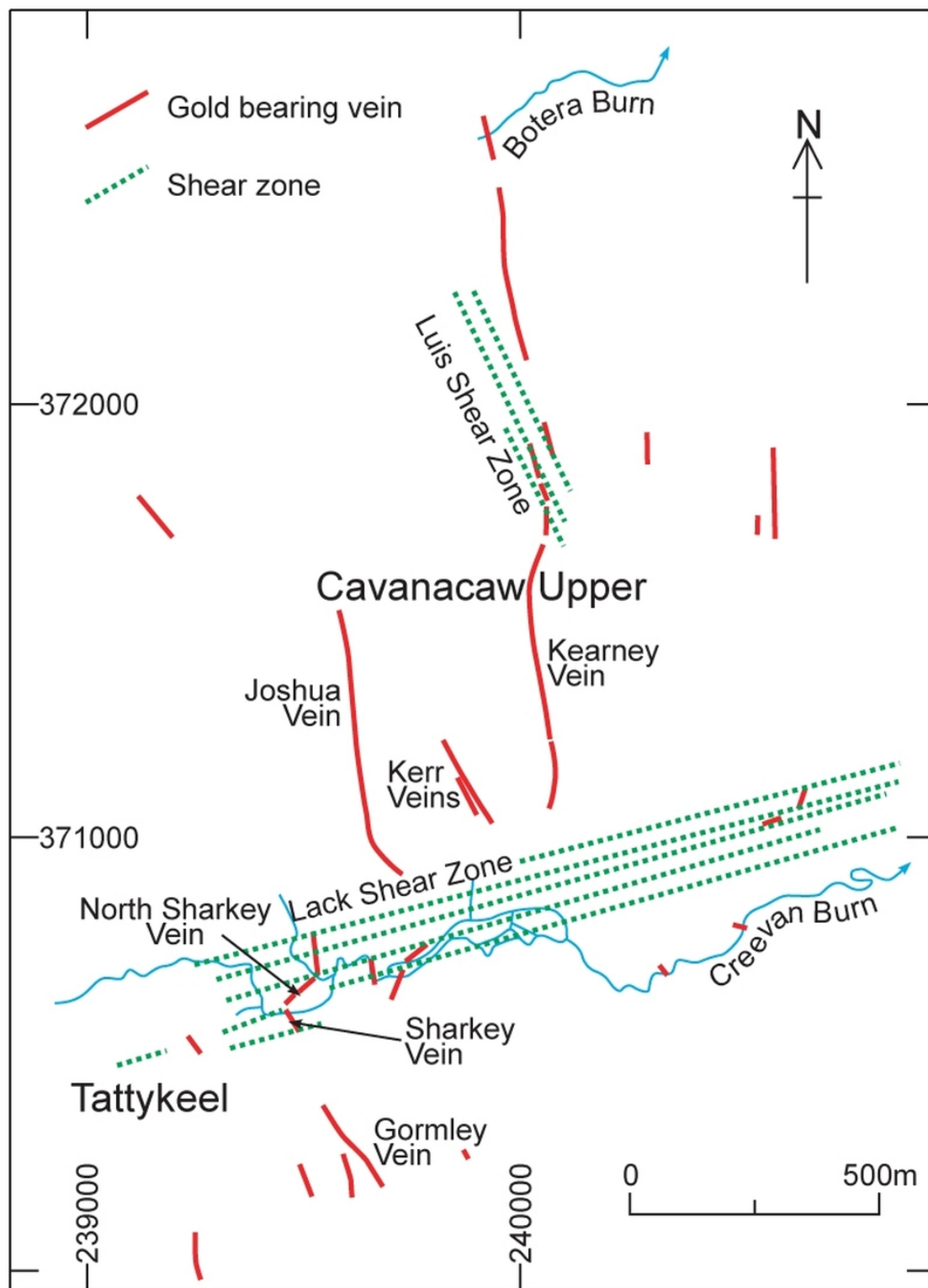


Figure 8.3. Orientation of vein structures at Cavanacaw, including Kearney Vein, Joshua, Kerr, Gormley, Sharkey and north Sharkey. The Lack Shear Zone is identified with a WSW-ENE general trend. (Woodham et al, 1989 modified and presented in Mitchell, 2004).

Geochemically, observations of interest to this study are presented by Parnell et al. (2000) and Earls et al. (2003). Parnell et al. (2000) note that Cavanacaw veins are richer in Ag than those hosting the Curraghinalt deposit, with wider dispersion of values on Au-Ag plots. As is recorded at values of up to 3.5 percent (sic), with higher Pb and Sb concentrations than at Curraghinalt also recorded. Au(-Ag) is associated with As, Ce, Cu and Pb (Earls et al., 2003). Within tested pyrite, trace amounts of As, Hg and Au were also detected (Parnell et al., 2000).

An overall structural control for Cavanacaw mineralisation is interpreted by Phelps and Mawson (2013) and Earls et al (2003), with an updated model that may explain differences with structure at Curraghinalt proposed by Shaw et al. (2019) (see Figure 8.4). The three principle controlling structures within the Lack-Curraghinalt area are the N-S trending Omagh Lineament, the SW-NE trending Omagh Thrust and the WNW-ESE trending Curraghinalt Lateral Ramp (Earls et al., 2003). The long-lived Omagh Lineament, a deep crustal structure, is suggested to form a ‘zone of influence’ affecting the position and orientation of Cavanacaw veins.

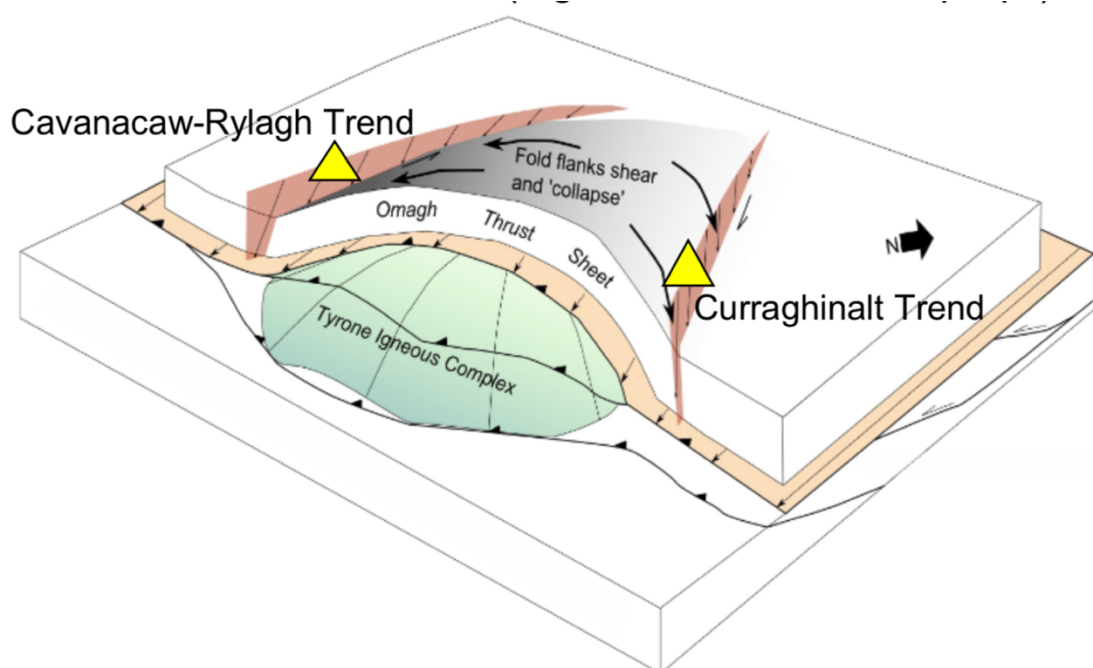


Figure 8.4. Structural model for the Sperrin Mountains Au deposits, proposed by Shaw et al. (2019). Trans-tensional shear zones are created through strain partitioning; shear zone and vein orientations are controlled by the geometry of thrusts and the topology of the subducting arc complex.

This is evidenced by Au and As anomaly distributions and the N-S orientation of mineralised veins themselves (Earls et al, 1996 cited in Phelps and Mawson, 2013). Shaw et al. (2019) have proposed that E-W striking (e.g. the Lack Shear Zone) and N-S trending shear zones (e.g. the Luis Shear Zone) are conjugate, and that the Grampian arc-continent collision resulted in localised trans-tensional deformation. Shear zones were generated by strain partitioning due to SE-directed late thrusting (D_3) controlled by the topology of the underlying arc. Space created accommodated mineralising fluids at both Curraghinalt and Cavanacaw, evidenced by the presence of extensional and dilational textures at both deposits.

Parnell et al. (2000) observe similar fluids at Cavanacaw to those recorded at Curraghinalt, within a narrow NE-SW trending zone from the Lack Inlier to Curraghinalt, c. 26 km and open to the SW. Phelps and Mawson (2013) emphasise that there are numerous proximal targets which had not yet been followed up at the time of their report: associated with boulder prospecting, soil sampling, and interpretations deriving from the Tellus integrated survey, led in the region by the Geological Survey of Northern Ireland. They advocate the prospectivity of Dalradian strata, particularly the Glengawna, Mullaghcarn and Dungiven Formations along with Lower Carboniferous basins in all directions, where sulphides have also been observed (Hitzman, 1986 cited in Parnell et al., 2000).

8.3.ii. The Cononish Au deposit, Scotland

The principle Cononish vein, historically known as the Eas Anie structure, is described as being poorly exposed and lacking in topographic expression; information until recently was largely sourced from diamond drilling (Tanner, 2012), however recent extensive mapping of the vein within the adit has been conducted by Lyell (2019). Two contrasting mineral assemblages are observed by Lyell (2019): the first, of main economic interest, includes pyrite, tellurides, chalcopyrite and galena within quartz, calcite, sericite and barite gangue; the second

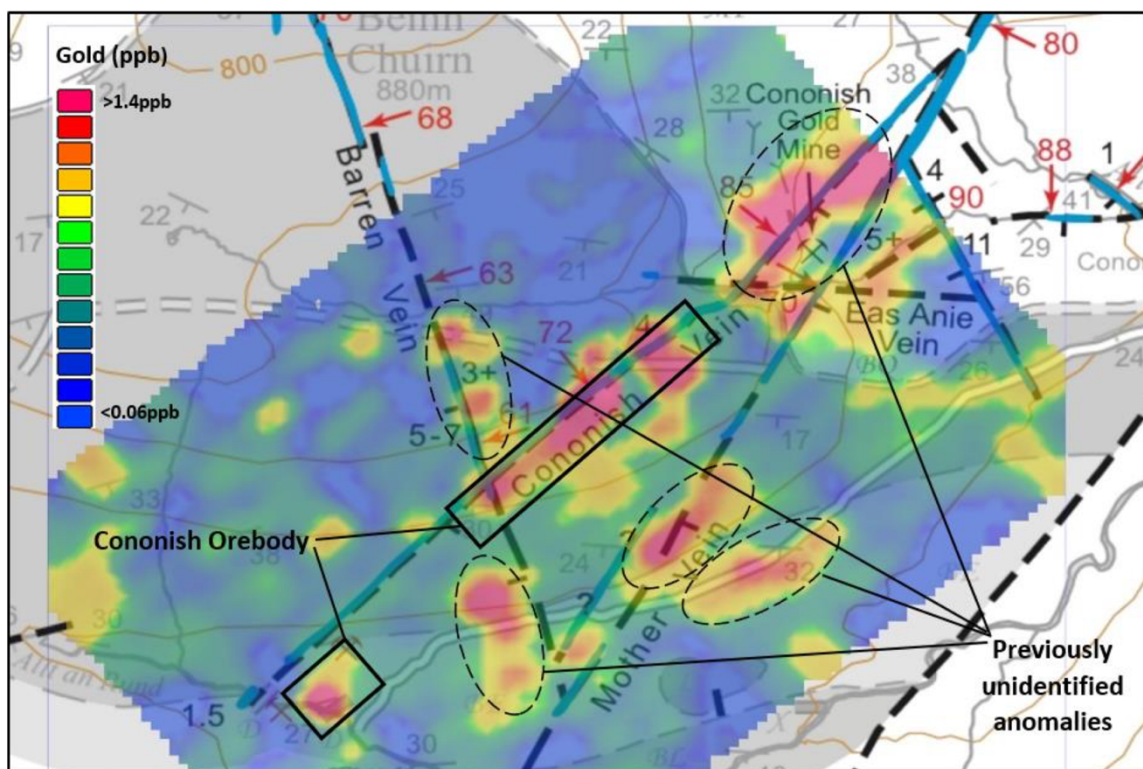


Figure 8.6. Soil anomaly map (static sodium cyanide leach) overlain on a structural and geographic map of the Cononish area, with anomalies identified prior to March, 2019 identified (Scotgold Resources Limited, 2019). A key is provided of colour on the map in relation to recorded gold concentrations.

assemblage is of oxide minerals, pyrite, pyrrhotite and chalcopyrite, within veins of quartz, carbonate and chlorite. This difference is attributed to changes in the oxidation state of ore-fluids. Visible gold occurs within grains of electrum intergrown with pyrite and galena, accompanied by silver-tellurides and native silver; <0.2mm native gold grains are also recognised as a minor phase (Parker et al. 1989; Earls et al. 1992; Treagus et al. 1999 cited in Tanner, 2012). The 15m-wide Eas Anie dyke composed of quartz and dolerite intersects the vein along with minor faults showing a >9m displacement (Tanner, 2012). Vein margins are characterised by sub-parallel quartz veinlets, and pink to red colouration of the country rock attributed to potassic feldspar alteration of chloritised and sericitised host rocks. A structural control on mineralisation is proposed by Tanner (2012), while the mobility and abundance of metals including Au, As and Sb is suggested to be controlled by an inverse relationship with metamorphic grade (Pitcairn et al, 2015).

Fluid types and sources are the subject of ongoing debate: two recent contributions by Spence-Jones et al. (2018) and Lyell (2019) support the involvement of magmatically derived fluids, while Hill et al. (2015; cited in Pitcairn et al., 2015) and Tanner (2012) note that both metamorphic fluids and magmatic fluids are likely to be involved. Key evidence presented by Spence-Jones et al (2018) includes detailed petrography, whole rock geochemical analyses of Te enrichment, SEM-EDS/EDX analyses of gold-bearing grains and $\delta^{34}\text{S}$ signatures of host pyrite. Results include elevated concentrations of Te, along with an increase in $\delta^{34}\text{S}$ from -2.0‰ to $+11.4\text{‰}$ throughout the paragenetic sequence. This is interpreted in their study as indicative of a primary low- $\delta^{34}\text{S}$ fluid carrying elevated Te, Au and Ag attributed to a magmatic source, followed by introduction of a high- $\delta^{34}\text{S}$ fluid containing relatively lower Te, Pb and Cu sourced from metamorphosed sedimentary exhalative horizons. Their evidence is supported by Lyell (2019) who observe that mineralisation was contemporary with high-K, Ba-Sr enriched alkaline magmatism through analyses of pyrite, interpreted as an indicator of mineralisation at epithermal temperatures c. 223 °C. Both the study of Spence-Jones et al. (2018) and Lyell (2019) question the validity of the ‘orogenic’ classification for Cononish deposit; Spence-Jones et al. (2018) note that Te enrichment may be an uncommon feature of orogenic deposits bearing a magmatic input, while Lyell (2019) suggests that while Cononish has much in common with orogenic deposits, it is likely to be distinctively magmatic in origin.

Regionally, host rocks Dalradian metasediments reached lower amphibolite facies grades of metamorphism, according to Tanner (2012), retrogression is observed, with alteration of biotite and garnet to chlorite evidenced. Pitcairn et al. (2015) describe significant mobility of Au, As and Sb within the Dalradian Supergroup of Scotland, noting that they have been affected by multiple fluid flow events. Key observations of interest to this study include: (i) that regional sulphide assemblages (pyrite, sphalerite, galena, cobaltite and gersdorffite) decrease in abundance with metamorphic grade; (ii) that concentrations of Au, As and Sb of sulphide assemblages decrease with metamorphic grade (proposed as a control on metal mobility), (iii) that chlorite may be important as a host mineral for As in metamorphic rocks at greenschist

facies, and (iv) that its breakdown may indirectly control the mobility of Au, As and Sb as it produces metamorphic fluid, which in turn drives the transition between pyrite and pyrrhotite (such fluid and element mobilisation is proposed earlier in this study in *Chapter Seven*).

Pitcairn et al. (2015) attest that Au is mobilised during metamorphism, and therefore there is potential for mineralisation as yet undiscovered within the Dalradian Supergroup of the Central and SW Scottish Highlands. They caution however that the amount of Au mobilised is likely to be lower than in comparable metasedimentary terranes; efficient fluid focusing and physical trapping would be required to form deposits. Also of interest to this study (particularly in light of the observation of elevated Zn in the precursor pyrite at Curraghinalt Py₁ in north-west Ireland, see *Chapter Five*), they note that stratabound Pb-Zn mineralisation hosted by the Argyll Group has been recorded by previous workers hosted by the Argyll Group, and throughout the Dalradian Supergroup: across the SW Highlands, and on the Isle of Islay (see Figure 8.1).

8.4. Samples and analytical methods

Petrographic work on samples from Cononish and Cavanacaw was principally focused on targeting of Au-hosting pyrite for microanalysis using Laser Ablation ICP-MS. All micro-analytical work was conducted at iCrag Lab@TCD (also known as the Centre for Microscopy and Analysis or CMA) and the Geochemistry Laboratories of Trinity College Dublin.

One hand sample of sulphide-bearing vein mineralisation from the Cononish deposit was acquired from the Trinity College Dublin collection for use in this study (designated CS01), while a limited set of 11 thin sections from the Cavanacaw mine released by Omagh Minerals Ltd (Galantas Gold Corporation). Of the 12 thin sections examined in this study, one was prepared as part of a batch from the Cononish sample (CS01a) by Thin Section Lab in Toul,



Figure 8.7. Underground drilling at Cononish (Scotgold Resources Limited, 2020b)



Figure 8.8. Society of Geology Applied to Mineral Deposits (SGA) visit to Cononish, August 2019 (author second from left; Scotgold Resources Limited, 2020b)

France at a width of 60 μm (suitable for LA ICP-MS analysis) with dimensions (25mm x 54mm). A selection of samples were mounted in resin prior to dispatch to avoid breakage.

A field visit was conducted to the Cononish mine in August, 2019 as part of a Society of Geology Applied to Mineral Deposits (SGA) Student Chapter tour hosted by Scotgold Resource Limited, prior to the SGA Biennial Meeting in Glasgow (August 27-30). At Cavanacaw in Northern Ireland, a visit to the project including an underground tour was facilitated by Omagh Minerals Ltd (Galantas Gold Corporation) in May, 2019 during which an additional 14 grab samples containing pyritiferous material were collected from within the adit and examined.

Optical microscopy was conducted using a Nikon Eclipse LV100 microscope with reflected and transmitted light capabilities, connected to a Märzhäuser Wetzlar TANGO desktop controller, with images processed using the Nikon NIS-Elements platform. LA ICP-MS spot analyses and raster element mapping were conducted using a Teledyne Cetac G2 193 nm Excimer ArF laser with a HelEx 2-volume cell, coupled to a ThermoFisher Scientific Elemental iCAPQs mass spectrometer. In total, 56 analyses were conducted on samples of pyrite from Cavanacaw (n=6) and Cononish (n=50). The number of analyses for Cavanacaw was limited; as such results are presented in this study with the caveat that (i) this suite of analyses was designed initially as a test, (ii) that they demonstrate the potential of this methodology and (iii) that they provide general results for the purposes of comparison with deposits across the trend. Analytes were selected with a view to consistency with previously conducted analyses so as to enable comparative work; ^{55}Mn , ^{59}Co , ^{60}Ni , ^{63}Cu , ^{66}Zn , ^{71}Ga , ^{75}As , ^{78}Se , ^{95}Mo , ^{107}Ag , ^{118}Sn , ^{121}Sb , ^{125}Te , ^{182}W , ^{197}Au , ^{202}Hg , ^{205}Tl , ^{208}Pb and ^{209}Bi . A variable volume in-house device was retro-fitted to the ablation cell, linking it to the ICP-MS torch for the purpose of smoothing the signal between the laser and the mass spectrometer. A flow of 3ml/min (for raster element maps) and 10ml/min (for spot analyses) of N_2 was introduced using this device which enhances signal sensitivity and reduces the formation of oxides. For Cavanacaw spots (n=6), a fluence of 1.43 J/cm² was used, while for Cononish spots (n=50) this was 1.0 J/cm²; a fluence of 1.2 J/cm² was used for Cononish raster element mapping.

Raster element mapping data were reduced in semi-quantitative mode using Iolite 3.0. The selected reference material was MASS-1, and the Trace_Elements data reduction scheme was used. A threshold of 5000 counts was used to mask low signals (attributed to neighbouring grains) and a beam-second sensitivity of 1 s. Zero seconds were trimmed before or after low signals and no outlier rejects were selected for these experiments. The same data reduction scheme was used for spot analyses, though an internal standardisation method was selected (^{57}Fe , 46.1 wt.%) for Cononish spot analyses, and signals trimmed where appropriate. A 2 x standard deviation (2SD) outlier reject option was selected for both baselines and normal selections. Reference materials used for all experiments were MASS-1, UQAC, NIST 610 and BCR-2G, except for Cavanacaw spots (n=6) where only MASS-1 was used; this was deemed sufficient due to the limited number of analyses being conducted. Mapping comprised 61 individual traverses at a repetition rate of 6 Hz. Fe standardisation was completed for Cononish samples using targeted spot analyses using Energy Dispersive X-Ray Spectroscopy spot analyses (n=6) in tandem with a TESCAN MIRA4 Field Emission Scanning Electron Microscope at iCRAG Lab@TCD in advance of Laser Ablation ICP-MS work.

8.5. Petrography

8.5.i. Cavanacaw underground and core reconnaissance

Vein samples acquired within the underground adit at Cavanacaw (zone between adit portal and Joshua vein) were of low to high density (qualitative) and contained variable amounts of galena, pyrite and chalcopyrite. Those with the highest density tended to be more Pb-rich, containing visual estimates of between 5 and 30 % galena. Wallrock was observed to be schistose and micaceous, with chlorite associated within the penetrative fabric. Galena within vein samples tended to be massive or semi-massive, with stringer-type textures also observed. Pyrite exhibited

Sample	Closest to	Density	Primary sulphide	Secondary sulphide	Tertiary sulphide	Fabric	Estimated position
CW01	Portal	High	Ga (20%) ■	Py (<1%) ■	-	No	Ore zone
CW02	Portal	High	Ga (10%) ■	Py (10%) ■	Cp (5%) ■	No	Ore zone
CW03	Portal	Low	Py (3%) ■	Cp (3%) ■	Ga (2%) ■	No	Ore zone
CW04	Portal	High	Ga (5%) ■	Cp (3%) ■	-	Yes	Veinlets cross-cutting fabric
CW05	Portal	V. High	Ga (30%) ■	Py (3%) ■	Sp ² (<1%) ■	No	Ore zone
CW06	Portal	High	Ga (30%) ■	Py (<1%) ■	Sp ² (<1%) ■	Yes	Ore zone
CW07	Portal	Low	Cp (<0.5%) ■	-	-	Yes	Wallrock, distal
CW08	Portal	High	Py (50%) ■	Ga (10%) ■	-	No	Ore zone
CW09	Portal	High	Py (20%) ■	Ga (20%) ■	-	No	Ore zone
CW10	Joshua	Low	Py (<1%) ■	Cp (<1%) ■	-	Yes	Veinlets in wallrock
CW11	Joshua	Low	Cp (3%) ■	-	-	Yes	Veinlets in wallrock
CW12	Joshua	Low	Cp (<1%) ■	-	-	Yes	Veinlets cross-cutting fabric
CW13	Joshua	Low	Py (<0.1%) ■	-	-	Yes	Veinlets cross-cutting fabric
CW14	Joshua	Low	Cp (2%) ■	-	-	Yes	Veinlets cross-cutting fabric

Table 8.1. Visual assessments of underground grab samples from the Cavanacaw deposit, including mineral abundance estimates, and an estimate of the location relative to the portal and the Joshua vein which the adit approaches, based on advice provided by guides during the underground tour.

matrix to disseminated sulphide textures. Proximal to the portal (Kearney zone), samples are richer in galena and pyrite, while distal from the portal en route to the Joshua vein, the most common mineralisation encountered were veinlets cross-cutting the penetrative fabric containing trace amounts of chalcopyrite and pyrite. Traces of sphalerite were also encountered, associated with galena-rich samples.

A limited amount of diamond drill-core was also inspected, though not sampled. Massive quartz and brecciated textures are observed within the ore zone, while conjugate veinlet arrays cross-cutting the fabric are observed distal to massive quartz. These veinlets were

observed to be mineralised, commonly with chalcopyrite, consistent with observations from within the underground infrastructure. The host fabric was observed to be highly micaceous (containing biotite and chlorite), with evidence of silicification and ductile deformation. Minor offsets in veinlets are visible, indicative of late movement.

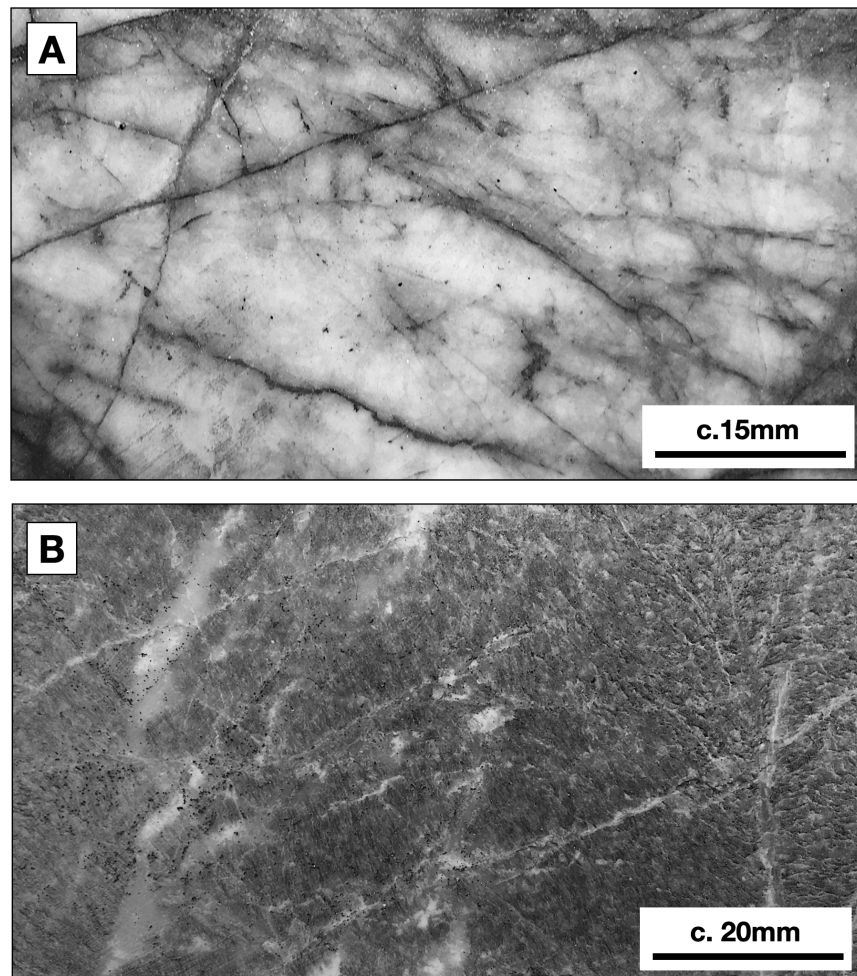


Figure 8.9. (A) Massive quartz texture within ore-zone in diamond drill-core; (B) millimetric quartz veinlets distal to the ore-zone in drill-core. (information on drill-hole ID and intersections is unavailable).

8.5.ii. Thin section petrography

Cavanacaw

A suite of representative ore sections from the Cavanacaw deposit were obtained from Omagh Minerals Ltd. (Galántas Gold Corporation) and examined using a reflected light microscope. While grain size and texture varies across the sample set, the Ga + Asp + Py assemblage observed is consistent throughout. Pyrite (Py₁) and galena (Ga₁) are the dominant sulphide minerals; certain observed regions Py₁ are texturally distinctive (exhibiting micro-scale surface deformation features and localised recrystallisation) and it partially replaces Ga₁ and arsenopyrite (Asp₁). The entire assemblage appears to have endured deformation typical of a shear zone: for galena, this is ductile, while for all other sulphide minerals deformation is cataclastic resulting in complex micro-fracturing.

Clearly identifiable fabrics are not observed within sections, precluding the identification of a coherent petrographic constraint, however samples were obtained from 'lode zones' which cross-cut deformation fabrics, and hence post-date Grampian fabrics. The host vein assemblage is dominated by quartz, while chlorite ± biotite ± phlogopite are observed within the wallrock where observed. Where sulphides are massive, they dominate thin section areas and may comprise up to 90% of the total section (e.g. OML-1; OML-3, see Figure 8.10). Where present within veinlets in discrete fractures, sulphide is observed as stringers (e.g. OML-8) or as finely disseminated grains (e.g. OML-10, OML-11).

It is hypothesised based on microscopic observations that following the emplacement of galena (Ga₁) under greenschist-facies conditions, arsenopyrite (Asp₁) and pyrite (Py₁) precipitated. Due to the ductile behavior of galena under greenschist conditions, mineral relationships have been obscured due its remobilisation throughout the metamorphic history at Cavanacaw; hence, a precise timing of galena within the paragenetic sequence is difficult to discern. Late micro-fracturing occurred synchronous with partial recrystallisation of Py₁ with a late fluid carrying Au and sulphosalts exploiting cataclastic, often orthogonal micro-fracture

networks cross-cutting arsenopyrite and pyrite phases. The observation of chlorite within the host assemblage also supports pervasive greenschist facies metamorphic conditions.

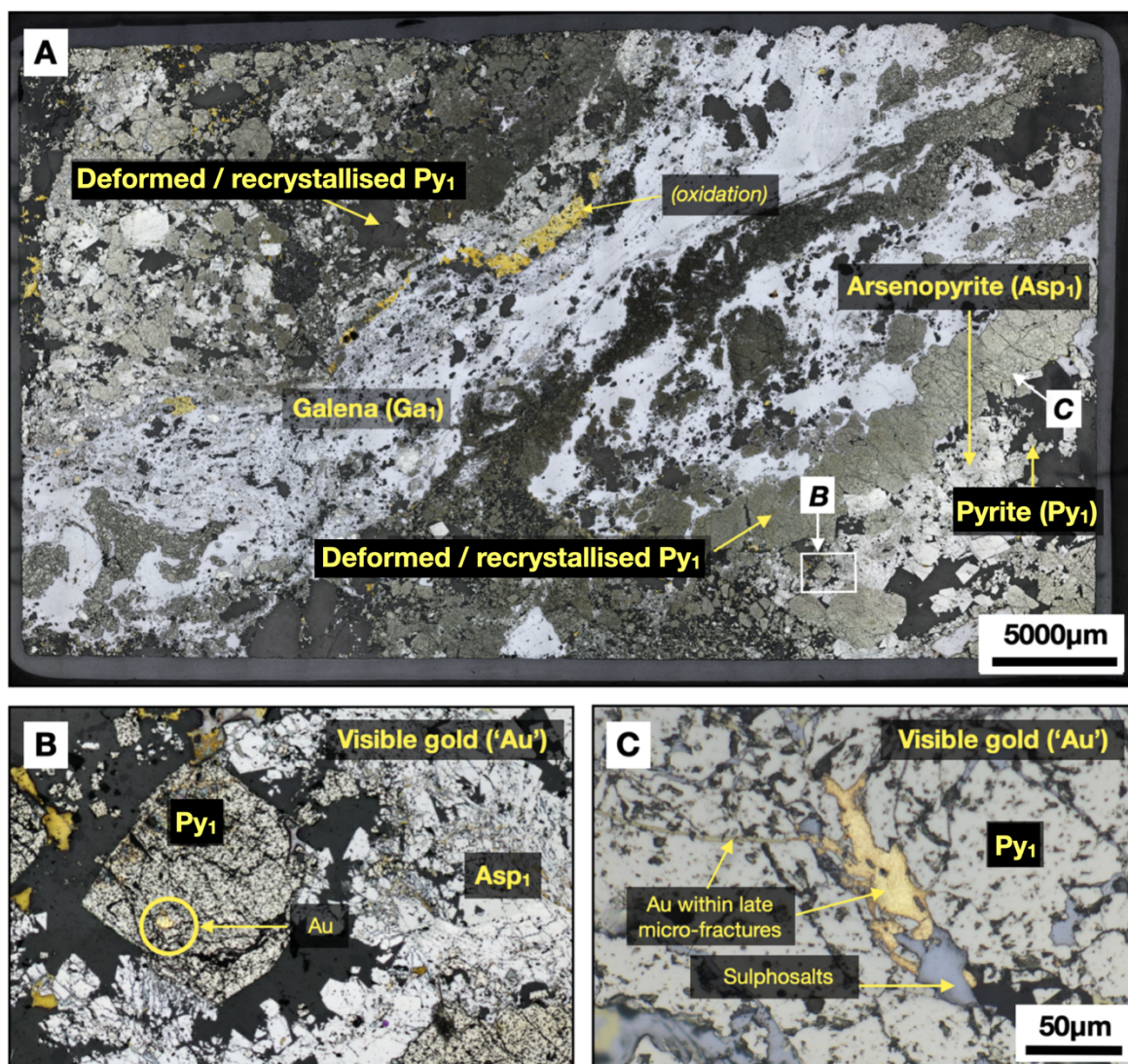


Figure 8.10. Representative thin section OML-3: (A) fully stitched image of the entire section, showing principle sulphide phases. Broad ductile deformation is observed across the section for the earliest recognised phase of galena (Ga_1). This has been replaced in the lower-right and upper-left of the section by arsenopyrite (Asp_1). Within specific regions orientated lower-right to upper-left, pyrite (Py_1) has been recrystallised. Visible Au is recognised within the lower-right of the image associated with pyrite : an area of interest, 'B' is indicated using a white box, while the location of 'C' is designated using an arrow; (B) visible Au associated with complex pyrite micro-fracturing; (C) visible Au observed within late micro-fractures carrying sulphosalts (likely to be tennantite-tetrahedrite) cross-cutting all pyrite and arsenopyrite.

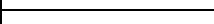
Sulphide / Au phase				
Galena (Gai)				
Arsenopyrite (Asp ₁)				
Pyrite (Py ₁)				
Sulphosalts				
Visible Au associated with microfractures				

Table 8.2. 'Ore-zone' assemblage: hypothesised paragenetic sequence for examined samples based on observations from reflected light optical microscopy. Relatively undeformed and unaltered pyrite (Py₁) is considered to be comparable in texture (relatively homogeneous with low-intensity micro-fracturing) to that observed at Curraghinalt (Py₃).

Cononish

Inspection of a thin section (CS01a) obtained from a sample of sulphide-bearing material from the Trinity College Dublin collection (CS01) reveals a comparable mineralogy, magnitude of deformation and paragenesis to late orogenic veins observed at Curraghinalt (see *Chapter Five*). Xenomorphic sub-millimetric grains of pyrite are cross-cut by visible micro-fractures evidencing cataclastic deformation; these have been exploited by fluids carrying visible Au and chalcopyrite. Visible tellurides and additional minerals are not observed within the specific section tested (see Figure 8.11). The occurrence of Au within micro-fractures varies, in certain instances infilling almost entirely, while in other areas Au is observed at the junctions cross-cutting fractures. Open spaces (or 'pores') containing quartz within micro-fractures are observed infrequently, indicating a physical process of rotation or variable strain intensity, or localised chemical dissolution of the surrounding pyrite. A simplified paragenetic sequence of visible phases is presented in Figure 8.12.

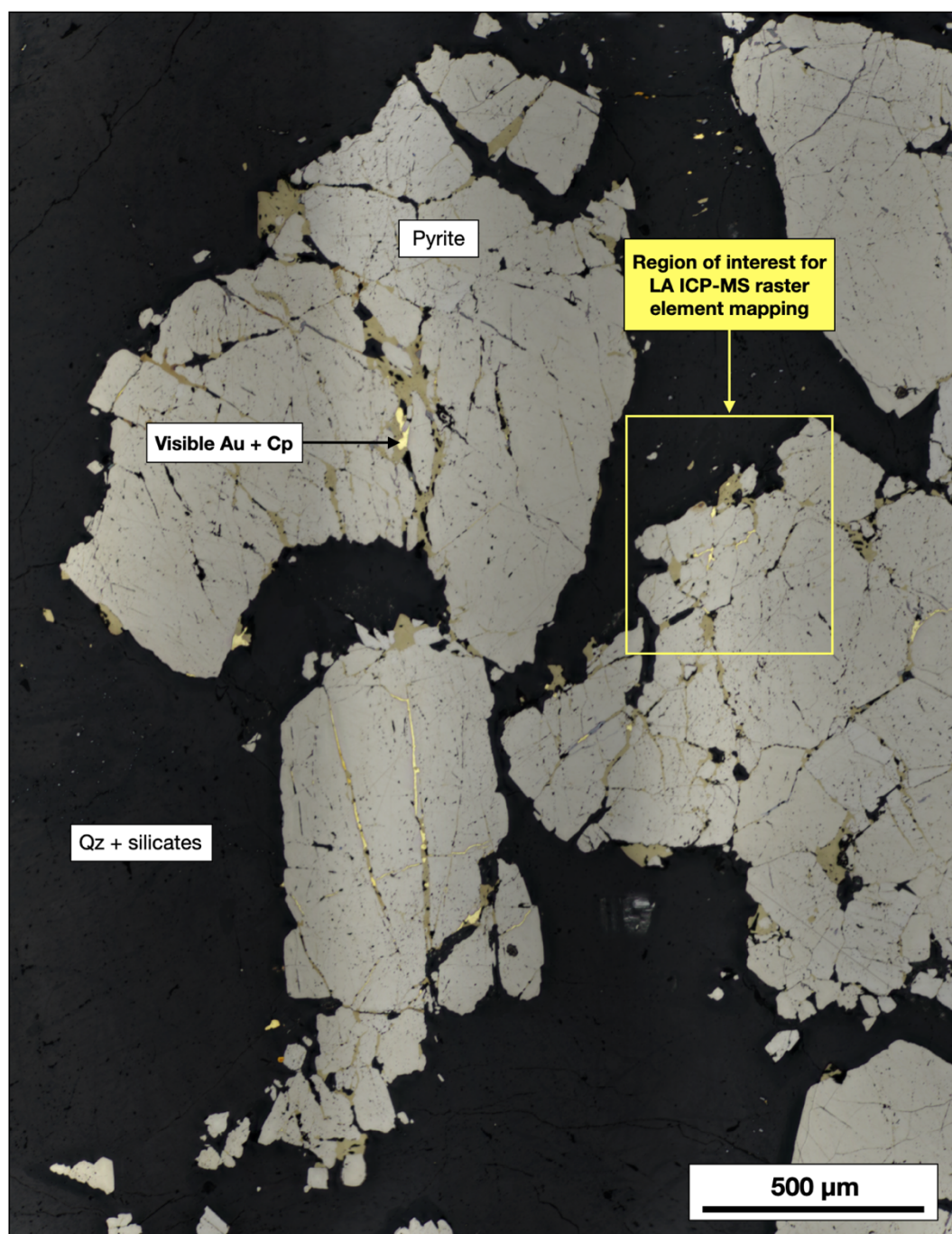


Figure 8.11. Reflected light image showing cataclastically-deformed pyrite in a quartz-silicate matrix, exhibiting micro-fracture infill by phases of visible Au, chalcopyrite (sample CS01, thin section CS01a, from the Trinity College Dublin collection). The representative, selected region of interest for LA ICP-MS raster element mapping is shown in the centre-right of the image. Maps for analytes of interest for this region are presented in Figure 8.18.

Sulphide / Au phase		
Pyrite		
Chalcopyrite		
Sulphosalts		■ ■ ■ ■ ■ ■ ■ ■
Visible Au associated with microfractures		

Figure 8.12. Paragenetic sequence of pyrite, chalcopyrite and visible Au within tested section of the Cononish deposit. Minor phases observed (e.g. sulphosalts within micro-fractures) require additional analyses to be placed in a comprehensive sequence.

8.6. Laser Ablation ICP-MS analyses

8.6.i. In-situ spot analyses

This section of the chapter presents key trace element abundances from the Cavanacaw and Cononish datasets, and examines in certain instances concentrations and trends in comparison Curraghinalt Py₃, a late orogenic phase hosting the largest estimated resource along the trend, (considered in detail in *Chapter Five*). The implications of these findings are considered later in the Discussion section of this chapter, along with how results support or contradict the model hypothesised in Figure 8.2.

General abundances and trends: Cavanacaw

Results from spot analyses targeted on Au-hosting pyrite from the Cavanacaw deposit (sample OML-3; n=6) show enrichments >100 ppm for As (median = 1,325 ppm; IQR = 285 – 8,398 ppm; n=6) and Pb (median = 907 ppm; IQR = 71 – 17,875 ppm; n=6). Mn, Co, Ni, Cu, Zn, Se, Ag, Sb and Hg report abundances between 10 ppm and 100 ppm, Sn and Au lie between 1 and 10 ppm, while Ga, Mo, Te, W, Tl and Bi report concentrations <1 ppm (median). The median value for Au is 3 ppm (IQR = 1.28 – 9.30 ppm; n=6), which is elevated compared with Curraghinalt Py₃ (<1 ppm; see Figure 8.13) demonstrating that Au within pyrite is one order of

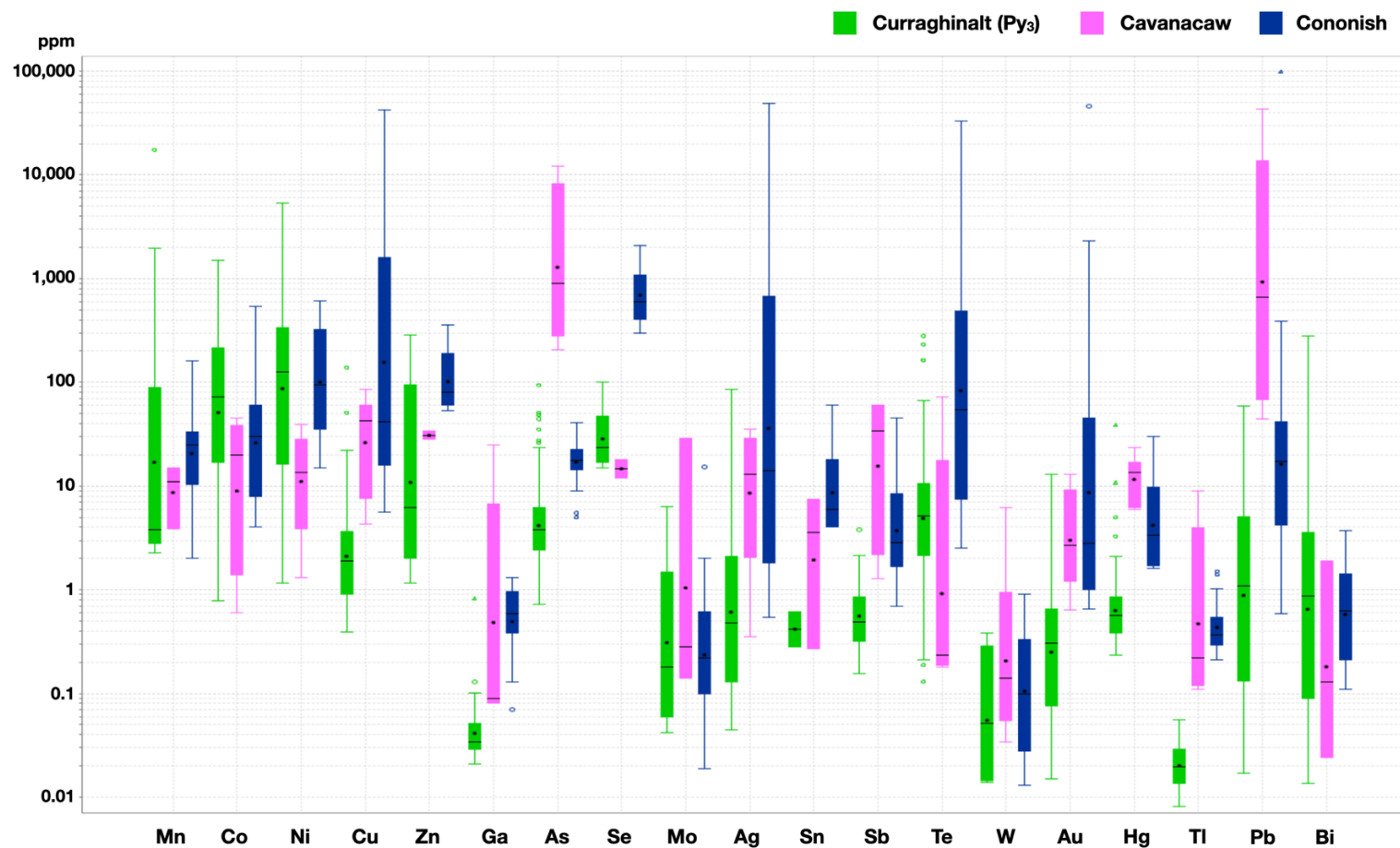


Figure 8.13. Box and whisker plots for trace element abundances (obtained using LA ICP-MS spot analysis) within pyrite from Cavanacaw (pink), Cononish (dark blue), with reference data from Curraghinalt Py₃ also shown as a reference (green; see *Chapter Five* for analytical conditions and petrographic information). The box is representative of the interquartile range (IQR), while whiskers represent extreme values which are not outliers.

magnitude more enriched. Examining how the relative enrichment of analytes across the dataset (see Figure 8.14 and Figure 8.15) compares with ore-associated Curraghinalt Py₃, this study notes that median concentrations are >800 ppm higher for As and Pb, with minor relative enrichments observed for Mn, Cu, Zn, Ag, Sn, Sb, Au and Hg. Co, Ni and Te are relatively depleted, with negligible differences observed for Ga, Mo, W, Tl or Bi.

While the reporting of correlations is to be approached with caution due to the low number of analyses at Cavanacaw (n=6), it is tentatively suggested that Au correlates positively with Hg ($\rho = 0.94$; Spearman rank) due to the high coefficient ($\rho > 0.9$). According to the model

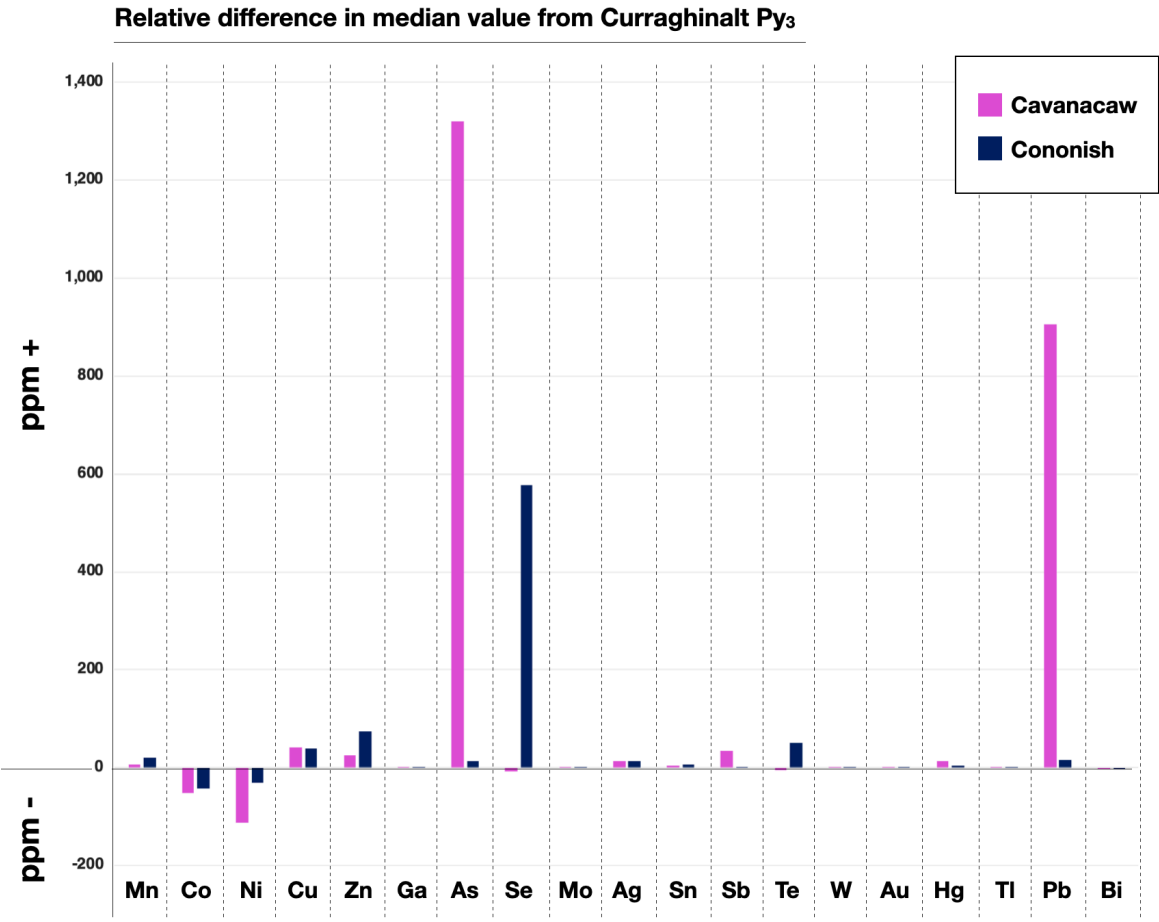


Figure 8.14. Relative abundance of selected trace elements compared to the median value recorded for Curraghinalt Py₃. The differences of greatest magnitude are observed for As (relatively elevated at Cavanacaw), Pb (relatively elevated at Cavanacaw) and Se (relatively elevated at Cononish).

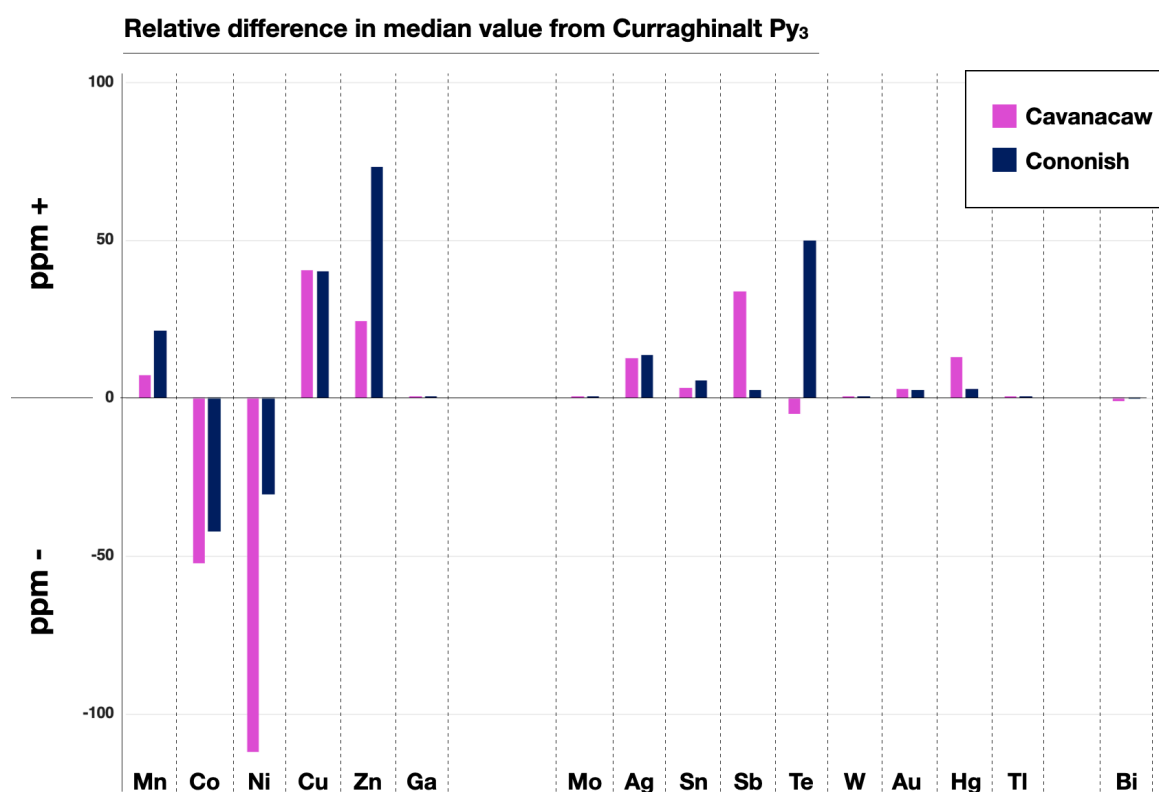


Figure 8.15. Difference in median concentrations of selected analytes: as previous figure, with As, Se and Pb removed to enable augmented visualisation of elements exhibiting lower relative differences.

for orogenic gold deposits presented by Goldfarb and Groves (2015), a Au-Hg(-Sb) signature may be indicative of epizonal formation depths c. 3km (lower greenschist facies conditions). Diagnostic of deposit formation at lower crustal depths is a positive correlation of Au with As (these do not correlate; $\rho = -0.086$), Te (no correlation coefficient is reporting), and W ($\rho = 0.7$) which does meet the criteria. It is suggested by this limited dataset that formation at the epizonal-mesozonal transition (3 km) is likely. Average element ratios for Au (presented in plots in Figure 8.16) include Au/As = 0.009 (n=6), Au/Ag = 0.68 (n=5), Au/Te = 13.8 (n=4), Au/Bi = 118.2 (n=3) and Au/Sb = 0.3 (n=6). The ratio of Au to elevated Pb is 0.01 (n=6). Co/Ni is an average of 1.38 (n=5; Figure 8.16A).

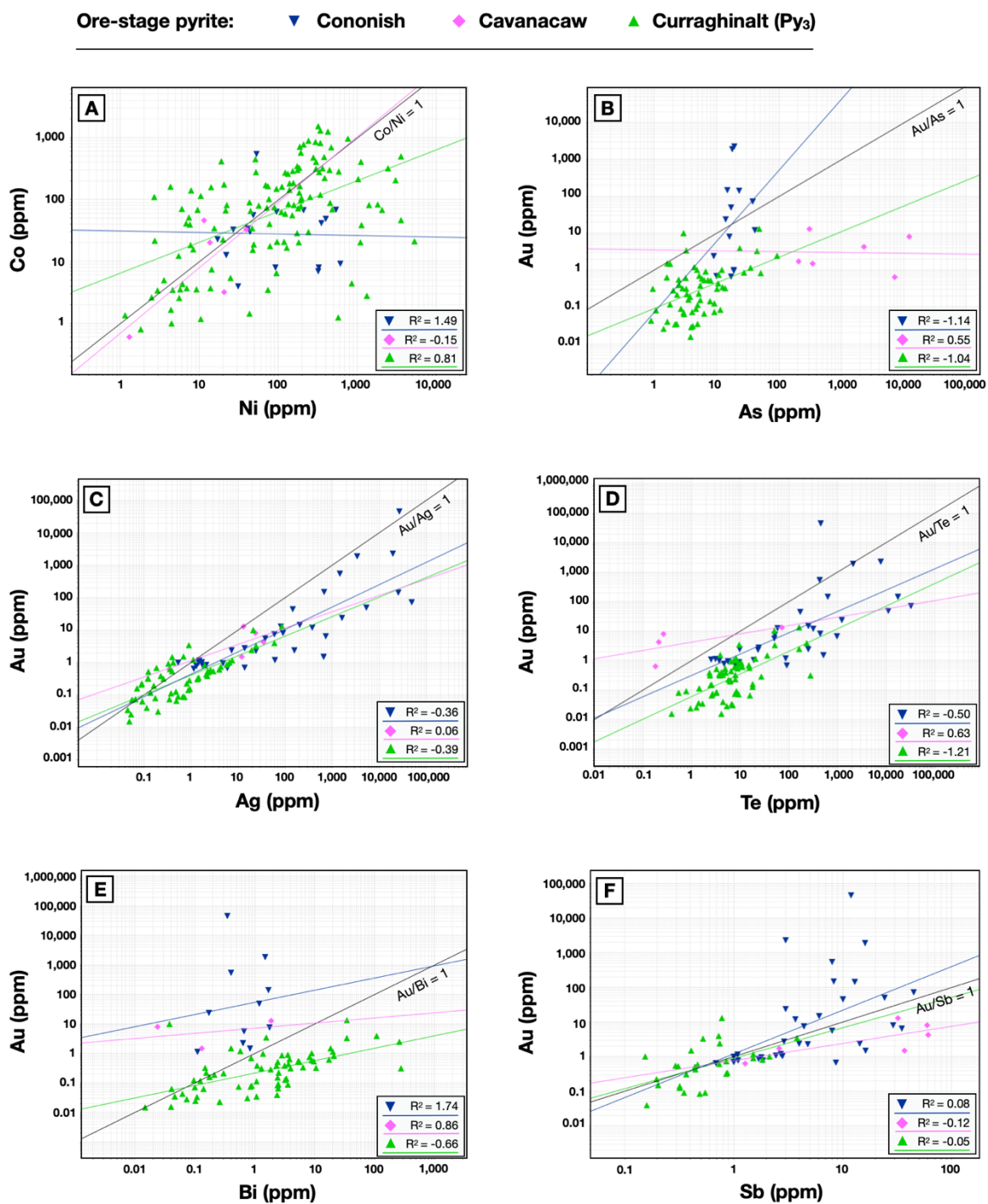


Figure 8.16. Trace element ratios within ‘ore-stage’ late-orogenic pyrite associated with visible Au from Cavanacaw (n=6) and Cononish (n=50), with data from Curraghinalt Py₃ (n=137; see *Chapter Five*) shown on plots as a reference.

General abundances and trends: Cononish

Tested Au-associated pyrite from Cononish (sample CS01a; n=50) is enriched at concentrations >100 ppm in Se (median = 600 ppm; IQR = 410 – 1,075 ppm; n=16). Median abundances between 10 and 100 ppm are recorded for Mn, Co, Ni, Cu, Zn, As, Ag, Te and Pb, >1 ppm for Sn, Sb Au and Hg, while Mo W, Tl and Bi report < 1ppm. The median concentration of Au is 2.8 ppm (IQR = 1 – 45 ppm; n=35), which correlates positively with Ag ($\rho = 0.88$; Spearman rank), W ($\rho = 0.86$), Te ($\rho = 0.8$), Hg ($\rho = 0.6$), Sb ($\rho = 0.66$), Pb ($\rho = 0.54$) and Cu ($\rho = 0.54$). Cross-referencing with the zonation model of Goldfarb and Groves (2015), the observed Au-Hg-Sb-Te-W association is suggestive of epizonal (c. 3 km) to mesozonal formation depths (> 3km) at greenschist facies conditions. The median concentration of Te recorded in Cononish pyrite is 55 ppm (IQR = 7.53 – 488 ppm; n=40), with an average Au/Te ratio of 3.37 observed (see Figure 8.16D). Trace element average ratios associated with gold include Au/As = 17.7 (n=14), Au/Ag = 0.32 (n=34), Au/Bi = 12,216 (n=11) and Au/Sb = 147 (n=33) (see Figure 8.16). The mean Co/Ni ratio for analyses is 1.04 (Figure 8.16A).

A comparison with the Curraghinalt Py₃ dataset presented in *Chapter Five* (see Figure 8.14 and Figure 8.15) shows that Cononish pyrite is relatively enriched in Se (>500 ppm; median concentration), Mn, Cu, Zn, Ag, Sn and Te. Also observed for Cavanacaw pyrite, Co and Ni are relatively depleted. Ga, Mo, W, Au, Hg, Tl and Bi show broadly similar concentrations.

Au solubility

Plotting LA ICP-MS spot analyses in Au-As space reveals two distinct fields with implications for the solubility of Au at each deposit. Five of six Cavanacaw analyses (mean Au/As = 0.009; n=6) plot below the solubility limit for orogenic systems (Deditius et al., 2014), indicating that Au is predominantly lattice-bound, while all analyses for Cononish reporting above detection (mean Au/As = 17.7; n=14) plot above the Au solubility curve (see Figure 8.17). It is interpreted that results from Cavanacaw indicate that the fluid carrying Au was largely undersaturated with respect to Au. Such conditions may be linked to early post-peak metamorphic conditions.

Further analyses (ideally $n \geq 50$) would be required to attain a definitive interpretation. Data from Cononish are indicative of retrograde metamorphic conditions (late-orogenic). A low-As, high-Au field above the solubility limit within Au^0 nanoparticle space confirms that the Au-transporting hydrothermal fluid at Cononish was supersaturated with respect to Au.

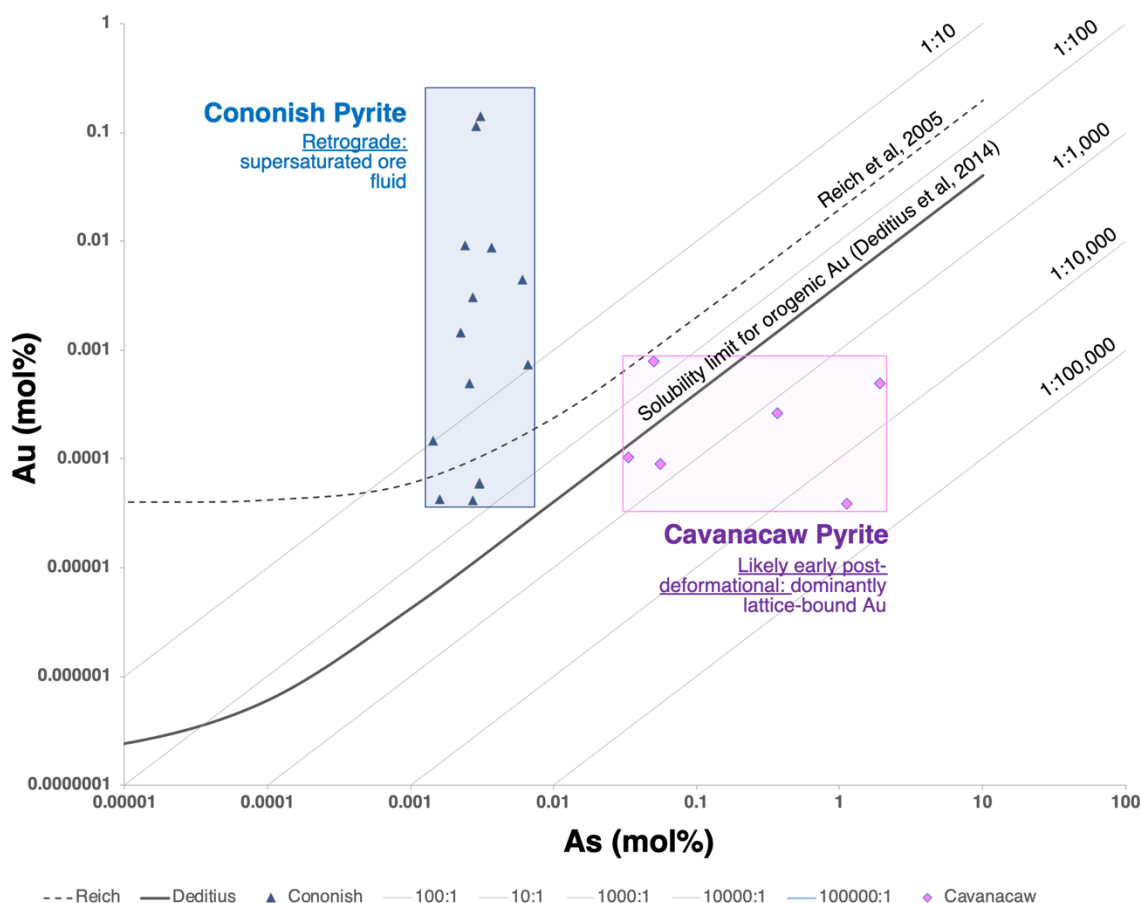


Figure 8.17. Au/As plot revealing Au solubility information for Cononish ($n=14$) and Cavanacaw ($n=6$) pyrite derived from LA ICP-MS spot analyses.

8.6.ii. Element raster mapping

LA ICP-MS raster element mapping was conducted on a region of interest measuring approximately $500 \mu\text{m} \times 500 \mu\text{m}$ on pyrite from Cononish (shown across two pages in Figure 8.18). The wider area within which this region is annotated in Figure 8.11. Data were

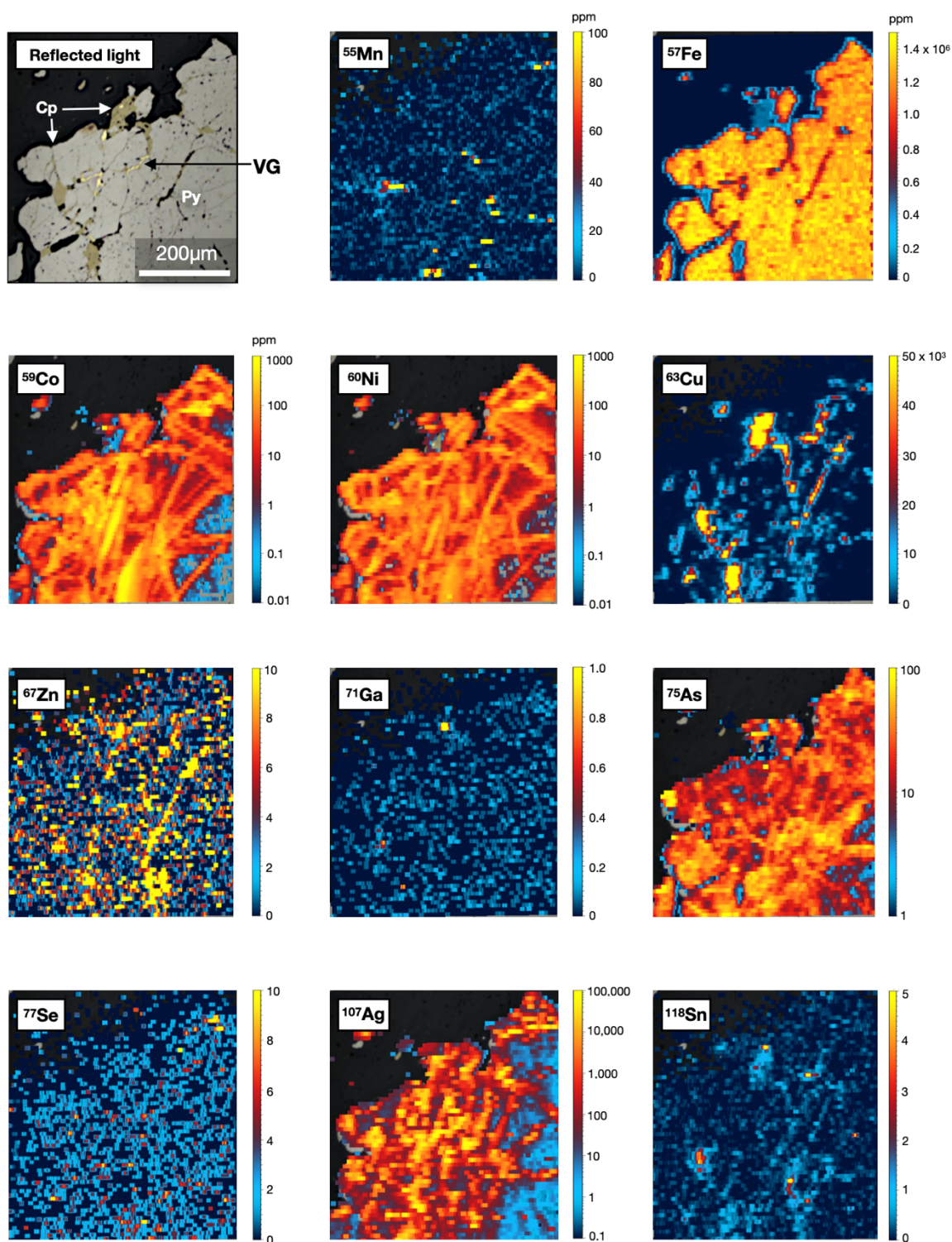


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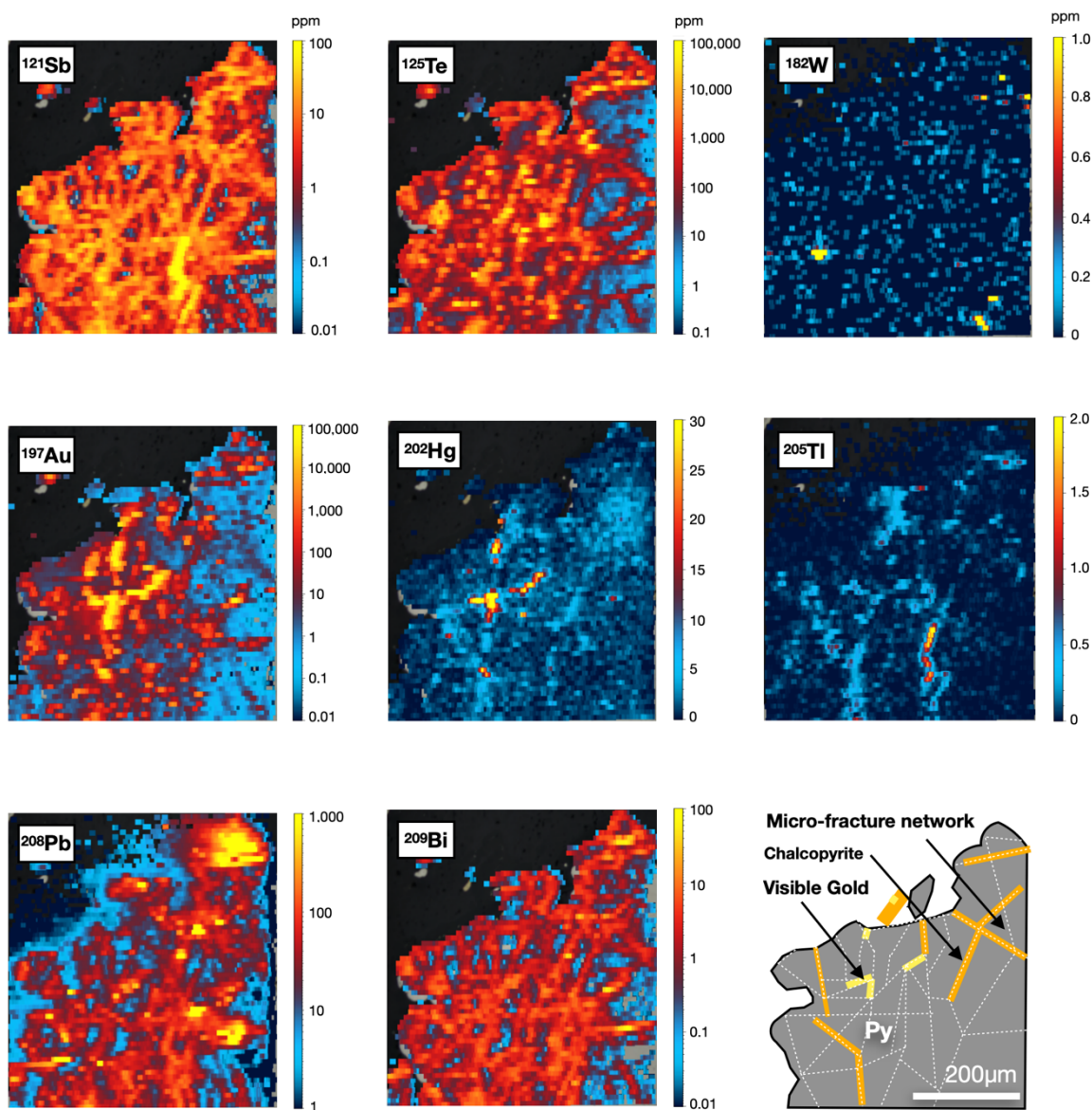


Figure 8.18. An annotated reflected light microscope image (top-left, previous page) of the selected region of interest (Cononish Au deposit, Scotland; sample CS01), followed by individual Laser Ablation ICP-MS raster element maps for a series of selected analytes. A model is presented at the end of the series at the bottom-right, which shows an association between visible gold (VG), chalcopyrite and the identified micro-fracture network revealed through elemental mapping. While the pyrite itself grain is depleted in trace elements, the micro-fracture network is enriched in Co, Ni, Cu, As, Ag, Sb, Te, Au, Hg, Pb and Bi with minor amounts of other elements. The highest enrichments localised within micro-fractures in Cu and Au correspond with the locations of visible gold and chalcopyrite, while enriched localised Mn, Sn, Te, W, Hg, Tl, Pb and Bi within the network indicates the presence of micro-particles including cassiterite, Bi-telluride, and galena. Three distinct chemical events associated with micro-fracture emplacement are interpreted in *Section 8.6.ii* of this chapter.

reduced in semi-quantitative mode using Iolite and a 5000 count mask applied so as to present data singularly from the pyrite grain and not surrounding gangue material (quartz). The most striking observations from maps are (i) the complexity of the micro-fracture network across the grains, and (ii) that the matrix of the original grain itself (right side of maps, Figure 8.18) is relatively depleted in trace elements. Micro-fracturing is highly concentrated, with spacing typically $< 50 \mu\text{m}$. They also show curvature, indicating that while this occurred during a brittle deformational event, there was strain accommodated by vein pyrite during cataclasis, likely associated with regional shearing. Areas of highest Au concentration coincide with micro-scale visible particles of Au: these particles are late and post-date brittle cataclastic fracturing of grains. Fractures enriched in Au are also enriched in Ag, however unlike Au, the Ag contained within this network is more homogeneously distributed, at concentrations frequently $> 10,000$ ppm. A schematic diagram showing the interpreted relationship of visible Au to the micro-fracture network is shown in the lower-right box of Figure 8.18.

Two late fluid infiltration events are interpreted to have proceeded Py_1 hosted in Cononish veins as observed within LA ICP-MS raster maps (Figure 8.18), bearing distinct geochemical signatures. The first of such infiltration events (I) is recognised in the broader geochemical enrichment observed throughout the grain appearing as a cryptic micro-fracture network. Elevated Co (>100 ppm), Ni (>100 ppm), As (>10 ppm), Ag (>100 ppm), Sb (>1 ppm), Te (>100 ppm), Pb (>10 ppm) and Bi (>1 ppm) are observed which this study interprets are associated with an early phase of cataclasis healed by pyrite: Py_2 (a Co-Ni-As-Ag-Sb-Te-Pb-Bi emplacement signature). This is corroborated by a patchwork of linear enrichments in Co-Ni where no fractures are visible (RL-optical); further discrete phases of Co-Ni minerals have not been recognized and anomalies are likely refractory signatures in a cryptic pyrite phase. The second event (II) corresponds to widespread late fracturing of the pyrite and infilling by visible Au, chalcopyrite and sulphosalts. These fractures cut across both Py_1 and Py_2 and may have been aided by a structurally weakened pyrite healed by Py_2 . This is corroborated by a region visually in respective maps of Au and Hg forming a ‘cross’ shape within two cross-cutting

fractures; with minor enrichment of Au within proximal fractures >10 ppm) which is slightly tilted to the right, with enrichment in those fractures internal to the grain and not observed close to its rim. This region while enriched in a large suite of elements, characteristically contains Au (>1,000-10,000 ppm coinciding with Au-particles observed in reflected light), Hg (>25 ppm) and Ag (>1,000-10,000 ppm) enrichments not observed across the wider network. Au-Hg-Ag emplacement may therefore be attributed to this event. It is considered that reactive surfaces are present within micro-fractures which were favourable for the emplacement of Au and nucleation of visible particles.

The determination of Au emplacement within micro-fractures coinciding with Hg and Ag is consistent with findings from LA ICP-MS spot analyses (see *Section 8.6.i*) of a positive Au-Hg(-Sb-Te) correlation (Spearman rank, $\rho \geq 0.5$. However, W, which also has a positive correlation in spot analyses of pyrite ($\rho = 0.86$) is not enriched within micro-fractures [while care was taken in spot analyses to avoid micro-fractures where visible, however their localised intensity suggests that they were inevitably partially intercepted, explaining these results].

8.7. Discussion

8.7.i. Objectives and parameters

The purposes of this phase of work are four-fold: (i) to consider a genetic relationship between Cavanacaw and Curraghinalt, (ii) to examine the relationship of Au with characteristic Pb signatures at Cavanacaw and Te at Cononish, (iii) to consider emplacement processes at the regional scale from a time immediately following the peak of Grampian metamorphism (+ c.10 Myr) to a period much later in the deformation of the orogen (+ c.40 Myr), and (iv) to test a modelled hypothesis based on review of literature indicating the circulation and interaction of brine fluids in the Sperrin Mountains, and magmatic involvement at Cononish (see Figure 8.2). This endeavour is approached with a limited dataset of petrographic and geochemical

observations and is largely attempted as an addition to more detailed work completed in earlier chapters. The contextual framework of evidence provided in this study includes thin section petrography of sections from ‘ore-zone’ material (with the caveat that these may or may not be fully representative of typical ore zone mineralisation) from Cavanacaw and Cononish, and geochemical data acquired using LA ICP-MS methods of in-situ spot analyses and raster element mapping within regions of interest. Questions are considered in the context of primary data acquired with reference to the literature.

8.7.ii. The relationship between Cavanacaw and Curraghinalt

Data presented in this chapter reveals mineralogical and geochemical distinctions between late sulphides at the Cavanacaw deposit and those from Curraghinalt addressed in *Chapter Five*. The principle petrographic differences are the observation of abundant galena and arsenopyrite in thin section microscopy which is not observed in late veins at Curraghinalt, the abundance of sulphide, and the observation of ductile deformation at Cavanacaw as evidenced in galena. In terms of similarities, ore stage pyrite at Cavanacaw (Py₁) is petrographically similar to Py₃ at Curraghinalt. Both Cavanacaw-Py₁ and Curraghinalt-Py₃ are relatively homogenous in appearance with limited brittle deformation and an association with visible Au. Py₁ at Cavanacaw has however undergone a later phase of recrystallisation which is not observed in tested post-deformational veins at Curraghinalt.

These observations pose the question of whether Cavanacaw-Py₁ and Curraghinalt-Py₃ are in fact the same phase, wherein comparable geochemical signatures ought to be observed (allowing for localised idiosyncrasies); further petrographic work is required, examination of vein sets outside the ore shell of Cavanacaw could reveal earlier phases of pyrite. This can be tested using geostatistical methods, specifically a two-sample t-test assuming for specific elements. Such a test assuming equal variance is used; results are provided as rudimentary and solely as an indicator of whether or not they are similar or different. Results show that

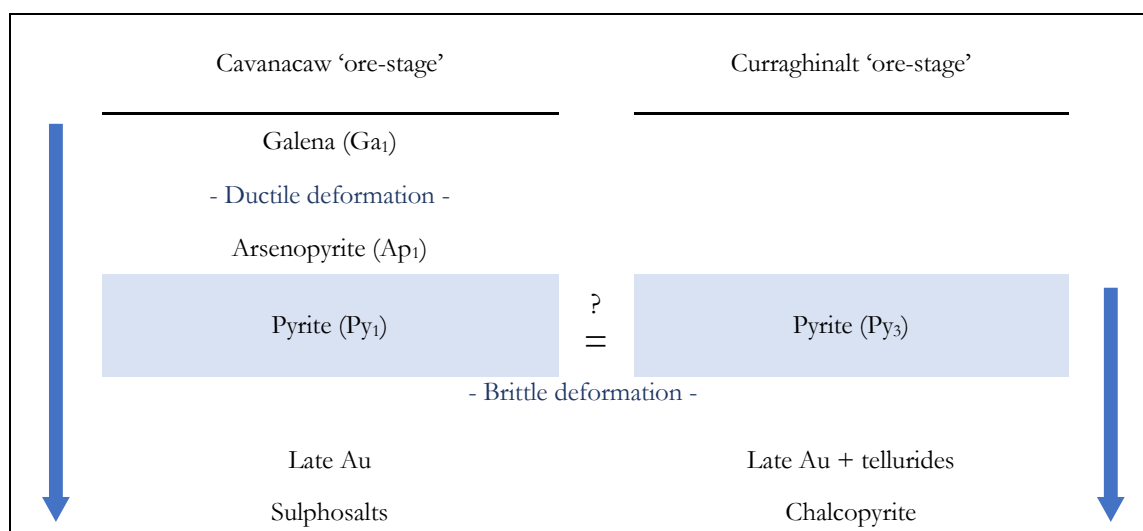


Figure 8.19. The hypothesis is tested that Cavanacaw Py₁ is the same phase as Curraghinalt Py₃, the blue arrows represent time and the relevant sequence of events at each occurrence is included.

population means of Ag ($P=.048$), Tl ($P=.03$), Ga ($P=.007$), Cu, As, Sb, Au, Hg and Pb ($P<.001$) (9 of 19 analytes) acquired from LA ICP MS spot analyses from Cavanacaw Py₁ ($n=6$) and Curraghinalt Py₃ ($n=137$) are significantly different (at the 95% confidence level), while there is no statistical difference at the 95% confidence level between population means for Te ($P=.878$), Zn ($P=.749$), Bi ($P=.693$), Mn ($P=.627$), Se ($P=.395$), Sn ($P=.304$), Ni ($P=.3$), W ($P=.262$), Co ($P=.201$) and Mo ($P=.075$) (10 of 19 analytes).

The test demonstrates that geochemically, ore-stage pyrite from Cavanacaw shows both similarities and differences to Curraghinalt Py₃: in the context of the genetic model for orogenic gold of (Goldfarb and Groves, 2015), the statistical differences observed for Au, Hg, Sb and As (at the 95% confidence level) suggest that trace elements may have been emplaced under relatively different metamorphic conditions, and that there may be partial but not full commonality of source. As aforementioned, a full suite of LA ICP-MS spot analyses is recommended for future work ($n\geq 50$), however it is proposed that these results show the potential of the methodology for investigations of mineral system evolution.

8.7.iii. Au and Pb at Cavanacaw

Pyrite at Cavanacaw is paragenetically linked to an abundant phase of galena (Ga₁) which is interpreted as an earlier phase in the overall paragenesis. Pb enrichment is also recorded in LA ICP-MS spot analyses of pyrite (Py₁), at a median concentration of 907 ppm (IQR = 71 = 17,875 ppm; n=6). The paragenetic relative timing of Ga₁ confirms that a Pb-rich source was available to the system prior to the emplacement of Au, which may have also enriched Py₁.

Results indicate that hydrothermal fluids accessed the Pb-rich source both during the Ga₁ and Py₁ emplacement. This source may be metamorphic, associated with deformation of the orogen; alternatively enrichment in Pb may be associated with magmatic fluids (e.g. El Dien et al., 2019) circulated during subduction of the inboard island arc during the Grampian orogen.

8.7.iv. Au and Te at Cononish

Much has been reported recently regarding tellurium at the Cononish Au deposit, and whether it may be an indicator of magmatic fluid interactions (e.g. Spence-Jones et al., 2018), and Te has in itself become a focus of economic interest (e.g. Goldfarb, 2014). Te is sometimes considered a critical metal (Ore Deposits Hub, 2020): these are a focus of active interest among the research community (e.g. Irish Centre for Research in Applied Geosciences, 2020a). The recent contribution by Spence-Jones et al. (2018) argues that a Te/Au ratio (from whole-rock geochemistry) of ≈ 2.4 (while for most orogenic Au deposits this is <1) from vein intersections indicates that Cononish is unusually Te-rich; coupled with $\delta^{34}\text{S}$ values acquired from samples of pyrite -2.0‰ to $+11.4\text{‰}$ through the paragenesis, their study considers that Cononish is polygenetic, sourcing metals from magmatic and sedimentary fluid components.

Results of LA ICP-MS spot analyses of pyrite in this study (n=50) show that average Te/Au for the tested sample is 58.1 (n=32) (see Figure 8.20, a plot of Te/Au). This is significantly higher than the value reported from bulk geochemistry by Spence-Jones et al. (2018), though has been acquired from pyrite directly, alleviating the dilution effects of bulk

methods. The median abundance of Te from spot analyses was 55 ppm (IQR = 7.53 – 488 ppm; n=40), however LA ICP-MS raster element mapping however demonstrates that Te is enriched in Py₂ (infiltration event I) within micro-fractures (> 100 ppm), and is relatively depleted within the host grain (< 100 ppm), emplaced prior to late Au (infiltration event II).

Examining these results in the context of findings of two discrete fluids by Spence-Jones et al. (2018) that account for an initial influx associated with a magmatic source, and a late fluid which they ascribe to metamorphosed SEDEX horizons: it is theorised in this study that two late fluids are responsible for emplacing the largest abundance of Te and Au forming the deposit, likely post-dating the initial magmatic event. Future analyses including a broad suite of pyrite grains from across the Cononish vein are recommended as a follow-up to this exercise in order to further test this hypothesis.

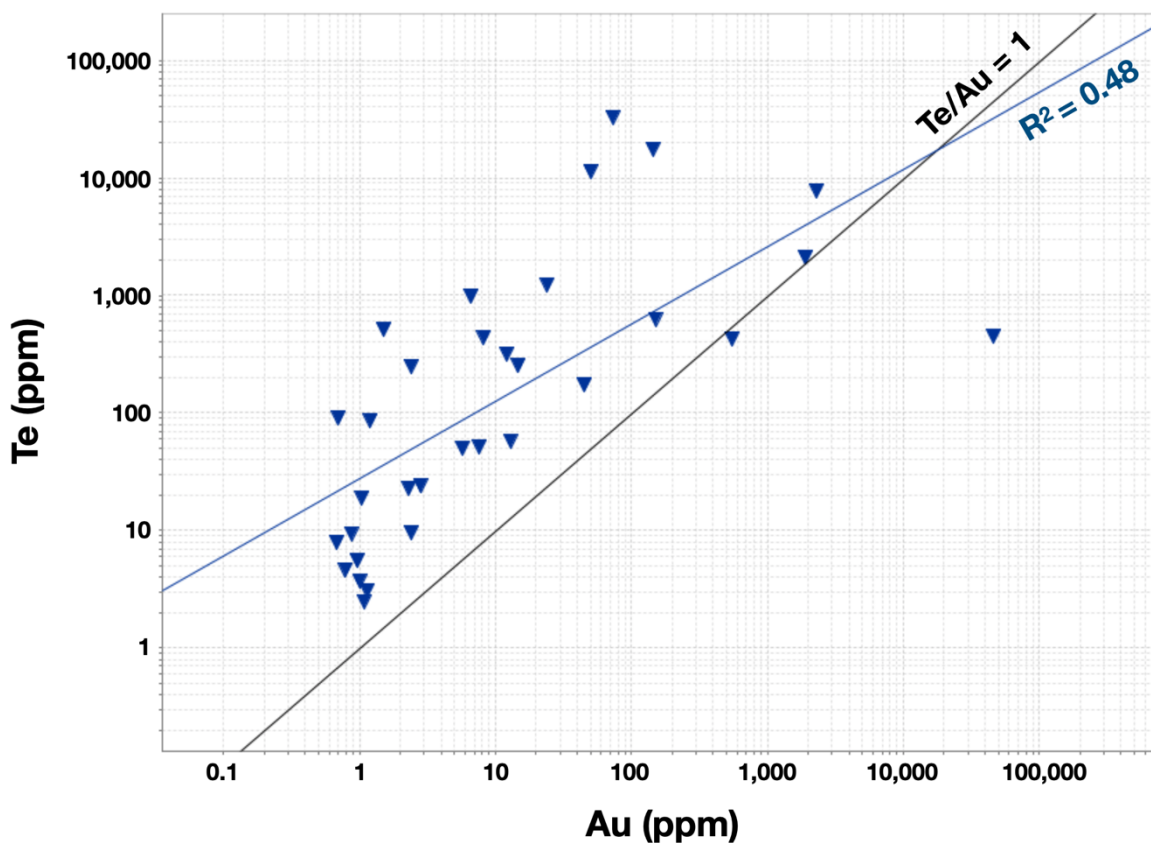


Figure 8.20. Te/Au plot for LA ICP-MS in-situ analyses of Cononish pyrite (n=32).

8.7.v. Emplacement mechanisms for Au

Data from this phase of work reveal initial Au emplacement at Cavanacaw and Cononish within pyrite itself, and within late micro-fractures at Cononish (this is supportive of findings from the Curraghinalt deposit where a similar two-phase emplacement process is observed in *Chapter Five*). Au deposition within orogenic, hydrothermal Au deposits is controlled by several physical and chemical mechanisms, as described by workers including Pokrovski et al. (2014).

Activity along the Omagh Thrust during the Grampian orogenic event resulted in movement along secondary faults, favourable for the emplacement of fluids and Au (e.g. Parnell et al., 2000). The recent structural model of Shaw et al. (2019) shows that such accommodating space may be created through localised strain partitioning during thrusting of host Dalradian metasediments over the colliding arc complex. The relative positioning of deposits on opposing flanks of a developing uplifted region resultant from thrusting may explain how different sources were accessed as the orogen collapsed. Vein emplacement at Cavanacaw is likely to be associated with fluid decompression due to rupture of proposed structures, with changes in fO_2 and pH likely having a role in the precipitation of Au. It is proposed that wall-rock interactions and fluid mixing may have played an important role across the Sperrins based on the work of several authors (e.g. Wilkinson et al., 1999; Parnell et al., 2000).

At Cononish, it is likely that movement of the Tyndrum fault created favourable pathways for early fluids carrying sulphur and trace elements, and a later fluid carrying Au along with Hg and Ag, preceding earlier metal emplacement events (e.g. Te in Py₂). Super-saturation of late fluid under retrograde metamorphic conditions enabled the free availability of Au⁰ nanoparticles which nucleated along the walls of micro-fractures and at junctions. Phase separation is a favoured mechanism, incorporating the description of a late fluid by Curtis et al. (1993) as CO₂-rich, homogenising at a temperature of between 290 and 340° C. Under this process, sudden decreases in pressure would lead to fluid immiscibility and the vapourisation of CO₂, resulting in the precipitation of Au. In both instances, changes in fO_2 or pH would also

result in the Au precipitation; fluid mixing which may have resulted from interactions with additional regional fluids can contribute to such changes.

8.7.vi. Timing of emplacement at Cononish

A proposed age of mineralisation at Cononish identified in review of the literature of between 428 and 425 Ma is considered by this study to be problematic. Described by Tanner (2012), dates were acquired using U-Pb (zircon) and Re-Os (molybdenite) dating of plutons and lavas ‘broadly synchronous’ with faults containing quartz and breccias associated with the deposit. It is considered in contemporary theory of orogenic systems that late intrusives may exploit the same pathways and regional fracture networks as those carrying fluids, though caution must be taken in (i) implying a genetic association of plutons with vein-gold deposits and (ii) suggesting synchronicity (e.g. Craw, 2013b). With respect to ore genesis, Groves et al. (2020) emphasise (citing Vielreicher et al., 2010) that while in certain instances lamprophyres and mafic intrusions do have a similar age to gold deposits, they are of too small a volume to have provided the fluids required to form those deposits.

8.8. Conclusions

This chapter presents petrographic and geochemical observations from a limited set of samples acquired from the vein-hosted Au deposits at Cavanacaw in County Tyrone, Northern Ireland, and at Cononish in the Stirling district of SW Scotland. Data from this study confirm the presence of visible Au phases hosted within pyrite, and characteristic enrichments of Pb at Cavanacaw, and of Te at Cononish. Visible Au is observed associated with pyrite at both deposits; LA ICP-MS spot analyses reveal that both carry Au within pyrite, at comparable concentrations (median., 3 ppm at Cavanacaw, n=6; median., 2.8 ppm at Cononish; n=35). Au is associated with Ag, W, Te, Hg, Sb, Pb and Cu at Cavanacaw, while at Cononish, an association

with Hg and Ag is recognised (micro-fracture emplacement phase II). A moderate As (0.01 – 10 mol% range) – moderate Au (10^{-6} to 10^{-4} mol%) trend at Cavanacaw suggests that emplacement occurred in the initial late orogenic stages, while a distinctive low As (0.001 to 0.01 mol%) – high Au (10^{-6} to 1 mol%) trend at Cononish is distinctively retrograde: indicative of cooling and the free availability of Au⁰ nanoparticles in the latter stages of orogenesis. Interpretation may be made based on element associations that Cavanacaw formed at shallower depths (at a lower metamorphic grade) than Cononish.

Cavanacaw is distinctive from the proximal Curraghinalt deposit (see *Chapter Five*) at the mineralogical and geochemical level, in having an observed paragenetic association with abundant galena and arsenopyrite, while Au-associated pyrite has statistically dissimilar concentrations of Ag, Tl, Ga, Cu, As, Sb, Au and Pb. However, both record the presence of visible Au within pyrite which is morphologically similar, and show statistically similar concentrations of Te, Zn, Bi, Mn, Se, Sn, Ni, W, Co and Mo. It is considered that at one time during the evolution of the Sperrin Mountains system during late orogenesis, these elements were carried by similar fluids, while at another (earlier) time, Cavanacaw pathways had access to a separate source which was Pb-rich. It is likely that the unique structural situation of Cavanacaw veins (with a dominant N-S orientation rather than WNW-ESE) is a factor in the potential sources available, one possible explanation is that Pb-rich fluids may have been sourced from fluids associated with the Tyrone Igneous Complex to the south.

It is proposed that at least three geochemically distinct metalliferous emplacement events are recognised associated with late infiltration of fluids into micro-fractures of Cononish pyrite: event I (Py₂; Co-Ni-As-Ag-Sb-Te-Pb-Bi) and event II (Au-Hg-Ag; synchronous with the emplacement of Cu and Sb). It is proposed that these data demonstrate the effectiveness of LA ICP-MS raster element mapping in determining more detailed understanding of metalliferous emplacement within grains showing deformational complexity, compared to solely relying on LA ICP-MS spot analyses which confer signatures which while indicative, do not provide the complete picture.

Given the possible late-orogenic timing of the Cononish deposit, c. 50 Myr after the peak of deformation, a secondary source is also invoked; however given the late timing of Au emplacement (relative to the precipitation of pyrite) evidenced in this study by LA ICP-MS analyses, and the suggestion in previous studies that metamorphically derived fluids circulated after magmatic fluids in the Tyndrum area, it is considered viable that an intrusive body may have catalysed the remobilisation of metamorphic fluids, late in the development of the orogen.

Chapter Nine: The potential of pyrite for vectoring and exploration strategy

9.1. The exploration context

The objective of mineral exploration is an economic discovery. The challenges are immense: ventures themselves are relatively high-risk investments, much depends on the median to long-term outlook for capital markets and the commodity of interest (which may itself depend on a suite of unknown factors), jurisdiction, labour, infrastructure, the availability of expertise and importantly access to sustainable sources of investment. This burden of risk is often taken by junior companies with a view to attracting the interest of mid-tier to major mining companies with the capacity to build an economic mine.

The challenges facing the industry over the past number of years have expanded and coalesced to a point where there is currently much discussion of ‘The Crisis in Mineral Exploration’. A 2015 report by the Boston Consulting Group (Koch et al., 2015), with contributions from MinEx Consulting, identifies the central problem: that exploration has too often not been considered a high priority, even a target for cost-reduction, and that this has led to the depletion of metal reserves. As stated in the report, exploration during the years preceding its publication had delivered little success relative to the scale of projected demand. Recommendations are made from the board room to the field team, highlighting the need for a focus on simple large targets in mineralised districts and a drill strategy aligned to return on

investment. An integrated approach is advised to mitigate risk and heighten the probability of discovery and delineating a resource at the necessary scale, with a focus on four key areas: (i) exploration strategy, (ii) exploration management, (iii) innovation and (iv) talent development and people management (see Figure 9.1). Technologies, for example: real-time down-hole ‘sensing’, novel approaches to the modelling of ore bodies, and the use of data and analytics are identified as key to optimising those strategies.

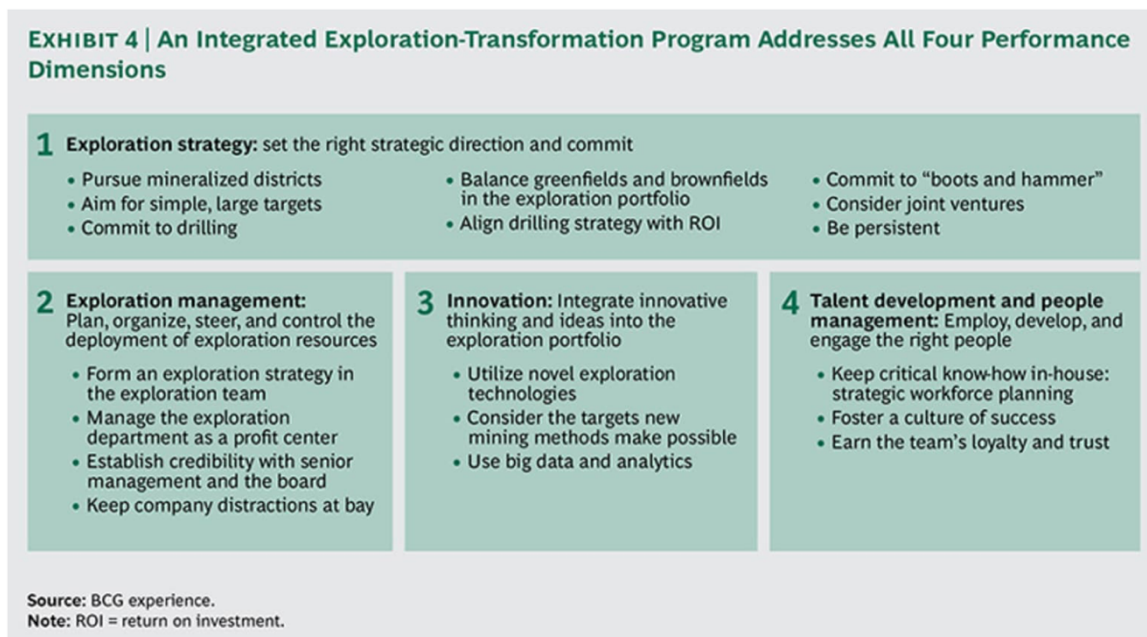


Figure 9.1. Exploration approach recommended by Boston Consulting Group (Koch et al., 2015).

The process of exploration includes four key stages: (i) *target generation*: this step seeks to define viable prospects through the review of available technical information, early interpretations of data, mapping, soil sampling, geophysical surveys and other geological activities aimed at enhancing geological knowledge; (ii) *target drilling*: with the objective of intersecting mineralisation, which may involve various methods including percussion, reverse circulation and diamond drilling; (iii) *resource evaluation drilling*: to define the three-dimensional extent of an ‘ore body’ and potential resource using drilling, and (iv) *feasibility studies*: the final step, through which integration of geological and socio-economic factors determines whether

the defined resource may be viable for extraction, to include metallurgical test work and statistical studies of the resource (Marjoribanks, 2010).

This study concerns the development of vein-hosted gold mineralisation associated with the Grampian arc-continent collisional event, hosted by the Dalradian Supergroup in north-west Ireland. It has generated insights into the evolution of a complex terrane-scale system of hydrothermal fluid and metal mobility through the examination of pyrite, utilising emerging technologies including Scanning Electron Microscopy (SEM) and Laser Ablation Inductively Coupled Plasma - Mass Spectroscopy (LA ICP-MS) in a novel, integrated capacity. At the regional-scale, results support the presence of a tectonically-driven system with the potential to mobilise fluid and metals from depth at the scale required to generate large ore-bodies (see *Chapter Seven*). At the deposit-scale at Curraghinalt, Northern Ireland, precursor phases of Au and base metal mineralisation have been discovered which may provide an indicator of localised system fertility, and a disconnect is identified between host pyrite and late orogenic mineralisation emplaced following brittle deformation and cataclasis (see *Chapter Five*). Geochemical distinctions have been identified between deposits exhibiting localised geological differences (e.g. host mineralogy, structural control and timing, see *Chapter Eight*), confirming the need to consider the larger genetic model, but to also be wary of applying broad generalisations at the local level: for example, while a consistent mineralogical and geochemical relationship between Au, As, Bi, Te and Ag is encountered at deposits and prospects across the trend, investigation of Au/As ratios reveals differences in solubility of Au in pyrite suggestive of differences in occurrence-scale physical and chemical conditions associated with emplacement.

At the level of the emerging prospect, at Cloonacool in the Ox Mountains, LA ICP-MS methods have enabled the identification of multiple episodes of fluid interactions, bearing different metal signatures. This has demonstrated that repeated opening and closure of fluid pathways occurred, and that trace elements including Au, As, Co, Ni, Sb, Te and Bi were mobile synchronous with deformation of the terrane during orogenesis.

The implications of this work for exploration are two-fold: (i) that insights gained from this research may benefit understanding of the geological processes and metal mobility from the deposit to the regional-scale, and (ii) that SEM and LA ICP-MS technologies may be used to rapidly evaluate mineral localities from the perspective of their Au potential and their relative position in the overall system (e.g. with respect to time, metamorphism, tectonics, element mobility). These are investigated in this chapter with reference specifically to the four stages of exploration aforementioned (target generation, target drilling, resource evaluation drilling and feasibility), prospectivity (including mineralogical and geochemical vectoring), and the use of novel technologies in an optimised approach. All of these are considered in the context of a challenging economic environment for exploration, with a view to enhancing potential for discovery.

9.2. Geochemical signatures and vectors across the Grampian orogen: Au and elements showing positive correlation

Results for Au report above detection in LA ICP-MS in-situ analyses for all tested generations of pyrite and pyrrhotite across the Grampian Terrane. These generations are hosted within veins throughout tested stratigraphy and stratabound within lower host formations of the Dalradian Supergroup. Au where observed as visible particles is found to have a mineralogical paragenetic association with Ag- and Bi- tellurides (e.g. at Curraghinalt within late micro-fractures of ‘ore-stage’ Py₃, see *Section 5.9*). As aforementioned, the geochemical association between Au and As has enabled the prediction of Au solubility within pyrite at different stages in the evolution of the orogen (see *Chapter Ten*, Figure 10.1). Within phases of pyrite, Au concentrations (refractory) are found to show a positive correlation (Spearman rank, $\rho \geq +0.5$) with Co, Ni, Cu, Mo, Ag, W, Hg (transition metals), Ga, Sn, Tl, Pb, Bi (base metals) and As, Sb, Te (metalloid), with systematic chemical variations observed for each pyrite generation tested (see subsequent

sections). These observations are summarised in Figure 9.1, which lists tested generations in order of the relative enrichment and depletion of Au concentration with reference to the median of all LA ICP-MS spot analyses (0.69 ppm; IQR = 0.2 – 2.11 ppm; n=284 reporting above detection for 520 individual analyses). The highest median concentration of Au while for analyses of pyrite was recorded for samples of Curraghinalt Py₂ (3.69 ppm, n=34; see Figure 9.2 and Figure 9.5). Au mobility from potential source strata into the system is discussed in *Chapter Seven* and *Chapter Ten*, however it is potentially important to note from an exploration standpoint that the pyrite phase ‘hosting’ mineralisation at Curraghinalt (within micro-fractures), Py₃, shows an Au concentration (refractory; 0.31 ppm, n=69) lower than the median for all pyrite analyses conducted in this study (0.69 ppm). This is a strong indication of the importance of late fluid interactions concentrating Au, observed in this study within micro-fractures as aforementioned (see *Chapter Five*, Figure 5.17).

Optimal exploration criteria for orogenic Au in the Grampian terrane include: (i) petrographic constraints within late veins (cross-cutting S₂/S₃ schistosity) in localised structural zones (e.g. dilation zones); (ii) low concentrations of trace elements within late-orogenic pyrite and the presence of cataclastic brittle fracturing; (iii) visible Au within late micro-fractures which may coincide with the occurrence of Bi- and Ag- telluride phases; (iv) greenschist to lower amphibolite facies host rocks; (v) evidence of pathway interactions with late fluids [these likely correspond to those with a H₂O-NaCl-CaCl₂ composition, e.g. Wilkinson et al. (1999)].

Favourable exploration criteria include (i) evidence of episodic fluid flux through syn-deformational fractures; (ii) positive correlation in pyrite of Au with Ag (Spearman rank, $\rho \geq +0.5$), (iii) Au/As plotting above or toward the solubility curve of Deditius et al. (2014), $C_{Au} = 0.004.C_{As} + 2 \times 10^{-7}$ (where C_x is the concentration in mol%), indicating the mobility of Au⁰ nanoparticles; (iv) the presence of precursor phases of pyrite containing lattice-bound Au indicating mobility of Au in early (prograde) metamorphically-derived fluids (carrying Au in HS-

complexes); (v) evidence of fluid mixing and interaction with host rocks; (vi) positive correlation of Au with Te in pyrite contained within syn-deformational veins (Spearman rank, $\rho \geq +0.5$).

Models are presented in individual chapters of this thesis which may be of value to explorers including (i) the mobilisation of Au from lower Dalradian Supergroup strata and structures (*Chapter Seven*, Figure 7.20) and (ii) a schematic model of Au incorporation into late micro-fractures (*Chapter Five*, Figure 5.17), (iii) conceptual transport pathways for fluids, Au and their association with pyrite growth zones (*Chapter Seven*, Figure 7.20) and (iv) a schematic 3-D overview of the overall Grampian system in north-west Ireland (*Chapter Ten*, Figure 10.7). Subsequent tables detail geochemical associations which may provide vectors, and key

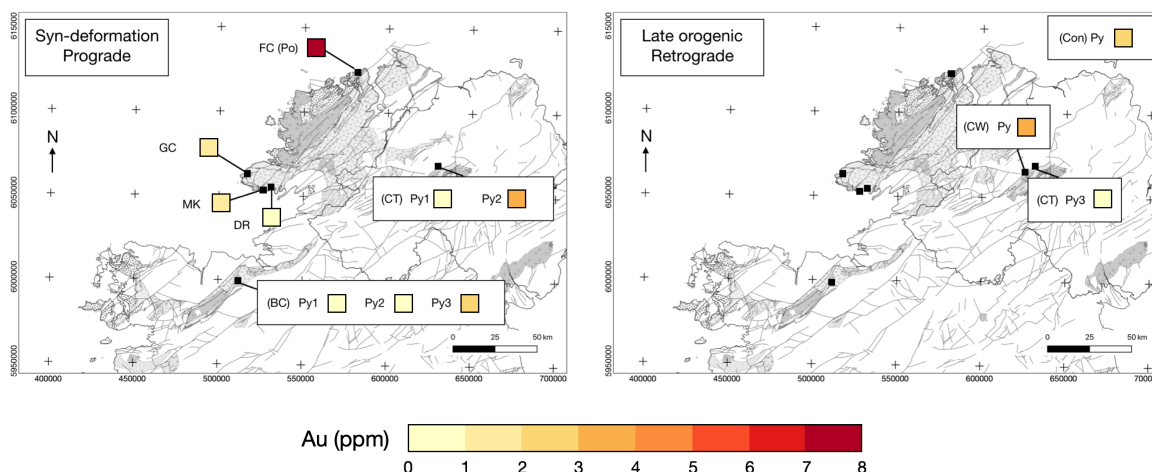


Figure 9.2. Spatial representation of median concentrations of Au from LA ICP-MS analyses ($n=284 > \text{LOD}$ for 520 analyses). recorded for generations of pyrrhotite and pyrite acquired; syn-deformational phases are on the left, while those which are peak- to late- orogenic are shown to the right (evidenced petrographically by their relationship with host fabrics; in the case of Cavanacaw and Cononish this is inferred with reference to the literature). Abundances are represented by a colour-scale. Abbreviations and concentrations reported: FC: Falcarragh (pyrrhotite; median = 7.8 ppm, $n=3$); GC: Glencolumbkille (pyrite; median = 1.4 ppm, $n=1$); MK: Muckros (pyrite; median = 1.75 ppm, $n=6$); DR: Derrylahan (pyrite; median = 0.91 ppm, $n=4$); BC: Cloonacool (pyrite; Py₁ median = 0.54 ppm, $n=59$; Py₂ median = 0.76 ppm, $n=30$; Py₃ median = 2.22 ppm, $n=5$); CT: Curraghinalt (pyrite; Py₁ median = 0.19 ppm, $n=35$; Py₂ median = 3.69 ppm, $n=34$; Py₃ median = 0.31 ppm, $n=69$); CW: Cavanacaw (pyrite; median = 3 ppm, $n=6$); Con: Cononish (pyrite; median = 2.8 ppm, $n=35$). The base map was created using QGIS using shapefiles acquired from the open-source Bedrock Geology Map of Ireland (1:500,000) published online by Geological Survey Ireland.

Identified pyrite phase (and chapter reference). (VG = visible Au, LT = lattice-bound Au)	Locality type	Vein /rock host	Host Group	km from FHCBL -HBF*	Spearman rank correlation ($\rho \geq +0.5$)	Dominant predicted solubility (using LA ICP-MS spots unless stated)	Syn-/late	‘Ore-stage’	Au ppm (median)	% + / -	n > LOD (spot)
● Curraghinalt Py ₂ (C.5) LT	Deposit	Vein	SOHI	<10	As, Tl	Lattice-bound	Syn-		3.69	+439	34
● Cavanacaw Py-Ore (C.8) VG	Deposit	Vein	SOHI	<1	Hg, W, Ni, Ga, Ag, Mo, Sn, Bi	Lattice-bound	Late §	✓	3.00	+337	6
● Cononish Py-Ore (C.8) VG	Deposit	Vein	GRAM -APPN	~35	Ag, W, Te, Hg, Sb, Pb, Cu	Au ⁰ NPs	Late §	✓	2.80	+267	35
● Cloonacool Py ₃ (C.6)	Prospect	Vein	ARGY	<1	Te, Hg, Cu	Lattice-bound	Syn-		2.22	+224	5
● SL - Muckros (C.7)	Shale	Rock	ARGY	~50	Co, Bi, Pb, Mn, Cu, As	Au ⁰ NPs **	Syn-		1.75	+156	6
● SL - Glencolumbkille (C.7)	Shale	Rock	ARGY	~60	n/a	Lattice-bound [±]	Syn-		1.40	+104	1
● SL - Derrylahan (C.7)	Shale	Rock	ARGY	~50	Sb, Tl	n/a **	Syn-		0.91	+32.8	4
● Cloonacool Py ₂ (C.6) VG	Prospect	Vein	ARGY	<1	As, Te	Lattice-bound	Syn-	✓	0.76	+11.4	30
Median, all data									0.69	-	284
● Cloonacool Py ₁ (C.6)	Prospect	Vein	ARGY	<1	Te, As, Ga, Bi	Lattice-bound	Syn-		0.54	-21.2	59
● Curraghinalt Py ₃ (C.5) VG	Deposit	Vein	SOHI	<10	Ag, Bi, Te, Sb, Pb	Au ⁰ NPs	Late	✓	0.31	-55.2	69
● Curraghinalt Py ₁ (C.5)	Deposit	Vein	SOHI	<10	As, Pb, Mo	Lattice-bound	Syn-		0.19	-72.6	35

Table 9.1. Relative percentage difference in median concentration of Au for each pyrite generation analysed using LA ICP-MS (spots). ‘Ore-stage’ pyrite is defined as the principle generation hosting visible gold, whether that is within pyrite as inclusions or within late cataclastic micro-fractures. Au solubility predictions are defined by the relationship of Au to As, as defined by Deditius et al. (2014) for high-temperature conditions appropriate to orogenic systems. SOHI = Southern Highland Group, ARGY = Argyll Group, APPN = Appin Group, GRAM = Grampian Group. LOD = Limit Of Detection, VG = Visible Gold, LT = Lattice-bound. “Syn-/late” refers to Grampian orogenic deformation. * Estimated at surface. [±] resolved using LA ICP-MS raster element mapping. ** This may be resolved by further LA ICP-MS raster element mapping. § with reference to literature.

observations for tested pyrite. It is recommended that explorers consider where observed pyrite is positioned within the regional system of orogenesis and deformation, and that prospects may exhibit localised variation which differ from regional trends, when considering prospectivity.

9.3. Exploration strategy

9.3.i. Overview

This study determines that the Dalradian Supergroup in both Ireland and Scotland, deformed during the Grampian arc-continent collisional event, is prospective for unknown large deposits of Au, through the determination of syn-deformational Au and trace element mobility (e.g. *Chapter Seven*), and emplacement subsequent to late brittle deformation (e.g. *Chapter Five*). Geographically, strata tested in this study are located in the north and west of Ireland extending into SW Scotland, however previous workers have also established continuity to the west, associating the Grampian orogenic event with the Taconic event of North America (e.g. Hollis et al., 2012) and to the north-east with deformed strata recognised in Norway (Yoshinobu et al., 2002). The suture of the orogen is a crustal-scale structure known as the Fair Head – Clew Bay Line in Ireland and the Highland Boundary Fault in Scotland, along which deposits are recognised in close proximity. Prolonged Au mobility along this trend is interpreted from phases synchronous with the formation of fabrics, driven by metamorphic processes with high fluid-rock ratios. Early pyrite is likely to have transitioned to pyrrhotite at the greenschist-amphibolite facies transition, driving the release of aqueous fluids carrying Au in HS-complexes which were distributed through available structures. Locally, fluid mixing is likely to have occurred including the mixing of formation waters with a low-temperature ($T_h = 120\text{ }^{\circ}\text{C}$) brine of $\text{H}_2\text{O}-\text{CaCl}_2-\text{NaCl}$ composition and with a salinity of 12-21 wt.% (Wilkinson et al., 1999). These fluids are observed by Wilkinson et al. (1999) to have an association with brittle tectonic reactivation, which likely resulted in cataclasis observed in this study at Curraghinalt (see *Chapter Five*). Their study interprets that $\delta^{18}\text{O}$ values (0 per mil) are most likely attributed to surface waters: seawater,

meteoric waters, or fluids derived from seawater, with high salinities most likely relating to evaporites or evaporated seawater. A recent proposal for the origin of brines is that they may be derived from a forearc basin geologically represented by strata at Pomeroy, south of Curraghinalt, or that they emanated from compression of the Tyrone Volcanic Group (Rice et al., 2016). A Carboniferous timing associated with reactivation was favoured by Wilkinson et al. (1999), however this is not supported by evidence presented by Rice et al. (2016) that all gold emplacement at the Curraghinalt deposit is confined to the Ordovician (462.7-452.8 Ma; derived from Re-Os (molybdenite) and $^{40}\text{Ar}/^{39}\text{Ar}$ dating (sericite) within cross-cutting micro-shears).

Information in this thesis builds a case for prospectivity and augmented exploration of the belt for Au deposits. Based on information attained in this research and work by others in comparable orogenic systems associated with tectonics and metamorphism such as the Otago Schists of New Zealand (e.g. Pitcairn et al., 2014), it is likely that the full potential of Au within the Grampian terrane has not yet been realised. It is recognised that additional work is required to establish calculations of the scale of fluid mobilised and the chemistry of those fluids across the terrane, this will involve systematic testing of regional veins across different metamorphic grades. It is also envisaged that phase discrimination of pyrite and pyrrhotite at upper greenschist to lower amphibolite facies is required to broaden the case for metamorphic devolatilisation. Nevertheless, this thesis provides an augmented platform upon which to deepen our understanding of Au mobility across the terrane through targeted petrographic and geochemical examination of Au-associated pyrite, at mineralised systems and in lower stratigraphy.

9.3.ii. How can pyrite geochemistry generate a positive exploration outcome?

Three key objectives are identifiable for which microanalytical strategies including geochemical analyses of pyrite are of value: (i) the identification of a prospective target with the potential to host resources at the desired magnitude (a high value outcome), (ii) a reliable vector toward a

potential deposit, and (iii) the fertility of structures hosting Au-transporting hydrothermal fluids (medium to high value outcomes). Pyrite geochemistry may aid other aspects of the exploration process, for example in resource definition tracking the variability of Au spatially within veins, or within metallurgical studies tracing deleterious elements. While also desirable these are not pre-requisite to the discovery of an ore deposit.

Target identification

Pyrite geochemistry can form part of an integrated approach in support of traditional targeting methods (e.g. mapping, regolith geochemistry), geophysics and the consolidation of historical spatial datasets. This study makes the following recommendations to assist in the identification and initial evaluation of targets:

LA ICP-MS mapping of pyrite to reveal the emplacement history: pathways within host-rock and grains themselves (e.g. micro-fractures) may be exploited multiple times by fluids bearing polymetallic compositions: The analysis of pyrite using microscopic and spectroscopic methods within individual veins and stockwork zones is advised to identify prospective vein types and pathways. The micro-analytical characterisation of Au-bearing (visible or refractory) pyrite phases may be introduced within early stages (e.g. reconnaissance mapping and sampling). For example, at the Cloonacool prospect in County Sligo, Ireland (see *Chapter Six*), LA ICP-MS raster element mapping was effective in this study in identifying cryptic Au-, Pb- and Zn-associated geochemical domains in grains which appear broadly homogenous with conventional microscopy. The identification of syn-deformational pathways exhibiting a Au-As signature is considered a positive outcome as it clearly defines auriferous hydrothermal fluid interaction with host rocks, while the observation of Pb- and Zn- bearing phases permitted a sequence of chemical emplacement events to be interpreted. As aforementioned, this record can be attained from field samples and may be a cost-effective prospecting tool, which may be followed up by macro-scale characterisation of vein network extent.

LA ICP-MS spot analyses of pyrite: e.g. Au and As can reveal information with regard to the solubility of Au and relative timing of sulphidation: As described in *Chapter Nine*, differing relative proportions of Au and As are associated prograde and retrograde metamorphic conditions. Syn-deformational pyrite carrying Au tends to lie below a solubility curve. The Au/As ratio may also be utilised as a proxy for such events where fabric constraints are unavailable or unclear.

Target identification: proposed workflow

Figure 9.3 presents a proposed workflow for the integration of micro-analytical techniques to aid targeting. The first sub-workflow, where brittle deformation and late micro-fracturing has been identified, shows how positive outcomes may be attained through petrography (e.g. the identification of visible Au and tellurides) prior to closer examination of those micro-fractures using SEM and LA ICP-MS techniques to characterise the metallic signature of late fluid interactions. This is most relevant to late veins (e.g. in the Sperrin Mountains geological setting). The second sub-workflow shows positive and negative outcomes which may result from micro-analysis of grains themselves.

Pyrite geochemistry using spot analyses is not a reliable stand-alone indicator of prospectivity for late orogenic veins: Au hosted by the ‘ore-stage’ generation of pyrite at the Curraghinalt deposit was found to be depleted (relative to median values encountered at sample sites across the trend) in Au (refractory) and all tested trace elements with the exception of Te, while at Cavanacaw, this is the case for all tested trace elements except As, Sb, Hg, Ag, Au and Cu. At Cononish, Pb, Te, Ag, Hg, Au, Cu, Sn and Sb were found to be relatively enriched, while As, Ga, Tl, Bi, Mo, Co, Ni and W are relatively depleted. It is recommended to integrate LA ICP-MS raster element

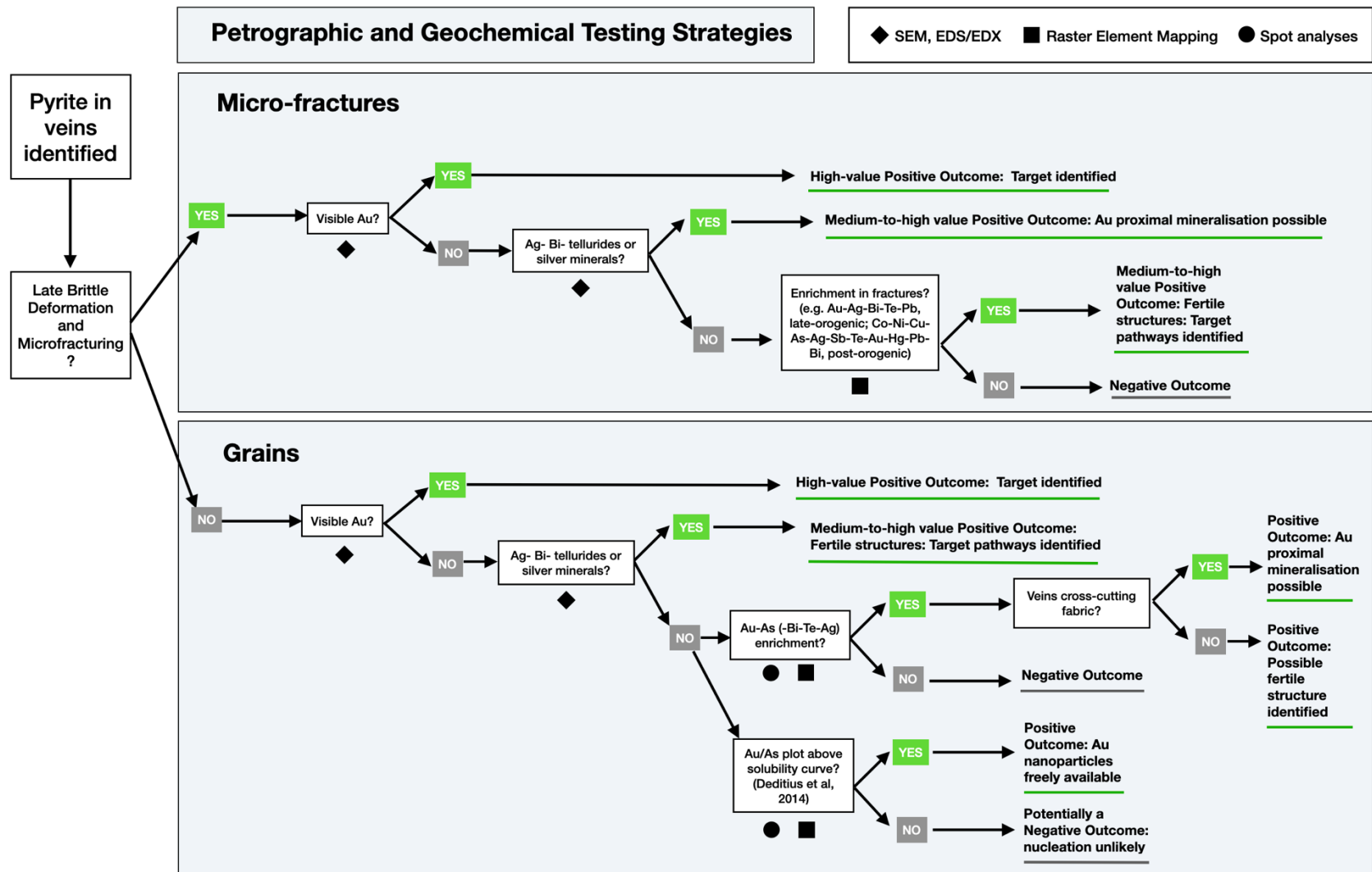


Figure 9.3. Example workflow for determining positive and negative outcomes using microanalytical techniques used in this study.

mapping into procedures as it has the capacity to reveal important information on late events (e.g. the infiltration of auriferous fluids into micro-fractures).

Vectoring toward a target

This study has determined that distal pyrite chemistry has limited applicability as a vectoring tool for mineralisation, however can provide valuable information regarding the early circulation of fluids bearing Au which may be pre-concentrated for later remobilisation.

Syn-deformational pyrite may pre-concentrate Au for later re-distribution and provide an indicator of horizon or structure fertility: The observation of syn-deformational pyrite carrying Au correlating positively (Spearman rank, $\rho > 0.5$) with As and Tl (Curraghinalt Py₂) in *Chapter Five* using LA ICP-MS spot analyses (see Table 5.4) and raster element mapping (see Figure 5.13 and Figure 5.14) is considered an important outcome of this study. The mobility of Au synchronous with the Grampian collision is supported by findings in *Chapter Six*, where visible Au is identified in syn-deformational veins at Cloonacool (correlating positively with As and Te, see Figure 6.17 and Figure 6.22), and *Chapter Seven*, where Au particles are observed in early Appin Group pyrrhotite (see Figure 7.11) and within the lattice of Argyll Group pyrite (correlating positively with Ga, Bi and Te). These observations point to broad mobility of Au and associated elements synchronous with the development of fabrics, examined in *Chapter Nine*.

Au concentrated in syn-deformational phases has the potential to form deposits, or act as a pre-concentrated cache from which it may be remobilised into later phases. Discovery of auriferous syn-deformational phases by prospectors may de-risk costly exploration activities (e.g. drilling) through integration of this data with macroscopic datasets which define the extent of host horizons and structures. In agreement with Groves et al. (2020), it is considered important to review province-scale architecture (e.g. using seismic reflection surveys to reveal structural information and magneto-telluric regional-scale surveys; the recent intra-

governmental Tellus survey may be a vital dataset) and district-scale fluid infiltration specifically along first-order lineaments: within the Grampian orogenic terrane, D₂ structures may be important initial carriers of fluids. Fluid focusing may be associated with anti-formal traps, for example Curraghinalt and Cavanacaw may be associated with the flanks of such a structure associated with the topology of the colliding island arc; see *Section 8.3*. District-scale fluid infiltration proximal to granite bodies is less applicable in general given our current understanding of the orogen, though may be an important future exploration target: Cononish may be associated with late intrusives, see *Chapter Eight*. It is also recommended to review deposit-scale stratigraphic traps and caps (rheological contrasts are likely to have facilitated fluid flow in the Grampian terrane, see *Chapter Three, Section 7.8*).

Wallrock pyrite proximal to veins has a syn-deformational signature and therefore cannot be used as a vector to late-orogenic mineralisation: This determination is made based on LA ICP-MS spot analyses of pyrite at the Curraghinalt deposit in Northern Ireland and is considered a vital observation for exploration. A test was conducted acquiring data from 20 x 20 µm spot analyses on 5 grains of wallrock pyrite (n=10) situated proximal (2,875-6,440 µm) to the ‘Grizzly’ vein hosting identified generation Py₃, associated with Au within micro-fractures (see *Chapter Five*, Figure 5.2). Equipment and techniques used for this test are the same as those described in *Chapter Five, Section 5.7.v*. A rudimentary comparison of results occurring within order-of-magnitude ranges (e.g. 1-10 ppm, 10-100 ppm, 100-1,000 ppm) reveals that between wallrock pyrite and Py₃, 8 of 15 tested elements lie within the same range (53%); between wallrock pyrite and Py₁, this is the case for 2 of 15 tested elements (13%), while comparing wallrock pyrite and Py₂, 11 of 15 elements report in the same order of magnitude (73%) suggesting a potential match.

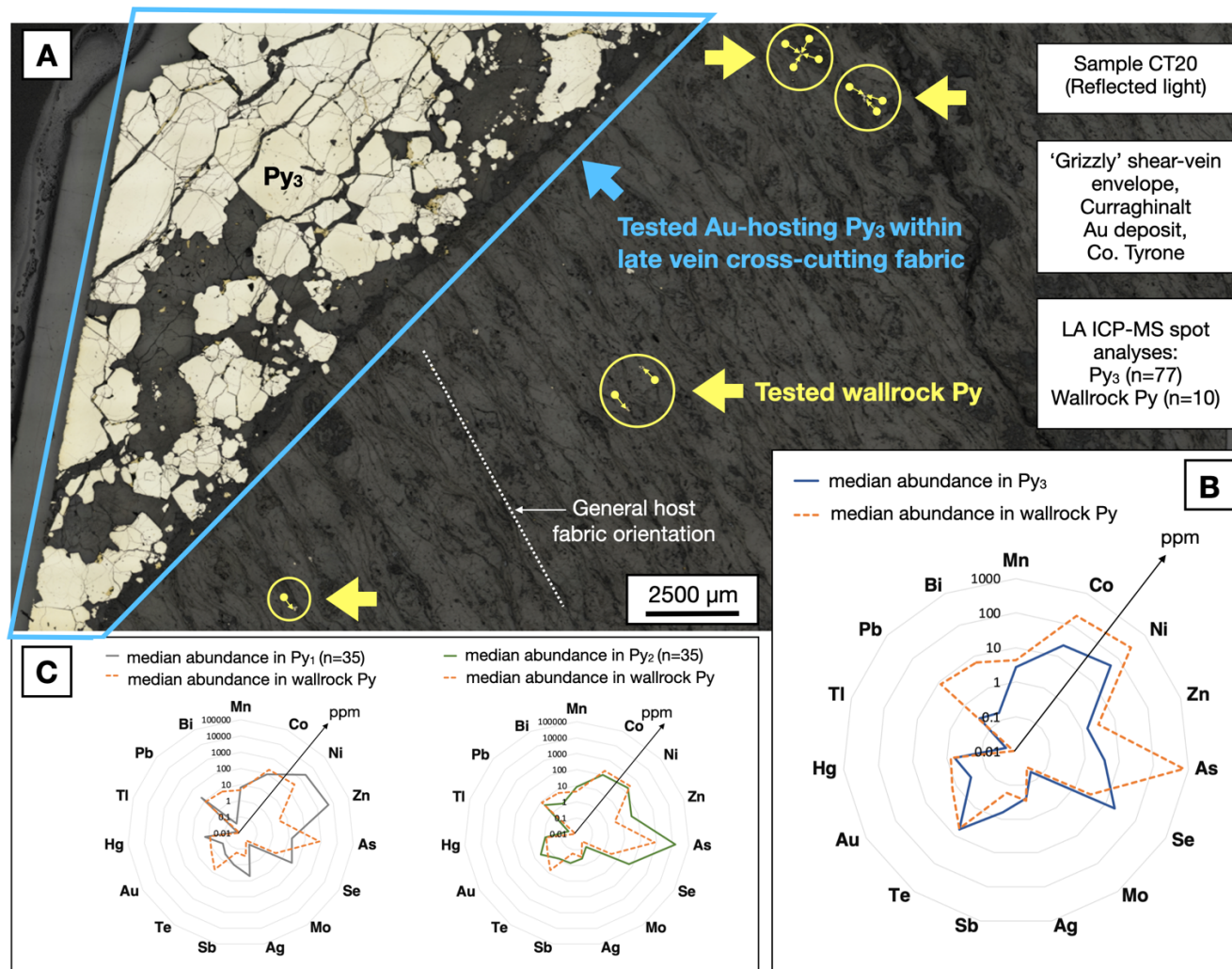


Figure 9.4. (A) Curraghinalt Au deposit sample CT20 (thin section in reflected light), showing the general location of LA ICP-MS spot analyses of 'ore-stage' Py₃ (n=77; blue annotation) and wallrock pyrite (n=10; yellow annotation), with the general orientation of host fabrics sub-perpendicular to the vein (white dashed line); (B) radar plot of trace element concentrations (in parts per million, ppm) of Mn, Co, Ni, Zn, As, Se, Mo, Ag, Sb, Te, Au, Hg, Tl, Pb and Bi (analytes reporting above detection in both populations), for Py₃ and wallrock Py; (C) a comparison of wallrock Py concentrations (in ppm) with earlier syn-deformational phases Py₁ (n=35) and Py₂ (n=35); radar plots visually demonstrate that wallrock Py contains more comparable abundances of trace elements to Py₂ than Py₃. Due to proximal wall-rock pyrite not containing an ore-stage Py₃ signature (with only comparable concentrations of Mn, Zn, Ag, Te, Hg and Bi), it cannot be used as a vector to mineralisation.

	ppm; wall-rock Py (n=10)	ppm; Py ₃ (n=77)	Same range? (e.g. 1-10 ppm)
Mn	4.40	2.69	Yes
Co	195	22.3	No
Ni	300	49.5	No
Zn	3.22	1.50	Yes
As	762	3.69	No
Se	3.10	19.5	No
Mo	0.04	0.05	Yes
Ag	0.29	0.24	Yes
Sb	0.17	0.63	Yes
Te	5.92	6.27	Yes
Au	1.30	0.31	No
Hg	0.79	0.60	Yes
Tl	0.01	0.02	Yes
Pb	8.20	0.26	No
Bi	6.30	0.17	No

	ppm; wall-rock Py (n=10)	ppm; Py ₂ (n=35)	Same range? (e.g. 1-10 ppm)
Mn	4.40	8.25	Yes
Co	195	105	Yes
Ni	300	191	Yes
Zn	3.22	39.0	No
As	762	14,680	No
Se	3.10	58.0	No
Mo	0.04	0.10	Yes
Ag	0.29	0.37	Yes
Sb	0.17	0.72	Yes
Te	5.92	0.78	No
Au	1.30	3.69	Yes
Hg	0.79	0.89	Yes
Tl	0.01	0.03	Yes
Pb	8.20	4.85	Yes
Bi	6.30	1.22	Yes

	ppm; wall-rock Py (n=10)	ppm; Py ₁ (n=35)	Same range? (e.g. 1-10 ppm)
Mn	4.40	6.60	Yes
Co	195	92.0	No
Ni	300	2,410	No
Zn	3.22	5,030	No
As	762	16.0	No
Se	3.10	45.5	No
Mo	0.04	0.08	Yes
Ag	0.29	5.12	No
Sb	0.17	1.04	No
Te	5.92	0.41	No
Au	1.30	0.19	No
Hg	0.79	1.73	No
Tl	0.01	0.02	No
Pb	8.20	17.9	No
Bi	6.30	0.04	No

Table caption overleaf

Table 9.2. (previous page). Median abundances of trace elements in tested wall-rock Py at Curraghinalt, compared to the ore-stage (Py₃), and earlier syn-deformational phases (Py₁ and Py₂). Comparison of ranges (defined by logarithmic order of magnitude, e.g. 1-10 ppm, 10-100 ppm, 100-1,000 ppm), shows that Py₂ (with only four elements reporting in a different range: Zn, As, Se and Te) is potentially a closer match than Py₃ (which has seven elements reporting in a different range).

It is considered likely that the wall-rock Py signature is comparable to Py₂ and therefore syn-deformational, precluding testing of wall-rock pyrite as a viable tool for vectoring toward late-orogenic mineralisation associated with late-fluid interaction observed at Curraghinalt. However, as Py₂ is determined in *Chapter Five* to be relatively auriferous, it may in the case of Curraghinalt be considered a viable indicator of early Au mobility and local system fertility as described elsewhere in this chapter.

9.3.iii. Integrating micro-analysis into exploration workflows

Micro-analysis including the use of Laser Ablation ICP-MS and SEM-EDS/EDX techniques has the potential augment geological knowledge throughout the four key stages of mineral exploration, from the generation of initial targets to scoping and feasibility. This technological capacity may de-risk exploration activities and provide mineral-scale insight of value to mineral processing studies.

A conceptual summary of how the use of such technologies may be integrated into exploration strategy is presented in Figure 9.5 and Figure 9.6. It is envisaged that during target generation and drilling (Figure 9.5), the deformation context and geochemical signatures of host sulphide phases may be established using petrographic, SEM, EDS/EDX and LA ICP-MS methods. This may be of significant economic value to explorers in establishing the position of sulphides within the overall orogenic system (e.g. with respect to metamorphism, tectonics, deformation) at an early point, using samples from outcrop or historic workings; favourable results may be established using specific agreed criteria which may then de-risk more costly exploration activities. Such endeavours may present ranked exploration targets, and

incorporating structural information (e.g. the dimensions of a physical trap), the potential scale of a target, a key investment consideration. Information on Au solubility obtained at this point in the process, through LA ICP-MS spot analyses of Au and As, may provide crucial information with regards potential ore processing methods. It is considered by this study that a robust geological model incorporating micro-analytical insights may present useful inventory to the prospector prior to initiating further activities.

LA ICP-MS analyses of samples can assist in establishing the variability of Au and trace element concentrations throughout a deposit. Systematic testing of veins at the resource evaluation and scoping stages (see Figure 9.6) may provide crucial data in the examination of mine feasibility, economic viability and processing.

9.4. Summary of exploration implications

During the Ordovician Grampian arc-continent collision event which uplifted and deformed strata of the Dalradian Supergroup of present-day Ireland and Scotland, gold and trace elements including Co, Ni, Pb, Zn, and As were mobilised from sedimentary horizons, transported through the developing structural network and emplaced in physical and chemical traps. Localised enrichments of Au and associated metals identified in this study are hosted by pyrite within veins, which may be exploited by multiple fluid episodes carrying different abundances of trace elements. In some tested samples visible Au is evident: aggregations of nano-particles positioned on the internal walls of microscopic fractures formed during brittle deformation, accompanied by Bi, Ag, tellurides and chalcopyrite. In syn-deformational samples, Au is generally cryptic and revealed only through spectroscopic analysis. These phases and associated abundances of As provide evidence of the transit of Au from its source toward potential traps.

For explorers, the information provided in this thesis of most crucial importance provided herein are the new and revised models of mobility and chemically-supported paragenesis. Au is variably associated with concentrations of Co, Ni, Cu, Mo, Ag, W, Hg (transition metals), Ga, Sn, Tl, Pb, Bi (base metals) and As, Sb, Te (metalloids) in pyrite and exhibit the effects of prolonged mobility. This study demonstrates that pyrite may be of limited value for vectoring (e.g. proximal wall-rock) though may provide indications of structure fertility (e.g. syn-deformational phases) which may augment prospectivity studies. This chapter has also demonstrated how micro-analytical techniques may be incorporated into exploration strategies to provide orogen-scale context to targets of interest.

It is the view of this study that geological and chemical conditions are favourable for large, undiscovered deposits across the Grampian terrane, with the most potential associated with late orogenic events.

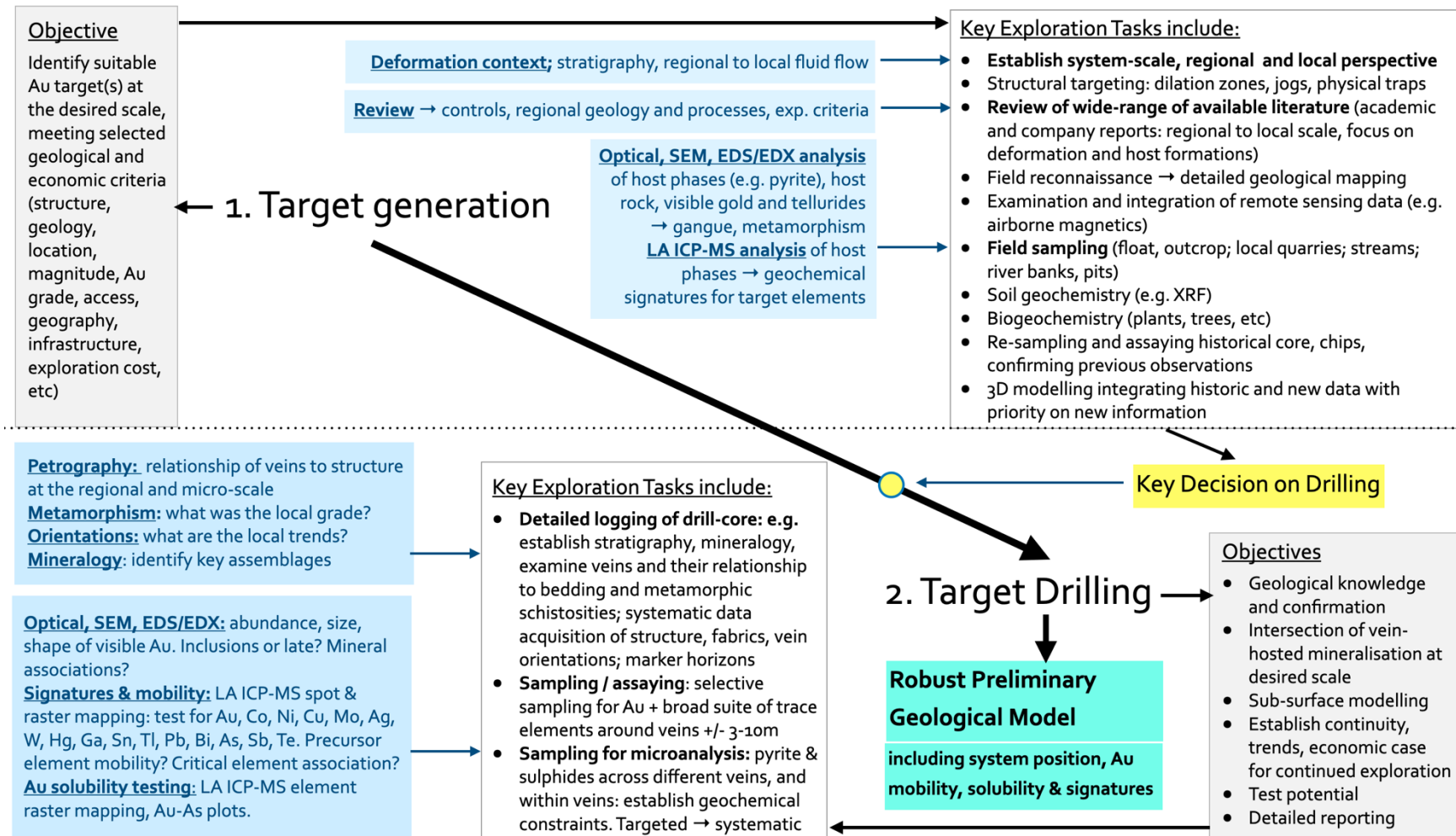


Figure 9.5. Integration of micro-analytical methods into Exploration Phase 1 and 2, with the objective of producing a robust geological model which includes information on the system context, relationships to deformation, metamorphism and regional sources, visible Au, mineral and element associations and Au solubility. Micro-analytical insights with minimal additional material required will provide key insights and allow augmentation of scientifically-informed decision-making.

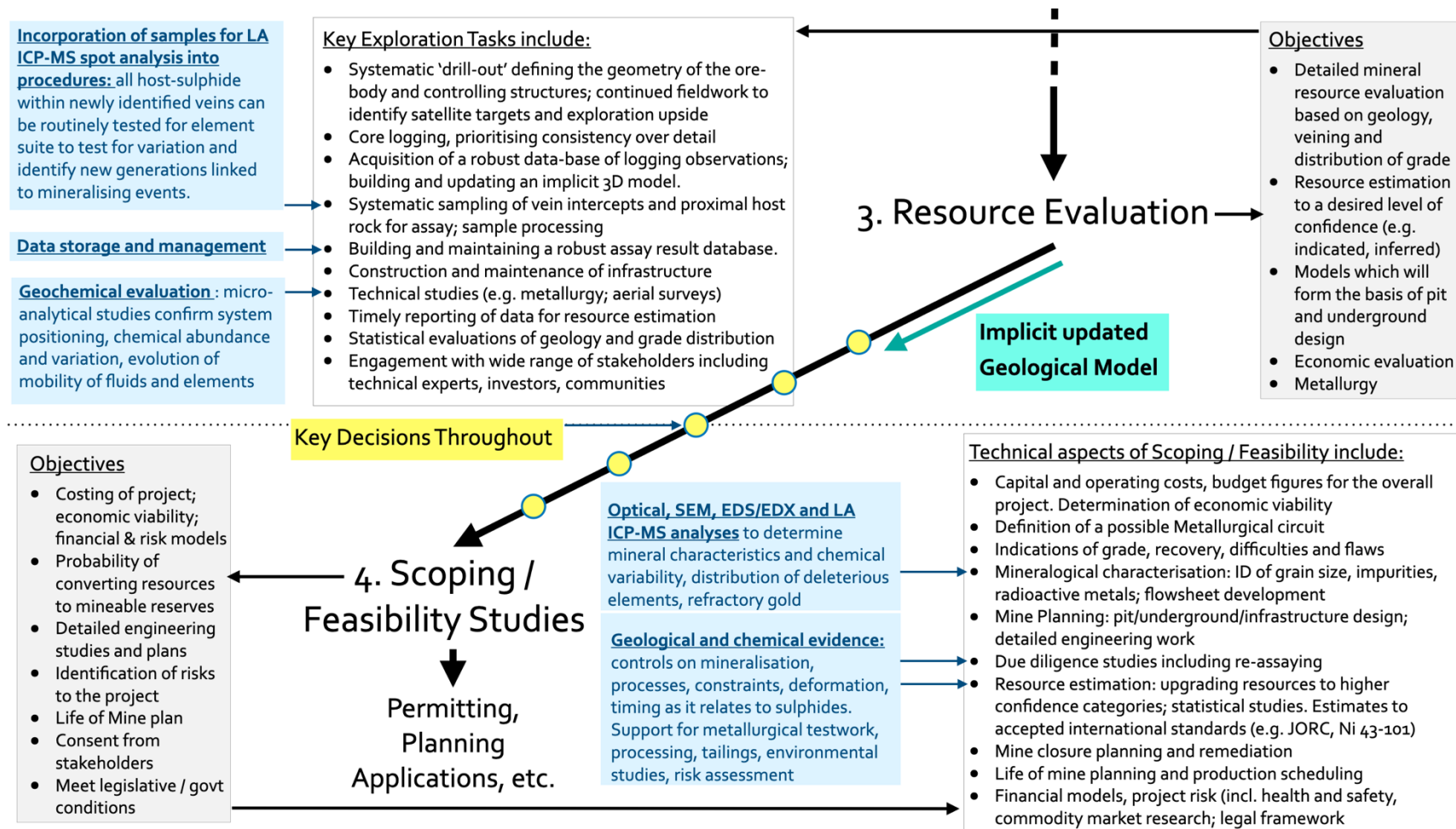


Figure 9.6. Integration of micro-analytical methods into Exploration Phase 3 and 4. Technical aspects and tasks includes information from Moon et al. (2006), New Zealand Petroleum & Minerals (2017) and SGS (2020).

Chapter Ten: Mechanisms for gold and trace element mobilisation: a model for gold emplacement in the Grampian Terrane

10.1. Introduction

Petrographic and geochemical data has been acquired from Au-associated pyrite at Curraghinalt deposit in County Tyrone, Northern Ireland (see *Chapter Five*) and the Cloonacool prospect in County Sligo, Ireland (see *Chapter Six*), along with regional data from pyrite and pyrrhotite hosted by sedimentary rocks along the Grampian Terrane which may represent a source of Au and associated geochemical signatures (see *Chapter Seven*). Results of these analyses and interpretations have been presented in previous chapters. This chapter seeks to address processes contributing to gold mobility and emplacement through the lens of specific research questions. A general model for Au mobility in north-west Ireland is presented at the end of this chapter.

10.2. On the mobility of gold and trace elements

10.2.i. Research question and overview

The first stated research question of this thesis asks:

“What is the extent of gold mobility and associated trace elements within the Grampian orogeny in Ireland and Scotland ?”

to include, “to what extent are orogenic Au signatures preserved in pyrite?

Both Au and trace elements exhibit protracted mobility throughout the Grampian Orogeny, with initial mobilisation recorded in pyrrhotite pyrite growths in the Appin and Argyll Groups to late enrichments in micro-fractures post-dating the latest generations of pyrite within veins cross-cutting deformation fabrics. While Au is observed at all stages, polymetallic signatures are also recorded which provide information on the broader history of metal mobility. Extensive spatial and temporal preservation of signatures across the Orogen has enabled the development of chemical and genetic models in this thesis.

This question is addressed in three preceding chapters: at the deposit-scale in *Chapter Five* which considers mineralisation at Curraghinalt in County Tyrone, Northern Ireland, in *Chapter Six* at an exploration prospect containing vein-hosted gold at Cloonacool, County Sligo, Ireland, and at the scale of regional fluid flow within the Grampian Orogeny in *Chapter Seven*. Principle conclusions are presented for the three scenarios. Within this section, data are also synthesised and interpreted enabling comparison of syn-deformational and late-orogenic pyrite geochemical signatures from the three chapters.

10.2.ii. Key findings and processes

Temperature and pressure acted as controls for early Au and initial trace element mobilisation:

Petrographic evidence of chloritised garnet porphyroblasts (see Figure 7.6) from the Glencolumbkille locality (Argyll Group) confirms that peak metamorphic grade reached lower amphibolite conditions favourable for garnet formation, before subsequently retrograding to chlorite. Garnet porphyroblast formation is indicative of amphibolite facies conditions where

temperatures exceeded 500 °C, while chlorite is stable below this temperature within the greenschist facies (and at higher temperatures within increased pressure (e.g. Nelson, 2011). This observation provides a qualitative indication of the range of temperatures endured during orogenesis, up to and exceeding 500 °C, consistent with the findings of workers including Alsop et al. (2001) who observe amphibolite facies conditions across the Donegal Inlier. [In the Sperrin Mountains Inlier, metamorphic conditions are interpreted to have reached 4.5 – 5.5 kbar (P) and 450 – 500 °C (T) (see *Section 5.6.*), while in the Ox Mountains Central Inlier, a broader range from <8 kbar (P) and 350 – 600 °C (T) is proposed by Yardley et al. (1987) for conditions associated with the Grampian event (see *Section 6.3.iii.*)]

Temperature is broadly proportional to Au solubility in aqueous fluids under specific conditions, wherein fO_2 and sulphur are buffered by sulphide mineral assemblages bearing pyrite and pyrrhotite as encountered in this study. Geochemical evidence of syn-deformational Au solubility is provided by examination of relative concentrations of Au and As using Laser Ablation ICP-MS spot analyses and raster element mapping of pyrite grains, within meta-sedimentary units from deeper structural (stratigraphic) levels, a potential source of gold for orogenic systems (see *Chapter Seven*). Such analyses and interpretations of solubility were also conducted on samples from metablastic and vein sulphide phases from Curraghinalt (*Chapter Five*) and Cloonacool (*Chapter Six*). The average Au/As ratio in pyrite constrained petrographically as synchronous with the development of deformational fabrics (broadly defined as ‘syn-deformational’ by this study) is 0.007 (146 results reporting above detection for both elements; n=327), with averages ranging from 0.0003 (Cloonacool Py₃; Ox Mountains Central Inlier; 5 results > detection for Au and As) to 0.09 (Muckros pyrite; Donegal Inlier; 3 results > detection for Au and As). A positive correlation is recognised between the two elements for syn-deformational phases ($\rho=0.75$, Spearman rank).

A bivariate plot of these data is presented in Figure 10.1 which compares ‘syn-deformational’ results (from Glencolumbkille and Muckros pyrite, Cloonacool Py₁₋₃ and Curraghinalt Py₁₋₂) to those of Curraghinalt Py₃, where pyrite is observed within veins cross-

cutting deformation fabrics (defined as ‘late orogenic’). Syn-deformational phases (of interest with respect to initial mobilisation and early emplacement) are relatively enriched in As, while showing comparable to moderately depleted concentrations of Au (the average Au/As ratio for late-orogenic Curraghinalt Py₃ is 0.17, while the Spearman rank correlation coefficient is 0.37). The plot, which includes the solubility curve of Deditius et al. (2014), identifies two broad trends when considering all data acquired (preceding chapters): a ‘Syn-deformational Trend’ associated with increasing temperatures and pressures due to collision, during which Au was incorporated into the structure of pyrite, and a ‘Late-Orogenic Trend’ linked to cooling and exhumation, wherein Au became supersaturated in fluids and precipitated as Au nanoparticles. It is theorised that these nanoparticles (Au⁰) contributed to the visible Au observed within late micro-fractures at Curraghinalt, and demonstrates that while late mixing with external fluids may have occurred, it was not required to concentrate gold in the Grampian Terrane.

Visible Au at Curraghinalt, the largest known deposit on the island of Ireland, is emplaced relatively late in the evolution of the Grampian orogen and is associated with Bi, Te and Ag, forming coeval tellurides: Targeted Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Spectrometry (EDS/EDX) and Laser Ablation ICP-MS methods have revealed critical information with respect to the emplacement of ‘ore-stage’ Au and associated trace elements at Curraghinalt, which challenge models presented by previous workers (e.g. Parnell et al., 2000; Rice et al., 2016; Wilkinson et al., 1999).

Key observations include: (i) the identification (using LA ICP-MS raster element mapping, see Figure 5.14 and Figure 5.15) of a complex micro-fracture network within Py₃ (pyrite within quartz-carbonate veins which cross-cut penetrative deformational fabrics)

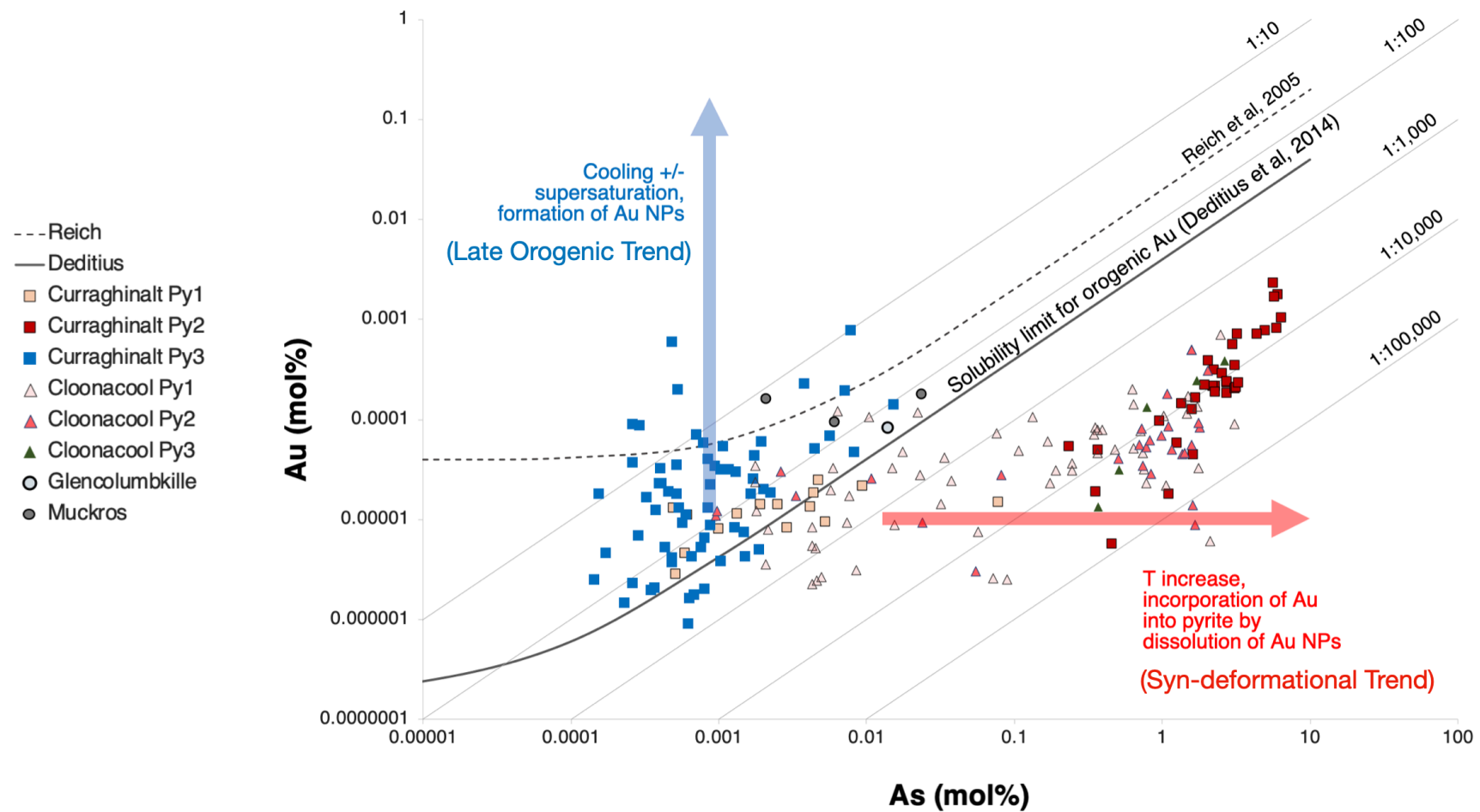


Figure 10.1. Solubility diagram for petrographically constrained early and syn-deformational phases (in shades of red and grey; $n=146 > \text{LOD}$ for both elements coinciding) and late orogenic phase Curraghinalt Py₃ (in blue; $n=64 > \text{LOD}$ for both elements coinciding). The solubility curve of Deditius et al. (2014) applicable for orogenic systems is shown as a bold line, while the line of Reich et al. (2005) is also included as a reference point.

enriched in Au and trace elements including Bi, Te, Ag, Pb, Cu; (ii) that those micro-fractures cross-cut internal growth zones (illustrated by Co and Ni concentrations, see Figure 5.17B) and that the signatures remain undisturbed by later fracturing and influx by auriferous fluids; (iii) that (using LA ICP-MS spot analyses; see Figure 5.10) Py₃ grains are relatively depleted in Au (<1 ppm); (iv) that mineral phases of Au, Ag, Te, Bi, Te and Cu are visible within the identified micro-fracture network, identified using SEM and EDS/EDX (broadly in sequence, Au → Ag → Te → Bi → Cu; see Figure 5.8); and (v) that Au and telluride particles nucleate on the walls of micro-fractures (a reactive surface) which are subsequently sealed by chalcopyrite (see Figure 5.9). Detailed interpretation of these observations is presented in *Section 5.12*. and form part of a revised paragenetic model presented in Table 5.5 (and graphically in Figure 5.17). This phase of Au emplacement at Curraghinalt is attributed as Au Stage II in this model.

Examination of Au and As trace element concentrations in Curraghinalt pyrite, acquired using LA ICP-MS spot analysis, show that late-orogenic pyrite (Py₃) contains low abundances of As (broadly < 10 ppm) relative to preceding phases (> 10 ppm); see Figure 10.1 and Figure 10.2B), and signatures lie mostly above the Au solubility curve of Deditius et al. (2014) for orogenic systems (Figure 10.1). Cross-referencing results with the observations of Deditius et al. (2014), these results form a low-As trend ('Late Orogenic Trend', Figure 10.1) which is indicative of free availability of Au⁰ nanoparticles in fluids derived from supersaturation and driven by cooling late in the evolution of the orogen, likely coincident with exhumation and its collapse. As aforementioned, evidence from LA ICP-MS mapping of Py₃ shows that signatures associated with its growth (e.g. cyclical Co and Ni) are undisturbed; this critical information demonstrates conclusively that while Au nanoparticles are recorded within Py₃, this record is indicative only of a chemical change in the system (supersaturation of late fluids with respect to Au) during late stages of orogenesis, and not that they were a source of ore-stage Au at Curraghinalt within those micro-fractures.

The late fluid event at Curraghinalt has been described by workers including Wilkinson (1999) as a brine, noting its salinity, and have ruled out metamorphic fluids. This study is inclined

to support the conclusion that the high-salinity brine recorded in fluid inclusions has a metamorphic origin. Goldfarb et al (2001), citing work by Yardley (1997) note that such brines may derive from basin or passive margin strata. Data acquired in this study resolutely points to supersaturation and the availability of Au⁰ nanoparticles, the liberation of which is controlled by temperature and pressure. Therefore, while accepting that fluid mixing (a mechanism associated with orogenic gold deposits) may have been part of the process, not ruling out external factors (e.g. involvement of the colliding arc), and accepting that analysis of fluids themselves is not part of this research, this study argues emphatically that the processes by which Au is mobilised and emplaced are the same which drive metamorphism.

Further interpretation of the early mobility of nanoparticles is presented in *Chapter Seven*.

Syn-deformational mobility of Au is detected at Curraghinalt which precedes the emplacement of 'ore-stage' Au. Au is lattice-bound, and is likely to have been emplaced by chemisorption of Au onto As-rich, Fe-deficient pyrite surfaces, facilitated by localised changes in semiconducting properties and grain-scale reducing conditions: Au is observed within Py₂ at Curraghinalt, an overgrowth of Py₁ detected within veins which are petrographically constrained to the development of S₂/S₃ composite schistosity (the principle deformational fabric). The concentration of Au derived from Laser Ablation ICP-MS spot analyses is the highest for the three tested generations of pyrite; a median abundance of 3.69 ppm (IQR = 2.02 – 10.1 ppm; n=35) is recorded, while in Py₁ and Py₃, Au is recorded at median concentrations < 0.5 ppm. The ratio of Au to Ag is 23.7 indicating significant relative enrichment of Au (see Figure 5.11A). LA ICP-MS raster element mapping (see Figure 5.13) confirms elevated Au within this phase, at concentrations >1 ppm and in part >10 ppm proximal to grain rims and the location of Bi- (and to a lesser extent Te-) enriched micro-fractures (attributed to the aforementioned late event).

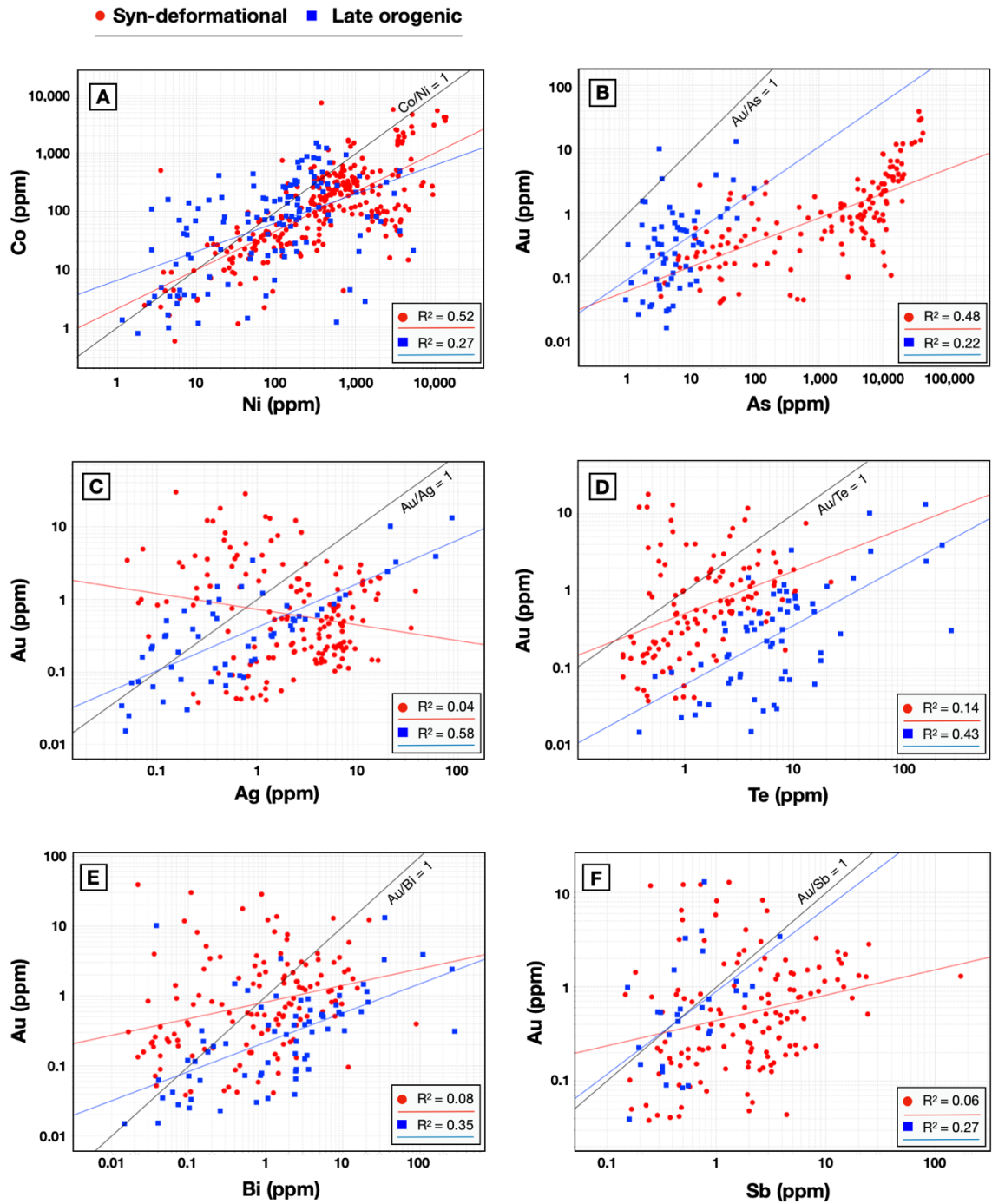


Figure 10.2. Ratio plots for recognised syn-deformational ($n=327$) and late orogenic ($n=137$) phases. Syn-deformational phases include Py_1 ($n=35$) and Py_2 ($n=35$) from Curraghinalt, Py_1 ($n=72$), Py_2 ($n=30$) and Py_3 ($n=5$) from Cloonacool, and pyrite from the Slieve League Peninsula ($n=150$), while the late orogenic phase recognised and included in these plots is Py_3 from Curraghinalt ($n=137$). (A) Co/Ni; (B) Au/As; (C) Au/Ag; (D) Au/Te; (E) Au/Bi; (F) Au/Sb.

Concentrations of Au and As viewed on a bivariate plot (see Figure 10.1, also Figure 5.18) show that values for Curraghinalt Py₂ lie below the Au solubility curve by Deditius et al. (2014) for orogenic systems, approximately following the 1:10,000 As:Au line; the median As concentration for this phase is 14,680 ppm (IQR = 8,250 – 20,800 ppm; n=35). Isothermal disequilibrium is confirmed by a correlation between Au and As in LA ICP-MS spot analyses of $\rho < 1$ (0.89, Spearman rank); the positioning of analyses in Au-As space also suggests that Au was incorporated into pyrite under locally prograde conditions (if isothermal equilibrium is attained, Au/As is constant; Deditius et al., 2014). Enrichment of As and the formation of an Fe-deficient surface promotes Au incorporation into pyrite in solid solution, as indicated in LA ICP-MS data from this study (evidenced by values plotting below the solubility curve in Au-As space). Mechanisms proposed by which Au may be incorporated into pyrite under these conditions by chemisorption onto the As-rich, Fe-poor surface, enhanced by variations in semi-conducting properties as a consequence of As incorporation. Surfaces are locally reducing, which may facilitate the destabilisation of Au-complexes and emplacement; pyrite enriched in Au and As may grow rapidly under non-equilibrium conditions (Maddox et al., 1998, Rickard and Luther, 2007, Reich et al., 2005; Deditius et al., 2008 and Qian et al., 2013 cited in Deditius et al., 2014).

Peak metamorphism associated with the Grampian arc-continent collision is placed at c. 468 Ma by previous workers (e.g. Chew et al., 2009b), indicating that Au mobility was protracted: while Au mineralisation has been temporally constrained to the Lower Ordovician by Rice et al. (2016) (462.7 – 452.8 Ma; Re-Os dating of molybdenite from late shears, also bearing Au and sericite, cross-cutting sulphides hosting emplaced Au which had been previously recognised) it is conceivable that Au was mobile in the broader system from an earlier point. Extending the interval to the peak of metamorphism, the interval of overall Au mobility (interaction of auriferous fluids with local pathways) at Curraghinalt may have been in the region of 16 Myr if one is to include refractory Au observed in precursor Py₂ observed in this study (Au ‘Stage I’ mobility is further explored in *Section 5.12.iv*).

The petrographic and geochemical investigation of pyrite and pyrrhotite grains from strata located structurally beneath the Southern Highland Group hosting the Curraghinalt deposit in *Chapter Seven* identifies a viable source for this stage of Au, along with potential mechanisms for the liberation and transport of auriferous particles in hydrothermal fluid, these are discussed in the subsequent section.

Zn and Pb are detected in syn-deformational phases of pyrite at Curraghinalt (Sperrins Inlier) and Cloonacool (Ox Mountains Central Inlier): Evidence presented from the Curraghinalt Au deposit and Cloonacool prospect, acquired using Laser Ablation ICP-MS spot analyses and mapping, are presented in *Chapter Five* and *Chapter Six* respectively. These data confirm syn-deformational concentration of Zn and Pb within early generations of pyrite, and the presence of sphalerite and galena. LA ICP-MS analyses are supported by petrographic work which includes the use of Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS/EDX) techniques. These findings are consistent with the findings of other workers in orogenic systems: interpretation of these results in *Section 5.12.vi.* describes how base-metal signatures are commonly observed within strata deformed by orogenic processes, for example in the Otago Schist in New Zealand (Hu et al., 2016; Pitcairn et al., 2010).

The observation of prograde base-metal mobility within the deformed Grampian terrane of north-west Ireland and its relationship to Au deposits is considered by this study to be new information and demonstrates that strata were fertile for base-metals in addition to Au. *Chapter Ten* includes information on trace element correlations and a graphical representation of concentrations, including Zn and Pb, in tested localities.

The value of using a combined analytical approach is also demonstrated in deciphering the relative timing of metalliferous emplacement and the relationship with trace elements. The use of four micro-analytical techniques in tandem (LA ICP-MS spot analyses and raster element mapping, SEM and EDS/EDX) has enabled the extraction of information on the spatial distribution and homogeneity of Zn and Pb, presented graphically in *Chapters Five and Six*. An

example of the use of a combined petrographic and geochemical methodology is provided in Figure 6.20 (*Chapter Six*, Cloonacool) which demonstrates how Pb concentrations decrease toward the edge of Py₂ masses where galena inclusions are observed. This decrease is accompanied by elevated Au, As, Bi and Te, while Cu and Ag record relatively lower abundances. Such observations provided a conceptual basis for internal geochemical zonation of these masses, which was then confirmed through LA ICP-MS raster element mapping presented in Figure 6.22.

Emplacement mechanisms across the Grampian Orogen include cooling, decompression, phase separation, wall-rock interactions, fracture-wall nucleation and mixing with external fluids. Seismicity is likely to have played an active role in quartz and Au emplacement: Au is emplaced at Curraghinalt, Cloonacool, Cavanacaw and Cononish within vein networks hosted by Neoproterozoic to Cambrian meta-sediments (Dalradian Supergroup) which were uplifted and deformed during the Grampian orogenic event. This study provides evidence for (i) the relative timing of emplacement with respect to deformation events (e.g. Curraghinalt Py₁-Py₂ vs. Curraghinalt Py₃, see *Chapter Five*), (ii) the abundance of Au hosted within pyrite, (iii) the solubility of Au, and (iv) mineralogical and geochemical information on trace elements associated with Au both within the pyrite lattice and within micro-fractures as visible phases. This evidence, considered in the context of regional scale tectonism, models of orogenic gold deposits produced by others in the field who have conducted systematic reviews and proposed physical and chemical processes, and information by previous workers relating to the evolution of the Grampian orogen, permits hypotheses to be put forward for mechanisms of Au emplacement along the orogen.

10.2.iii. Au emplacement at the scale of the orogen

Described by Pokrovski et al. (2014), five main processes are recognised which influence Au precipitation during the evolution of hydrothermal fluids in the crust. These are cooling, decompression, phase separation, interactions with rocks, and mixing with external waters. These mechanisms along with HS^- activity effect changes in pH and oxygen fugacity ($f\text{O}_2$) which may result in Au precipitation.

Before addressing possible scenarios, it is worth considering the reminder provided by Gaboury (2019) that an orogenic Au system requires five key constituent parameters, which if not all present, will result in aborting of the mineralising system. These are (i) fluid generation, (ii) ligand availability (re. complexing), (iii) Au availability, (iv) active faulting and (v) precipitating mechanisms (to be examined here). To form an orogenic Au deposit all of these criteria must be achieved. These criteria may be considered as a function of depth and time; fluid generation may occur at depths of <30 km at the start of the process, while precipitating mechanisms come into play at much shallower depths and after timeframes of 0.1 – 1 Myr (Cox, 2016 cited in Gaboury, 2019). Questions of source and transport are considered in subsequent sections.

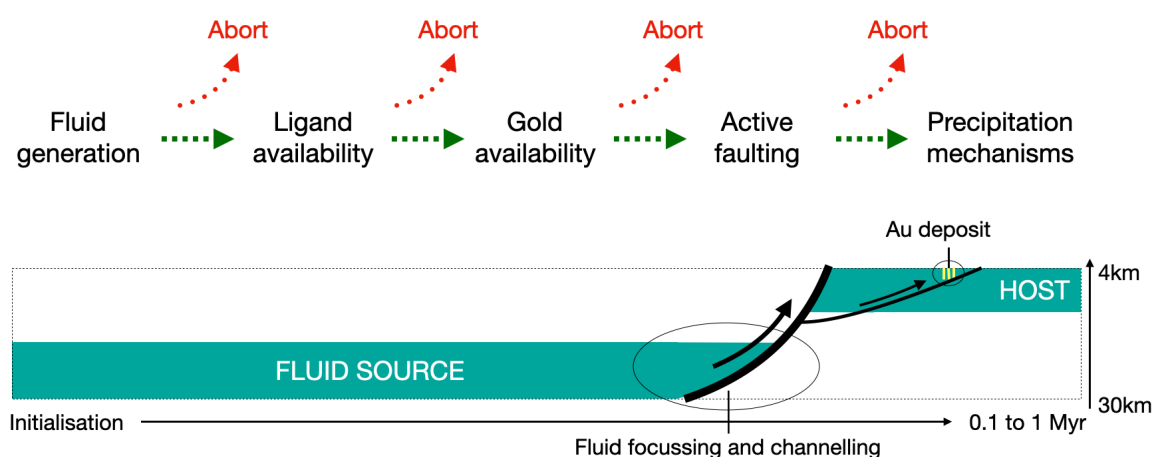


Figure 10.3. Key criteria for the formation of orogenic gold deposits, conceptual system representation adapted after Gaboury (2019) including information on relative timing by Cox (2016).

Cooling

Pokrovski et al. (2014) advocate that a temperature decrease is a highly effective mechanism controlling Au precipitation; this however is complex, and requires consideration of additional parameters.

The cooling of an acidic, saline fluid (as proposed by previous workers for the late auriferous fluid that formed the Curraghinalt deposit, see *Chapter Five*) is considered to be viable for the precipitation of Au, due to the dependence of Au behaviour upon reduced sulphur concentrations in such a fluid. Pyrite and chalcopyrite precipitation (due to an excess of ferrous Fe and Cu over sulphur in the fluid) will lead to removal of sulphur, and the precipitation of Au. This process is cited as particularly relevant to porphyry, VMS and epithermal systems, however may also be appropriate in this context of aqueous fluids along the Grampian orogen due to (i) the observed association with pyrite and chalcopyrite in tested systems (e.g. at Curraghinalt, see *Chapter Five*).

Decompression

The second mechanism of relevance to the Grampian orogen is *decompression*, based on the principle that changes in fluid pressure are linked to changes in the solubility of metals in that fluid (Migdisov and Williams-Jones, 2013 cited in Weatherley and Henley, 2013). Decompression mechanisms are likely to have been crucial in the emplacement of quartz veins and metals along the orogen; all tested deposits are hosted by vein arrays associated with faulting and shear zones. Along the Fair Head – Clew Bay line (FH-CBL), there is evidence for late growth of porphyroblastic albite, which has been linked to decompression (and in correlatives in Newfoundland) (Chew et al., 2009b; Jamieson and O'Beirne-Ryan, 1991).

Pokrovski et al. (2014) observe that pressure changes are associated with both mechanical and chemical changes in the system favourable for Au precipitation. Earthquakes are discussed by their study, noting that a large pressure drop may follow a seismic event along a fault, resulting in the creation of empty space. This can lead to rapid quartz formation and Au

precipitation along with that of other metal precipitates. The mechanism of ‘flash vapourisation’ (see Figure 10.4), wherein a fluid phase may expand by several orders of magnitude to a low-density compressible fluid due to rapid fluid decompression has been suggested for the formation of quartz vein arrays and the deposition of metals (Weatherley and Henley, 2013). Under such conditions, rock fractures are rapidly expanded causing the evaporation of fluids, resulting in Au deposition which can be ‘almost instantaneous’ (Craw, 2013a). Gaboury (2019) note skepticism however, that the process is either necessary or viable, due to the extraordinary magnitude of the pressure drop required (below hydrostatic pressure), and that minor pressure decreases may be sufficient to result in pH changes which can lead to Au precipitation. Weatherley and Henley (2013) consider that flash vapourisation following seismic slip may be a simple process which underpins up to 80% of Au deposits, including those outside of mountain belts and derived from seismogenic crust beneath ancient volcanoes, e.g. porphyry Cu-Au deposits.

It is considered likely that decompression is a key mechanism in the positioning of late-orogenic veins carrying Au which cross-cut penetrative Grampian fabrics (the principle S_2/S_3 composite schistosity) in the north-west of Ireland and in Scotland, in terms of the precipitation of quartz. In the Sperrins Inlier of County Tyrone, Northern Ireland, where the Curraghinalt Au deposit (see *Chapter Five*) and to a less detailed extent, the Cavanacaw deposit (see *Chapter Eight*) have been tested as part of this thesis, veins are present as arrays within dilational structural zones bound by shears. Vein arrays with a WNW-ESE orientation at Curraghinalt and a N-S orientation at Cavanacaw are associated with second-order faults, contemporaneous with movement along the Omagh Thrust. It is conceivable that frequent seismic activity along the Omagh Thrust during subduction of the orogen resulted in episodic rupture of faults and decompression, resulting in an influx of fluid to newly created dilational space. Vein arrays within the Sperrins contain multiple quartz phases (e.g. at Curraghinalt, see *Section 5.12*). It is likely that these formed within the general framework presented by Weatherley and Henley (2013) as a result of pressure decrease and rapid supersaturation of fluids (see Figure 10.4B).

Fault jogs resulting from physical movement along structures, as observed in the Sperrin Mountains Inlier along strike from Curraghinalt (recognised for example within information from the inter-governmental Tellus survey), are considered to be highly prospective exploration targets (Lusty et al., 2009).

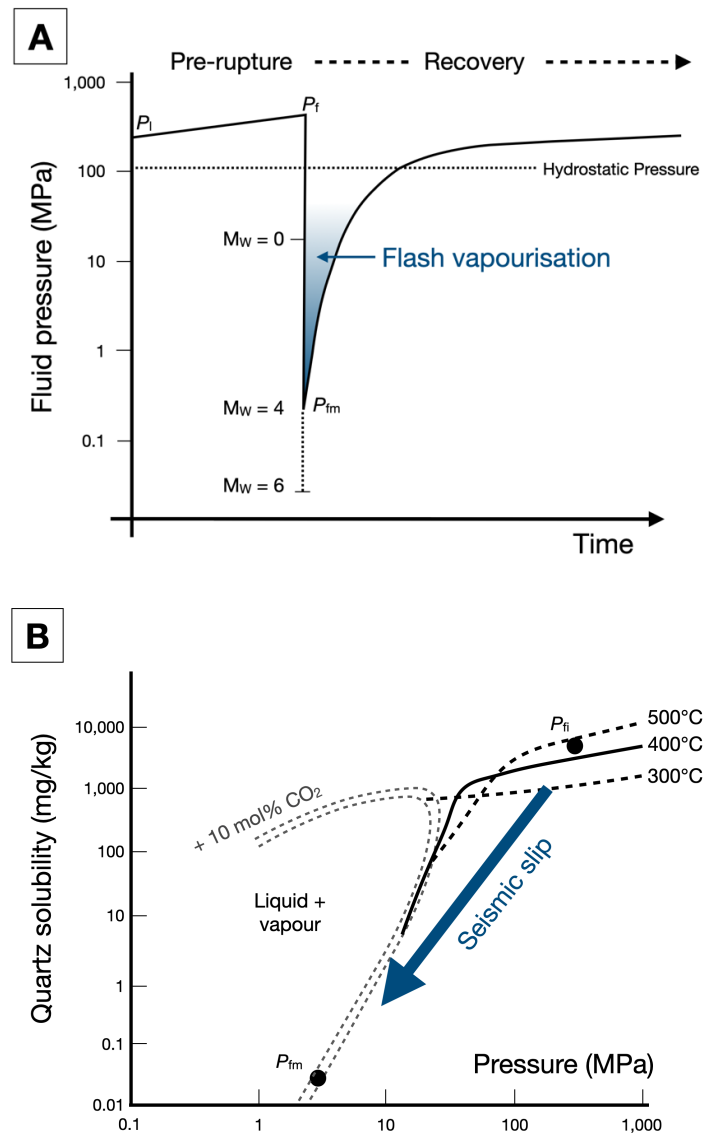


Figure 10.4. (A) Changes in fluid pressure resulting from deviatoric crustal stress during an earthquake cycle of magnitude ($M_W=$) 4, leading to failure (to P_m = minimum fluid pressure) and flash vapourisation triggering fluid expansion. During recovery, fluid flows into the newly created dilational zone until pore fluid pressure (P_f) = lithostatic pressure (P_l); (B) a diagram of the solubility of quartz as a function of pressure and temperature in pure water, showing extreme supersaturation due to flash vapourisation following rupture from an example of an initial condition (P_{fi}) to a minimum condition (P_{fm}). Diagrams modified after Weatherley and Henley (2013) who modelled data from the Revenge Au deposit in Western Australia.

This study proposes that visible Au was emplaced within late micro-fractures as nucleations of Au⁰ nanoparticles at Curraghinalt (the largest estimated resource considered) and Cononish, constituting the principle deportment. The presence of Au⁰ nanoparticles was determined using LA ICP-MS spot analyses of Au and As, while fracture- wall nucleation of associated tellurides is observed in SEM raster mapping at Curraghinalt which this study suggests is also an emplacement mechanism for Au (see *Chapter Five; Section 5.9; Figure 5.9*). Cathodoluminescence imaging at Curraghinalt demonstrates that late Au is associated with a late quartz fluid phase (syn-brine; associated with Bi- and Ag- tellurides, and chalcopyrite, see *Section 5.9; Figure 5.8*).

Episodic pressure fluctuation associated with ‘seismic pumping’ (a suggested mechanism for Au emplacement in the Otago schists of New Zealand and the Lachlan belt in Australia, e.g. Bierlein and Maher, 2001; Pitcairn et al., 2006) is likely to have driven the emplacement of late quartz and additionally, the precipitation of Au and emplacement of associated trace elements at Curraghinalt, Cavanacaw (where zoned galena, arsenopyrite and pyrite mineralogical phases are observed, with pyrite hosting visible Au, see *Section 8.7*), and Cononish (where Au is also emplaced within late micro-fractures, see *Section 8.7*). Seismicity is proposed as an active mechanism for the thickening of en-echelon, tensile fractures and the growth of veins hosting Au at the Croagh Patrick occurrence in County Mayo, western Ireland: this occurrence is located geologically within the footwall of the Fair Head – Clew Bay Line terrane boundary which extends into County Tyrone where the Sperrin Mountains deposits are situated (Wilkinson and Johnston, 1996). The link between seismic pumping and Au mineralisation is explored by Sibson and Scott (1998) who describe the formation of Au-bearing lodes in accretionary, compressional terranes late in the orogenic cycle; over-pressurised ($P_f > \sigma_3$) mineralising fluids infill structural traps in the mid-crust controlled by stress, resulting from the mis-orientation of low-angle thrust faults (‘domino steepening’), which occurs during progressive crustal shortening. They note that switches from compressional to extensional

regimes may result in massive fluid discharge and mineralisation, and that such conditions are observed in the Juneau Au belt in Alaska, USA.

Based on observations including the confirmation of Au within late micro-fractures at Curraghinalt (see *Chapter Five*) and Cononish (see *Chapter Eight*) in this study, and information provided by Wilkinson et al. (1999) in relation to the late saline H₂O-NaCl-CaCl₂ fluid phase (Q4) which likely corresponds to the fluid observed in this study at Curraghinalt, it is hypothesised that (i) fluid depressurisation due to fault rupture led to the initialisation of quartz vein growth in the Sperrin Mountains Inlier, though different processes may be responsible for the circulation of the late fluid which exploited late micro-fracture networks, and (ii) that this sequence may be replicated at Cononish in Scotland. At Cloonacool (see *Chapter Six*), multiple phases of fluid injection are observed exploiting the same fractures with different geochemical signatures (determined by LA ICP-MS methods). It is hypothesised by this study that episodic rupture and seismic pumping is likely candidate mechanism for the introduction of fluids across the orogen and a contributing factor to the precipitation of Au.

Misorientation of faults is noted as a common feature of mesothermal (sic) gold deposits (Cox, 2010); while the structural geology of faults is not a specific focus of this thesis, it is recommended that the orientation of structures may be a viable path of future research (through systematic re-examination of faulting) and a useful prospectivity tool in the search for late orogenic Au mineralisation proximal to the Omagh Thrust (and the broader Fair Head Clew Bay Line – Highland Boundary Fault) bounding the south of the Grampian Terrane.

10.2.iv. Au emplacement at the scale of a deposit

Phase separation ('boiling')

The process of phase separation is a recognised control for Au deposition in orogenic systems (Gaboury, 2019), along with porphyry, magmatic and epithermal mineralising systems at temperatures between 300 and 350 °C (Pokrovski et al., 2014), and is linked to decompression;

phase separation is derived from a sudden decrease in pressure leading to fluid immiscibility. A consequence of boiling, CO_2 [a constituent of initial one-phase water-carbonic acid (H_2CO_3 , HCO^- , CO) fluids provided in an example by Gaboury (2019)] are removed, resulting in pH changes in the resultant fluid. According to Gaboury (2019) who specifically addresses *orogenic systems*, the loss of CO_2 results in fluids becoming more acidic, and the precipitation of free Au. This acidification results in the formation of muscovite proximal to Au-bearing veins, and an association of muscovite with visible phases of Au. Pokrovski et al (2014) note that for fluids in *epithermal systems*, loss of CO_2 results in fluids becoming more alkaline, resulting in the precipitation of galena, sphalerite, chalcopyrite, pyrite and argentite, citing the example of the El Callao mining district in Venezuela (Velásquez et al., 2014) where boiling at temperatures of c. 250 °C (lower than temperatures encountered in orogenic systems) is considered a key mechanism in the precipitation of Au and arsenian pyrite. As observed by Gaboury (2019), variations in $f\text{O}_2$ will result in rapid Au precipitation, while any change in pH from neutral conditions will induce Au precipitation (see Figure 10.5). Changes in $f\text{O}_2$ or temperature on both bi-sulphide and chloride complexes of Au will also result in precipitation, and both oxidation conditions and the stability of sulphides may be predicted, if conditions of oxygen fugacity ($f\text{O}_2$) and temperature for an ore fluid are known (see Figure 10.6).

Experiments in this study of orogeny-associated Au deposits post-dating peak Grampian metamorphism and deformation reveal information on solubility, along with mineralogical and geochemical associations (e.g. Figure 10.1). This information considered in the context of observations with respect to regional fluid flow in the Sperrin Mountains Inlier by workers including Wilkinson et al. (1999) and Parnell et al. (2000), and in the Tyndrum area of SW Scotland by Curtis et al. (1993), permit some general interpretations with respect to phase separation:

Sperrin Mountains Inlier, Northern Ireland: (i) at Curraghinalt, late Au emplacement observed within micro-fractures associated with a late phase of quartz (see *Section 5.11.iv*) is likely

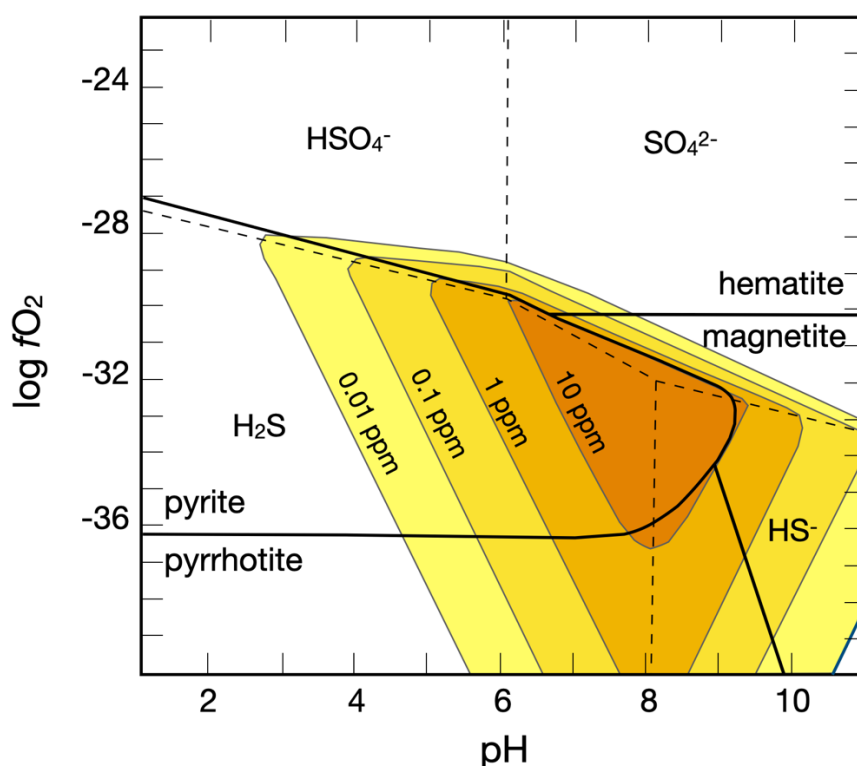


Figure 10.5. Gold solubilities (expressed as contours in ppm) for Au bi-sulphide complexes, calculated as a function of pH and oxygen fugacity ($\log f_{\text{O}_2}$). Temperature = 300 °C, total sulphur = 0.05 mol. Modified after Roberts (1988), data from Seward (1973) and Seward (1984).

to be associated with the circulation of a H₂O-NaCl-KCl fluid (Q3) mixed with a late H₂O-CaCl₂-NaCl brine (Q4), neither of which has determined values of CO₂ (Wilkinson et al., 1999): assuming Q3-Q4 (including the late brine) is the same as the late fluid phase observed in this study, this therefore may disqualify phase separation of CO₂ as a mechanism specifically for *late* Au emplacement at Curraghinalt; (ii) grains of pyrite and chalcopyrite are observed at both Sperrins deposits (Curraghinalt, see *Section 5.12.i* and Cavanacaw, see *Section 8.5*), along with galena and arsenopyrite at Cavanacaw. The precipitation of host sulphide phases may be achieved through phase separation: i.e. the loss of CO₂ from an earlier fluid due to boiling, resulting in a change in pH (e.g. Gaboury, 2019); unlike Q3-Q4, CO₂ is a recognised component of the precursor Q2 phase at Curraghinalt (H₂O-CO₂-NaCl-KCl; Wilkinson et al., 1999), supporting this hypothesis. This study interprets that phase separation *is not* likely to be responsible for Au emplacement in the Sperrin Mountains (derived from the late saline fluid

and hosted within pyrite micro-fractures), however it *is* likely that phase separation had an active role in the precipitation of host sulphides.

SW Scotland: This study presents evidence of late Au forming within micro-fractures of pyrite at Cononish Au deposit (Tyndrum, SW Scotland; see *Sections 8.5* and *8.6*) associated with late chalcopyrite infill and a Te, Co, Ni, Cu, As, Ag, Sb, Hg, Pb and Bi signature. Research of regional fluid circulation in the Tyndrum area by Curtis et al. (1993) concludes that fluids within veins hosting Au mineralisation at Tyndrum (sic) are typically CO₂-bearing, and have salinities of between 6 and 7 wt% NaCl equiv., which were homogenised at temperatures of c. 290-340 °C and pressures of c. 1kbar (equivalent to depths of c. 3.5km). Phase separation is

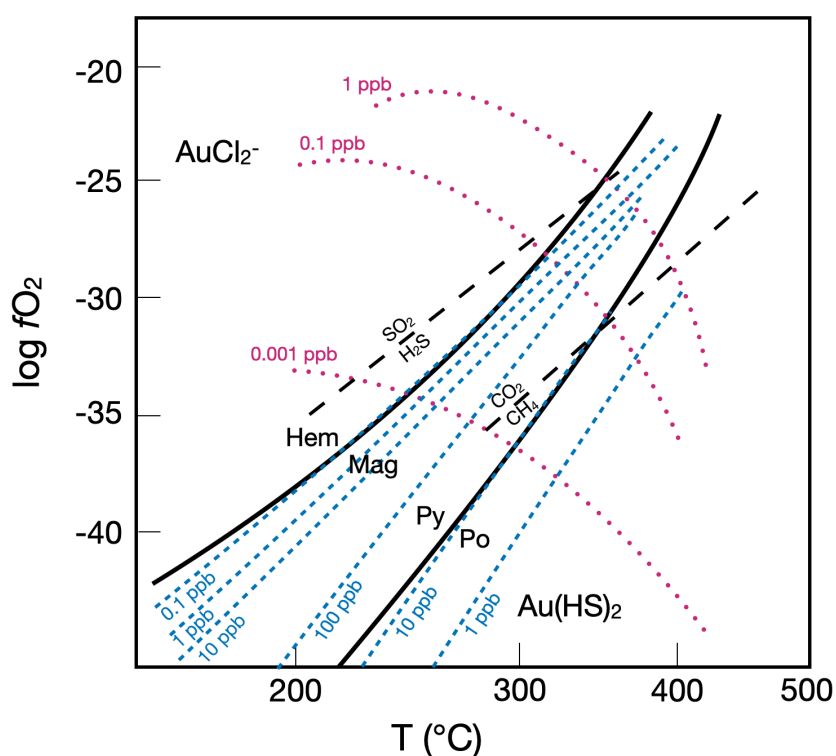


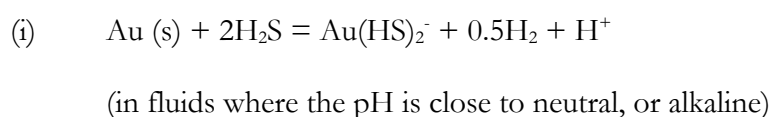
Figure 10.6. Solubility of Au as a function of temperature and oxygen fugacity, at a fluid pH of 6, NaCl of 6% and 320 ppm S (parameters reported for fluids associated with Au deposits of the Brazilian Gurupi Belt). Dashed lines (in blue) are solubility curves for bi-sulphide complexes Au(HS)_2^- , dotted lines (in purple) are for chloride complexes. The limits of stability fields for hematite (Hem), magnetite (Mag), pyrite (Py) and pyrrhotite (Po) are represented by heavy lines (in black). Long-dashed lines (in black) are gas buffers. Modified after Klein (2014); diagram conditions: 6 wt.% NaCl, pH 6, 320 ppm S.

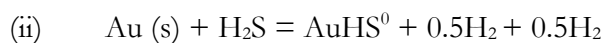
therefore a viable component mechanism for the precipitation of sulphides and Au at Cononish and is also suggested as a constituent process for Tyndrum (sic) Au mineralisation by Curtis et al. (1993).

Ox Mountains Central Inlier, Ireland: Visible Au mineralisation is observed to be hosted in grains of pyrite within syn-deformational veins at Cloonacool, County Sligo (see *Chapter Six*). Further research relating to the composition of fluids hosting mineralisation is required. However, it is reasonable that fluctuations in oxygen fugacity and pH (see Figure 10.5) played a role in the precipitation of host pyrite and supersaturation of the fluid leading to precipitation of Au. Geochemical observations from the study of a potential source reservoir favour early mobility of Au in bi-sulphide complexes, synchronous with fabric development (e.g. S₂/S₃) resulting from the main deformational stages of the Grampian orogen (see *Chapter Seven, Section 7.8*). Au within HS-complexes may have been introduced to strata of the Ox Mountains Inlier, supporting the phase separation model presented in Figure 10.5.

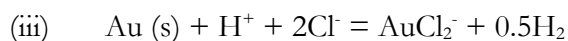
Fluid-rock interactions

Interactions with wall-rock may influence the development of orogenic Au deposits by changing the pH of fluids and modifying the content of sulphide; wall-rock sulphidation is considered to be the primary control on the deposition of metals in deep and high-temperature systems (Pokrovski et al., 2014). With decreasing depth, phase separation (described in the previous section) is considered to be influential in Au precipitation. Interactions with rocks rich in Fe^{II} can affect the precipitation of pyrite and pyrrhotite, acting as a sink for H₂S: as it is consumed from the fluid, Au precipitates as a result of the following reactions controlling Au solubility shifting to the left:





(acidic fluids)



(acidic saline fluids, brines)

Precise fluid conditions are not assessed as part of this study, however it is considered likely that syn-deformational and late-orogenic Au was transported by HS-complexes (see *Chapter Seven*) for which reactions (i) and (ii) are significant. Fluids attributed to Au precipitation in the Tyndrum area of Scotland (including Cononish) are not considered ‘saline fluids’ (Curtis et al., 1993), therefore reactions (i) and (ii) would also be applicable depending on the pH of those fluids. Reaction (iii) *could* become important with respect to late brines, however this is not considered to be significant.

Fluid mixing

Mixing of fluids with a different pH is considered to be a viable process indirectly effecting Au precipitation, a process considered most significant in low-sulphidation epithermal and IOCG (iron-oxide copper gold) systems (Pokrovski et al., 2014). For deposits hosted by the Grampian Terrane in Ireland and Scotland, previous workers have proposed any number of fluids including metamorphic fluids, magmatic fluids, saline brines, and meteoric waters interacting during the evolution of the orogen (including Curtis et al., 1993; Parnell et al., 2000; Wilkinson et al., 1999), mixing is thus likely to have contributed to Au precipitation.

Conclusion: dominant mechanisms associated with the Grampian event of the Caledonian Orogenic Cycle

There are three entirely distinct steps involved in the emplacement of Au, to which different processes may be attributed. Firstly, the opening of pathways and the introduction of a

hydrothermal fluid; second, the precipitation of sulphide minerals (e.g. pyrite) which may host mineralisation; third, the precipitation of Au from the fluid and its final emplacement. The facilitation of these events may require one or more mechanisms to successfully form a deposit. This study proposes that episodic rupture caused by decompression and seismic pumping are dominant in the injection of fluids into pathways formed through tectonism and localised faulting, that phase separation mechanisms are most important in the precipitation of host sulphides, while cooling, fracture-wall nucleation and in certain contexts (e.g. the Sperrin Mountains deposits) fluid-rock interactions, are dominant processes in late Au emplacement.

10.3. On the source of gold and trace elements

10.3.i. Research question and overview

The second stated research question of this thesis asks:

“What is the source of gold north-west Ireland?”, and whether pyrite itself is a source of gold.

In *Chapter Seven*, a regional-scale study, pyrrhotite and pyrite porphyroblasts were examined within geological formations in the Donegal Inlier which may provide a reservoir for gold and associated trace elements in north-west Ireland. These horizons lie within the Appin and Argyll Groups, stratigraphically below the Southern Highland Group which hosts Au deposits within the Sperrins Inlier. It is proposed that tested formations are viable for the source of Au observed in veins which formed synchronous with deformation fabrics, and may contribute to remobilised Au associated with ‘late-orogenic’ pyrite. Pyrite is a viable origin of gold at the earliest stages of the Grampian collision, distal to known deposits, however in the ‘late-orogenic’ context to which the majority of discovered ounces are ascribed, pyrite at the

deposit-scale is not considered by this study to be a source. Study of micro-fracturing of pyrite within veins at Curraghinalt and Cononish (*Chapter Five* and *Chapter Eight*) has revealed Au emplacement and metalliferous enrichment therein; evidence supports the late infiltration of fluids preceding those from which pyrite precipitated.

Key concepts and findings presented draw on methodologies by Thomas et al. (2011) and Deditius et al. (2014), among other workers.

10.3.ii. Key findings and processes relating to the sourcing of Au

It is considered by this study that redox conditions are likely to have been favourable for Au mobility in both the Neoproterozoic-Cambrian sedimentation environment (e.g. Planavsky et al., 2011) and during the Ordovician (contemporary with the Grampian arc-continent collision, c. 475-460 Ma), cross-referencing with work conducted by Pokrovski et al. (2014) which identifies a proportionality between Au solubility and oxygen fugacity. The solubility of Au within pyrite may be probed by examining ratios of Au and As concentrations using the methodology of Deditius et al (2014) and Reich et al. (2005). Examining pyrite from Glencolumbkille, Co. Donegal (Argyll Group), data was acquired from regions of interest within LA ICP-MS raster element maps using the ‘Monocle’ add-on script for Iolite processing software. This technique enabled the identification of trace quantities of Au in solution, and a trend toward super-saturation (and the formation of Au⁰ nanoparticles) with evolution of the system (see Figure 7.19).

Interestingly, Au solubility may be viable as a proxy for redox conditions: given the proportionality with fO_2 , results are indicative of a trend from anoxic conditions toward more oxidising conditions, which may be interpreted as consistent with post-peak (deformation) uplift and exhumation of the orogen.

Fluid and metals were mobile within the Appin and Argyll Group synchronous with deformation, driven by orogenic processes at the greenschist-facies transition: *Chapter Seven* presents petrographic and geochemical data from the Appin and Argyll Groups of mid-Dalradian Supergroup stratigraphy which have enabled the development of a viable model for the mobilisation of fluid and trace elements at the greenschist-amphibolite facies transition. This model is discussed in detail in *Section 7.8*. A graphical representation of this model and its key elements is presented in Figure 7.20.

A central component to this model is the examination of pyrrhotite and gangue minerals which confirm that strata were subjected to pressures and temperatures indicative of greenschist-amphibolite facies conditions before reverting to a retrograde path. This evidence includes the observation of garnet porphyroblasts exhibiting chloritic alteration at Glencolumbkille (Argyll Group), confirming observations made by previous workers and presented in the *Petrography* section of the chapter, *Section 7.5*. Geochemical analysis using LA ICP-MS methods have enabled the integration of Au solubility and trace element mobilisation data into the model.

Orogenic fluids were likely to have transported gold in $\text{AuHS}_0 + \text{Au}(\text{HS})_2^-$ complexes under retrograde conditions as temperatures decreased from 450°C. Rapid exhumation and depressurisation would have provided favourable conditions for Au solubility. Petrographic and geochemical information was attained from pyrite and pyrrhotite hosted by sequences of carbonaceous shales within the Appin and Argyll Groups of the Dalradian Supergroup in north-west Ireland. It was hypothesised that such horizons may provide a viable source for gold and trace elements. Observed pyrrhotite within the Appin Group shales and trace element enriched phases of pyrite within the Argyll Group, showing a relationship with deformation fabrics, is indicative of a viable framework for the mobilisation of fluid and metals when considered in the context of physical and chemical conditions and structural networks. A genetic model is presented in *Section 7.8.iv*. (illustrated in Figure 7.20), while viable processes for the mobilisation

of Au are considered in *Section 7.8.vi*. It is considered most likely that Au was transported in fluids within bi-sulphide complexes as the dominant species in metamorphic fluids between 200 and 450 °C; at high temperatures associated with peak temperature conditions, Cl-complexes are also likely have contributed (see Figure 10.6).

10.4. On gold, deformation and metamorphism

10.4.i. Research question and overview

A third research question is considered by this thesis:

“What is the relationship between gold emplacement, deformation and metamorphism?”

While this question relates to the specific environmental conditions and processes constrained by the geological evolution of the Grampian orogen, it is considered that proposals from this study may have implications for research of active and ancient orogenic systems further afield.

This study presents new evidence supporting metamorphism and deformation as the principle controls on the mobilisation of Au and trace elements in the Grampian Terrane. At Curraghinalt and Cloonacool, considered in *Chapter Five* and *Chapter Six*, the geological framework includes grain-fabric relationships which provide relative timing constraints on early prograde generations of pyrite. This has enabled geochemical results to be constrained to events in the P-T history. *Chapter Seven* examined the metamorphic conditions at the regional scale and identified a viable framework for the sourcing and mobilisation of Au bearing hydrothermal fluids. Conclusions from this work are discussed in the following pages.

10.4.ii. Key findings and processes associated with structural and metamorphic controls

Fluids released during pyrite to pyrrhotite conversion reactions initiated at the greenschist-amphibolite transition. These fluids originated in the Appin Group and were capable of transporting Au. It is hypothesised in this thesis that pyrrhotite, identified in this study within the Appin Group and petrographically examined in *Section 7.5.iii*, formed as a result of metamorphic conversion reactions described by Phillips and Powell (2010). This is supported by evidence including: (i) textural observations including their peculiar morphology and recrystallised rims (see Figure 7.8), (ii) the observation of elevated Au and Ag peaks within Laser Ablation ICP-MS spot analysis output signal indicative of auriferous particles which were likely to have derived from original precursor pyrite (see Figure 7.11), (iii) the petrographic observation of chlorite-altered garnet within overlying Argyll Group strata indicate peak metamorphic conditions at the greenschist-amphibolite facies transition, at which such conversion reactions would occur (see Figure 7.6).

Environmental retrograde conditions were likely to have been a result of exhumation and depressurisation of strata, and as proposed in *Section 7.3.ii*. (see also Figure 7.2), a favourably oriented structural framework was present for the distribution of metamorphic fluids which take the form H₂O-CO₂-H₂S.

D₂ thrust and nappe structures may have provided a suitable pathway network at the scale required for long-distance transit of hydrothermal fluids; Au was mobile synchronous with the development of deformation fabrics. It is considered by this study that the regional-scale structural network associated with early deformation of the Grampian orogen (e.g. D₁ and D₂ lineations identified in County Donegal (e.g. Alsop et al., 2001; see Figure 7.2) may have provided favourable pathways for the mobilisation of fluids carrying Au and trace elements. Evidence from LA ICP-MS spot analyses conducted during this study demonstrate consistent enrichments (>100 ppm) in Co, Ni ± As and Pb within early phases of pyrite which may have

been mobilised from basin stratigraphy within the Appin Group. Gold values exceeding 1ppm are also observed in these phases. Petrographic and geochemical evidence from the Cloonacool prospect demonstrate that localised pathways associated with deformation may have been exploited by multiple fluids carrying differing geochemical signatures (see *Chapter Six*).

Late orogenic Au at Curraghinalt was carried by a fluid which exploited micro-fractures which formed during a phase of extensive brittle deformation. It is considered likely that there is a genetic association between the dehydration of Appin and Argyll Group strata, the earliest recognised phase of Au at Curraghinalt (Py₂; see *Chapter Five*) and auriferous veins at Cloonacool (see *Chapter Six*). Evidence from the Curraghinalt deposit, is consistent with findings by previous workers that significant Au emplacement is also likely to have been derived from sources associated with late saline fluids associated with dehydration of the Laurentian margin proximal to the suture of the orogen. Mineralisation hosted within late micro-fractures observed in this study, was likely to have been transported in bi-sulphide complexes.

10.5. Model framework for Grampian orogenic Au

A schematic model for the orogenic mineralising system in north-west Ireland (not inclusive of extensive host strata deformation or late phase enrichments) is presented in Figure 10.7.

Initial conditions (Neoproterozoic-Cambrian) favoured the solubility of Au in pyrite, which was later transported due to metamorphism and deformation (Ordovician) toward physical traps, with chemical processes including phase separation, cooling and fluid-rock interactions effecting sulphide and Au emplacement within vein networks generated as a result of episodic seismicity along pathways. ‘Syn-deformational’ (prograde) Au is characterised by soluble phases within pyrite, while late fluids associated with retrograde metamorphism were super-saturated. Median concentrations of Co, Ni, As and Pb show enrichments in syn-

deformational phases, which may have derived from the Appin Group where enrichments of Mn, Co, Ni and Zn are recorded in pyrrhotite. It is likely that As was mobilised with Au from this stratigraphic level.

As, Pb and Ni enrichments are reported in late orogenic pyrite: the lowest average abundance of Au in pyrite is recorded in late orogenic pyrite at Curraghinalt, which hosts the largest estimated resource along the trend, supporting the hypothesis of Au enrichment from fluid which included a late brine component.

For a full breakdown of LA ICP-MS analytical methods, results and sample populations, see *Chapter Five* (Curraghinalt), *Chapter Six* (Cloonacool), *Chapter Seven* (Appin and Argyll Group potential sources), and *Chapter Eight* (Cavanacaw).

Au model framework for north-west Ireland

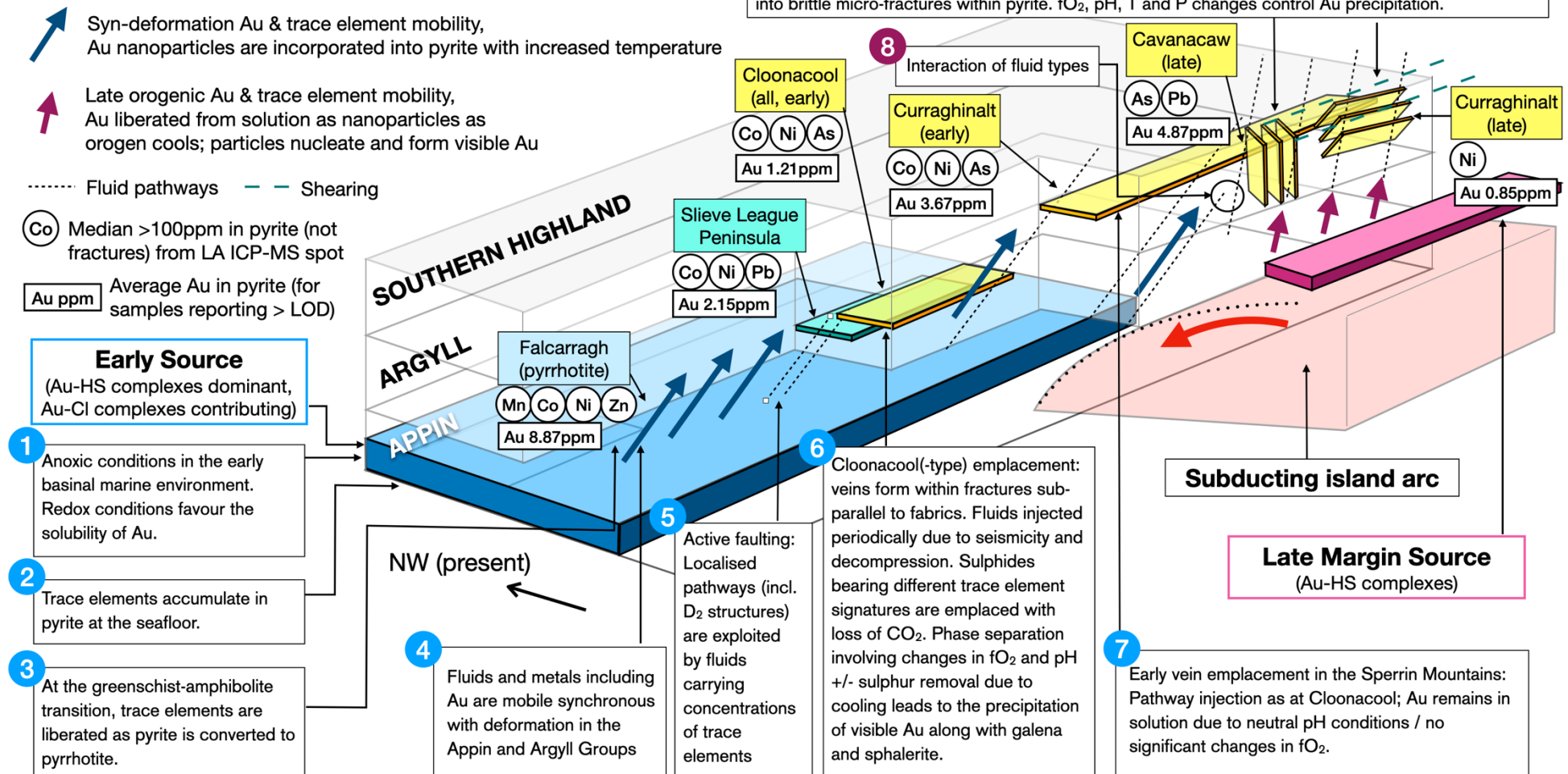


Figure 10.7. Schematic model for Au source, transport and emplacement associated with the Ordovician Grampian Orogeny in north-west Ireland.

Chapter Eleven: Conclusions

Geological context to the study

Vein networks in north-west Ireland and Scotland host gold mineralisation, associated with the Grampian arc-continent collisional event (475 - 460 Ma) of the Caledonian Orogenic Cycle (475 – 405 Ma). This study has sought to augment understanding of the mobility of gold and trace elements, potential sources, and the relationship between gold emplacement, deformation and metamorphism associated with Grampian collisional tectonics.

Model development and microanalysis

Models are developed and presented in this study which provide new insight into the genesis of ore deposits and may aid exploration of the Grampian terrane for gold and the realisation of its full potential. The results of petrographic and geochemical analyses of Au-hosting pyrite from the Curraghinalt and Cavanacaw gold deposits (Sperrin Mountains; County Tyrone, Northern Ireland), the Cloonacool occurrence (Ox Mountains; County Sligo, Ireland) and the Cononish deposit (Stirling, SW Scotland), along with pyrite (and pyrrhotite) grains from potential source strata within the mid-to lower- Dalradian Supergroup (County Donegal, Ireland). The principle techniques used in this work were optical microscopy, Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS/EDX), and Laser Ablation Inductively Coupled Plasma Mass Spectroscopy (LA ICP-MS). All analytical work was conducted in-house at Trinity

College Dublin laboratories (iCRAG Lab@TCD; Geochemistry Laboratories, Pearse Street, Dublin).

Petrographic summary and the extent of gold mobility

Quartz and carbonate are identified within veins at deposits and occurrences which typically contain abundant pyrite and chalcopyrite; local assemblages may also include galena, arsenopyrite and sulphosalts. Au-bearing veins are observed sub-parallel to regional S_2/S_3 fabrics (categorised in this study as '*syn-deformational*') and cross-cutting those fabrics, post-dating their development ('*late-orogenic*'). Late-orogenic mineralisation is considered to be most significant in terms of Au resources, visible phases of gold have a characteristic association with cryptic micro-fracture networks resulting from cataclastic deformation.

LA ICP-MS analyses of pyrite (spot analyses, $n=530$; raster element mapping) and pyrrhotite (spot analyses, $n=50$) have revealed that Au and trace elements were mobile throughout the evolution of the Grampian orogen, from the earliest stages of deformation-fabric development to relatively late timing associated with orogenic collapse. Refractory Au concentrations are recorded in pyrite across the Grampian trend with a median abundance of 0.69 ppm (IQR = 0.2 – 2.17 ppm; 294 analyses reporting above the limit of detection or LOD). These abundances are shown to correlate positively (Spearman rank, $\rho \geq 0.5$) with transition metals (Co, Ni, Cu, Mo, Ag, W and Hg), base metals (Ga, Sn, Tl, Pb and Bi) and metalloid elements (As, Sb and Te), with discrete localised variations observed across the trend.

Early gold and base metal mobility at Curraghinalt, Northern Ireland (see Chapter Five)

The Curraghinalt Au deposit in County Tyrone, Northern Ireland is the largest estimated resource discovered to date along the trend (>6 Moz) and was the subject of extensive petrographic and geochemical work in this contribution. Early phases of pyrite which formed synchronous with the development of regional S_2/S_3 fabrics are recognised within quartz-ankerite veins (also carrying galena and chalcopyrite) which carry polymetallic signatures.

Compositional zonation is recorded, which shows early Zn (median = 5,030 ppm, IQR = 4,000-7,400 ppm; n=35) and Ni (median 2,410 ppm, IQR = 1,850-3,420 ppm; n=35) enrichment in the initial phase of pyrite, Py₁, which is overgrown by a later phase exhibiting refractory enrichment of Au with a median concentration of 3.69 ppm (IQR = 2.02 – 10.1 ppm; n=34), confirmed by LA ICP-MS raster element mapping as heterogeneous. This enrichment demonstrates that Au was mobile in the Sperrin Mountains during earlier stages of the Grampian Orogeny which may have coincided with peak metamorphic conditions (c. 468 Ma).

Syn-deformational metal emplacement along-trend in the Ox Mountains (see Chapter Six)

In the Ox Mountains (County Sligo, Ireland), visible Au is observed hosted by samples of pyrite in quartz veins sub-parallel to regional fabrics at Cloonacool, a recently discovered occurrence at the exploration stage. LA ICP-MS spot analyses and raster element mapping reveal that these veins have also been exploited multiple times by fluids exhibiting varying geochemical signatures, including of Au; concentrations > 1 ppm Au coincident with As > 1,000 ppm are recorded within a discrete phase which is cryptic under a reflected light microscope and only observed using LA ICP-MS methods.

A metamorphic source for Au in lower Dalradian Supergroup stratigraphy (see Chapter Seven)

It is considered from this study that geochemical analyses of pyrite and pyrrhotite from County Donegal, the Sperrin Mountains (Curraghinalt) and the Ox Mountains (Cloonacool) in Ireland show that a viable source is present within the Appin and Argyll Groups; Au (and As) were mobilised, likely facilitated by reduction, which was transported within hydrothermal networks (tens of kilometres) in fluids released due to metamorphism, navigating a complex structural architecture (including D₂ thrusts and nappes). It is feasible that these fluids sourced from tested strata enriched phases of pyrite observed within early syn-deformational veins at Curraghinalt, Cloonacool, and at other localities across the terrane.

Modelling of geochemical data from sedimentary horizons within the Appin and Argyll Groups (County Donegal) shows that uncommon Au particles are recorded within Blair Atholl Subgroup pyrrhotite (median = 7.30 ppm; IQR = 6.90 – 12.4 ppm; n=3) associated with elevated concentrations of Ag (e.g. coincident peaks including 161 ppm Au, 141 ppm Ag, Au/Ag = 1.14; 46.6 ppm Au, 25.3 ppm Ag, Au/Ag = 1.84). Elevated concentrations are also recorded in Easdale Subgroup pyrite which exhibits chemical zonation. LA ICP-MS raster element mapping reveals that outer phase Py₂ at Glencolumbkille is relatively enriched in Co, Ni, Bi and Te compared to cores (Py₁), and using a novel technique to extract quantitative information from those maps for Au and As, growth phases show subtle enrichment in refractory Au and progressive trends toward supersaturation of fluids, liberating Au⁰ nanoparticles which it is hypothesised have been subsequently transported in hydrothermal fluids. Supported by petrographic evidence, it is proposed that Au is likely to have been mobilised with fluids as a result of dehydration reactions at the greenschist-amphibolite facies transition, during collision of the incumbent arc with the Laurentian margin.

Late orogenic Au emplacement within pyrite micro-fracture networks (see Chapter Five and Chapter Eight)

LA ICP-MS raster element mapping of ‘late orogenic’ phases of pyrite at Curraghinalt (the ‘ore-phase’, Py₃) and Cononish has revealed Au enrichment within cryptic, brittle micro-fracture networks which post-date the precipitation of host pyrite. At Curraghinalt, visible Au coeval with Bi- and Ag- telluride is observed within fractures carrying enrichment of Cu, Ag, Te, Au, Pb and Bi, while pyrite micro-fractures at the Cononish deposit in Scotland bear a more diverse enrichment of Co, Ni, Cu, As, Ag, Sb, Te, Au, Hg, Pb and Bi. Concentrations of tested analytes within Cononish pyrite are relatively depleted, however at Curraghinalt, these micro-fractures are clearly observed to cross-cut earlier growth zones of cyclical Co and Ni, with little disturbance of those zones. Observations from the Curraghinalt deposit challenge the previously held interpretation that late Au is sourced and remobilised in situ from the interior of grains. Evidence acquired from this study suggests that the main stage of Au is not genetically

associated with the growth of pyrite at Curraghinalt, furthermore, no discrete sulphide phases are found in association with Au at Curraghinalt. Gold is derived from an external source, likely related to dehydration of the Laurentian margin and interactions with seawater; at Cononish, local intrusives may be contribute to late enrichments of Au.

A partial overlap in source for the Curraghinalt and Cavanacaw deposits (see Chapter Eight)

A comparison of the proximal Curraghinalt and Cavanacaw deposits in the Sperrin Mountains has revealed petrographic and geochemical similarities (e.g. the presence of visible Au associated with fractures within pyrite, a partial overlap in chemical signatures for Te, Zn, Bi, Mn, Se, Sn, Ni, W, Co and Mo), and differences (in sulphide composition and enrichments, e.g. of Pb) suggesting partial synergy of ore sourcing and emplacement processes.

A model for metal emplacement at the Cononish deposit

Geochemically distinctive metal emplacement events are identified at the Cononish Au deposit (Stirling, SW Scotland) which are likely to be attributed to episodic infiltration of late fluids. These events have an identifiable chemical signature: event I (associated with Py₂ within pyrite micro-fractures; Co-Ni-As-Ag-Sb-Te-Pb-Bi) and event II ('ore stage'; Au-Hg-Ag, synchronous with Cu and Sb mineral phases). It is considered that the late timing of emplacement phases at Cononish within pyrite micro-fractures supports the hypothesis of late circulation of metamorphic fluids, which may have been catalysed by local intrusives.

Insight into processes which emplaced gold (see Chapter Nine)

Episodic rupture caused by decompression and seismic pumping is likely to have facilitated the injection of fluids into pathways (structural weaknesses), with phase separation mechanisms (including fluctuations in fO_2 and pH) and fluid-rock interactions aiding the localised precipitation of sulphide and Au. Orogenic fluids are most likely to have carried Au over long

distances (10s of kilometres) as bisulphide complexes; exhumation and depressurisation of the orogen provided favourable conditions for Au solubility, while seismicity is considered to have had a significant role in the injection of fluids into structural pathways. Emplacement of gold is likely to have been facilitated by temperature decreases under reducing conditions aiding supersaturation of Au-bisulphide complexes and the liberation of Au nanoparticles. Au observed within micro-fractures of pyrite at the deposit scale was emplaced by fracture-wall nucleation of particles on reactive surfaces under localised reducing conditions.

Exploration: fertility and vectoring (see Chapter Ten)

It is considered that while analyses of precursor and wall-rock pyrite phases may be of significant value to explorers as an indicator of local fertility, it is not likely to be a viable tool for vectoring toward a deposit. It is determined that wall-rock pyrite tested within millimetres of late Au-hosting veins do not bear geochemical signatures matching pyrite hosting mineralisation within late orogenic veins which cross-cut host fabrics. Positive exploration outcomes from the use of LA ICP-MS mapping may include (i) the elucidation of metal emplacement histories, (ii) information on the solubility of gold and (iii) the relative timing of sulphidation.

Future work

Additional analyses are recommended to reveal the full paragenetic history at Cavanacaw and Cononish, systematic sampling and micro-analysis across stratigraphic horizons, of fluid pathways and fertile structures, and at the deposit-scale between vein envelopes is recommended to test regional and deposit-scale models. The use of Secondary Ion Mass Spectroscopy (SIMS) may be of value in testing mobility of hypothesised nanoparticles across the Terrane and localised emplacement mechanisms within pyrite micro-fracture networks. Additional localities of interest not examined by this study include gold occurrences on the Inishowen Peninsula in County Donegal, Ireland, and in the Aberfeldy area of Central Scotland. Analysis of samples from these localities, and particularly of host formations with different

metamorphic grades may lead to a more comprehensive genetic model. Four-dimensional modelling of structure, ore fluid and metals, will enable precise targeting for exploration.

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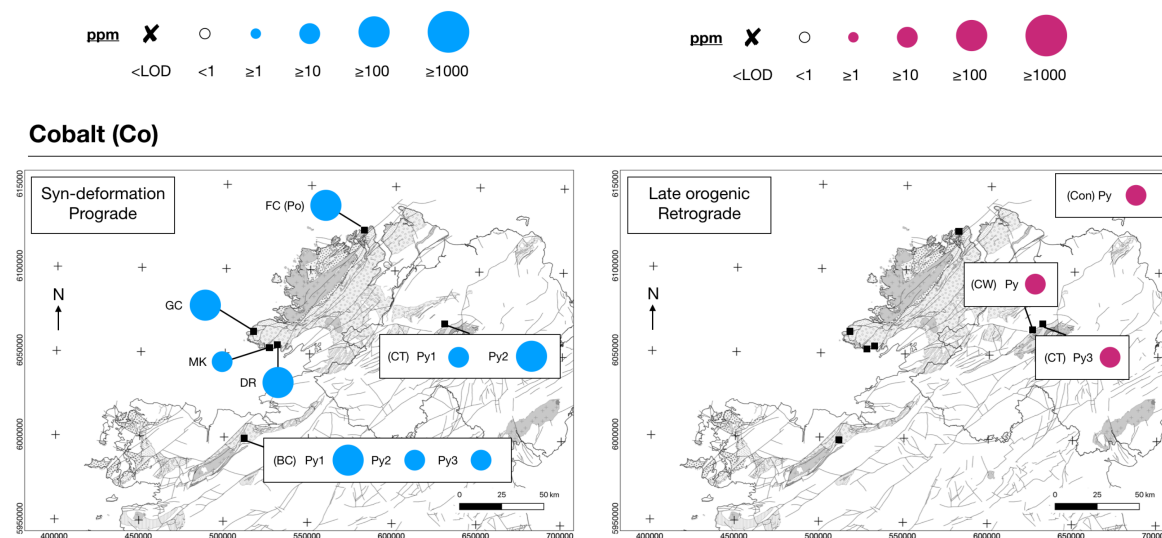
Appendix 1: Project and sample locations

Locality	Sample Prefix	Geographic region	Latitude (N)	Longitude (W)
Curraghinalt	CT-	Sperrins, N. Ireland	54° 43' 19.15"	7° 08' 58.73"
Cloonacool	BC-	Ox Mtns., Ireland	54° 06' 16.96"	8° 46' 26.72"
Cavanacaw	CW-	Sperrins, N. Ireland	54° 35' 04.16"	7° 22' 51.50"
Cononish	CS-	West Highlands, Scotland	56° 25' 06.77"	4° 46' 17.79"
Derrylahan	DR-	Slieve League Peninsula, Ireland	54° 38' 15.25"	8° 37' 29.35"
Glencolumbkille	GC-	Slieve League Peninsula, Ireland	54° 42' 23.79"	8° 45' 38.18"
Muckros	MK-	Slieve League Peninsula, Ireland	54° 37' 3.85"	8° 35' 27.30"
Falcarragh	FC-	N. Donegal, Ireland	55° 9' 53.37"	8° 3' 59.57"

Appendix 2: Geochemical signatures for elements of potential economic interest (excluding Au)

14.1.i. Cobalt (Co)

 **Critical Raw Material for the European Union** (European Commission, 2017)

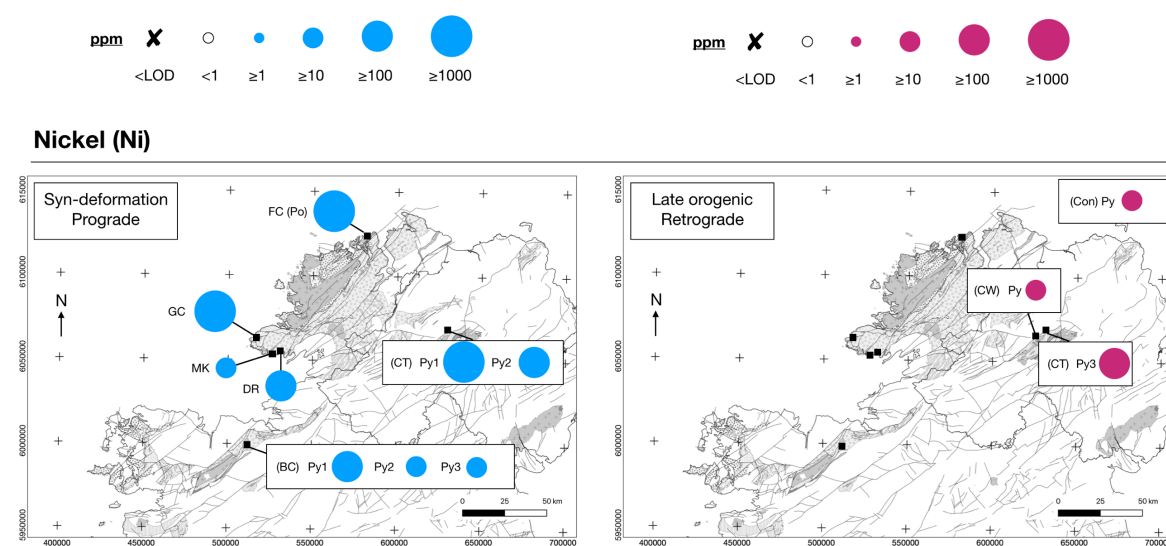


Proportional circle map for Co median in pyrite and pyrrhotite (ppm) for 435 LA ICP-MS analyses reporting > limit of detection (n=520).

Identified pyrite phase (and chapter reference). (VG = visible Au, LT = lattice-bound Au)	Spearman rank correlation ($\rho \geq +0.5$)	Spearman rank correlation with Au ($\rho \geq +0.5$)	Co ppm (median)	% +/-	n > LOD
● SL - Glencolumbkille (C.7)	Cu, Ni, Tl, Pb, Ag	✗	500	+510	33
● SL - Derrylahan (C.7)	W, Ni	✗	186	+127	41
● Cloonacool Py ₁ (C.6)	Ni	✗	140.5	+71.3	72
● Curraghinalt Py ₂ (C.5) LT	Ni, Zn, As	✗	104.5	+27.4	32
● Curraghinalt Py ₁ (C.5)	n/a	✗	92.2	+12.4	35
Median, all data			82	-	435
● Curraghinalt Py ₃ (C.5) VG	Ni	✗	72.3	-11.8	129
● SL - Muckros (C.7)	Ni, Au	✓	45	-45.1	35
● Cononish Py-Ore (C.8) VG	n/a	✗	30	-63.4	25
● Cloonacool Py ₃ (C.6)	Bi, Pb, Ni	✗	28	-65.9	5
● Cavanacaw Py-Ore (C.8) VG	As, Pb, Ag, Sn	✗	20	-75.6	5
● Cloonacool Py ₂ (C.6) VG	Ni, Ga	✗	14.7	-82.1	23

Summary for tested pyrite including relative abundances and correlative elements.

14.1.ii. Nickel (Ni)



Proportional circle map for Ni median in pyrite (ppm) for 442 LA ICP-MS analyses reporting > limit of detection (n=520).

Identified pyrite phase (and chapter reference). (VG = visible Au, LT = lattice-bound Au)	Spearman rank correlation ($\rho \geq +0.5$)	Spearman rank correlation with Au ($\rho \geq +0.5$)	Ni ppm (median)	% +/-	n > LOD
● SL - Glencolumbkille (C.7)	Co, Cu	X	3,285	1,101	28
● Curraghinalt Py ₁ (C.5)	As	X	2,410	781	35
● SL - Derrylahan (C.7)	Co, W, Sn	X	490	79.2	43
● Cloonacool Py ₁ (C.6)	Co, Se	X	443.5	62.2	72
Median, all data			274	-	442
● Curraghinalt Py ₂ (C.5) LT	Co, As	X	191	-30.3	32
● Curraghinalt Py ₃ (C.5) VG	Zn, Co	X	126	-54.1	128
● Cononish Py-Ore (C.8) VG	Zn, W	X	95.0	-65.3	29
● Cloonacool Py ₃ (C.6)	Co, Pb	X	78.0	-71.5	5
● SL - Muckros (C.7)	Co	X	69.0	-74.8	37
● Cloonacool Py ₂ (C.6) VG	Co, Bi	X	27.1	-90.1	28
● Cavanacaw Py-Ore (C.8) VG	W, Cu, As, Au, Hg, Tl	✓	13.6	-95.0	5

Summary for tested pyrite including relative abundances and correlative elements.

14.1.iii. Copper (Cu)

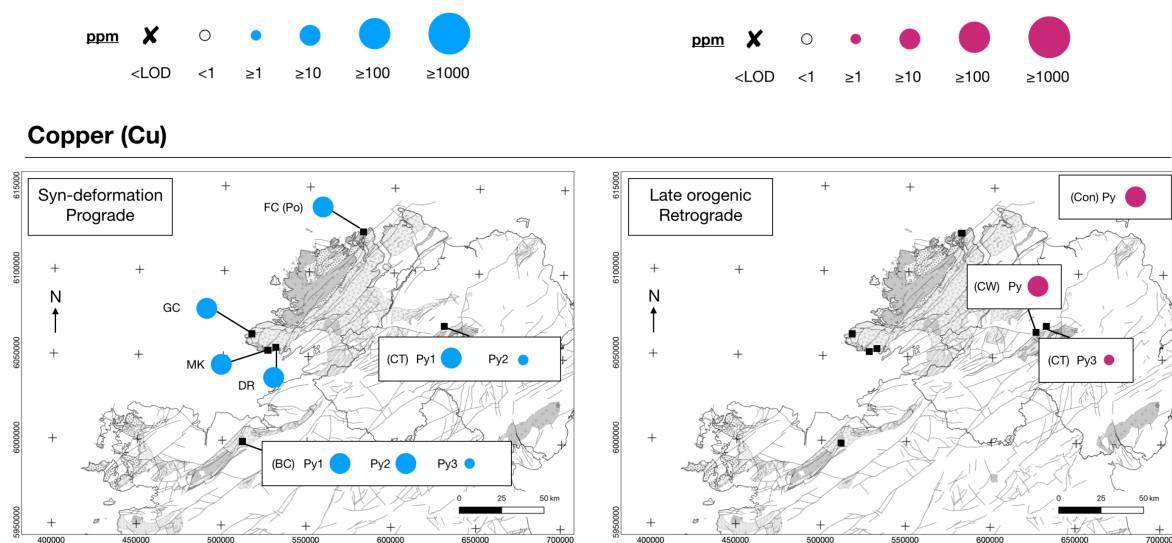


Figure 14.1. Proportional circle map for Cu median in pyrite (ppm) for 389 LA ICP-MS analyses reporting > limit of detection (n=520).

Identified pyrite phase (and chapter reference). (VG = visible Au, LT = lattice-bound Au)	Spearman rank correlation ($\rho \geq +0.5$)	Spearman rank correlation with Au ($\rho \geq +0.5$)	Cu ppm	% +/-	n > LOD
Curraghinalt Py ₁ (C.5)	n/a	X	50.0	+276	35
● Cavanacaw Py-Ore (C.8) VG	Te, Ni, Pb, Sb, Mn, Ga, Sn, W	X	42.4	+219	6
● Cononish Py-Ore (C.8) VG	Sb, Hg, Tl, Ag, Pb, Te, Sn, Au	✓	42.0	+216	38
● SL - Glencolumbkille (C.7)	Zn, Co, Bi, Ag, Tl, Ni	X	28.2	+112	38
● SL - Derrylahan (C.7)	Se, Mn	X	15.8	+18.4	42
● Cloonacool Py ₁ (C.6)	Ag, Pb, Bi, Te, Sb, W	X	15.3	+15.0	67
Median, all data			13.3		389
● SL - Muckros (C.7)	Hg, As, Pb, Bi, Ag, Se, Au	✓	12.5	-6.02	35
● Cloonacool Py ₂ (C.6) VG	Ag, Sb, Hg, Zn	X	12.4	-6.77	25
● Cloonacool Py ₃ (C.6)	Hg, Te, Ag, Au, As, Sb	✓	8.00	-39.9	5
● Curraghinalt Py ₂ (C.5) LT	W, Ag, Pb, Ga, Hg, Sb, Mo, Bi, Zn	X	4.93	-63.0	32
● Curraghinalt Py ₃ (C.5) VG	Mn, Se, Bi, Sb, Tl, Pb, Ag	X	1.91	-85.6	66

Summary for tested pyrite including relative abundances and correlative elements.

14.1.iv. Molybdenum (Mo)

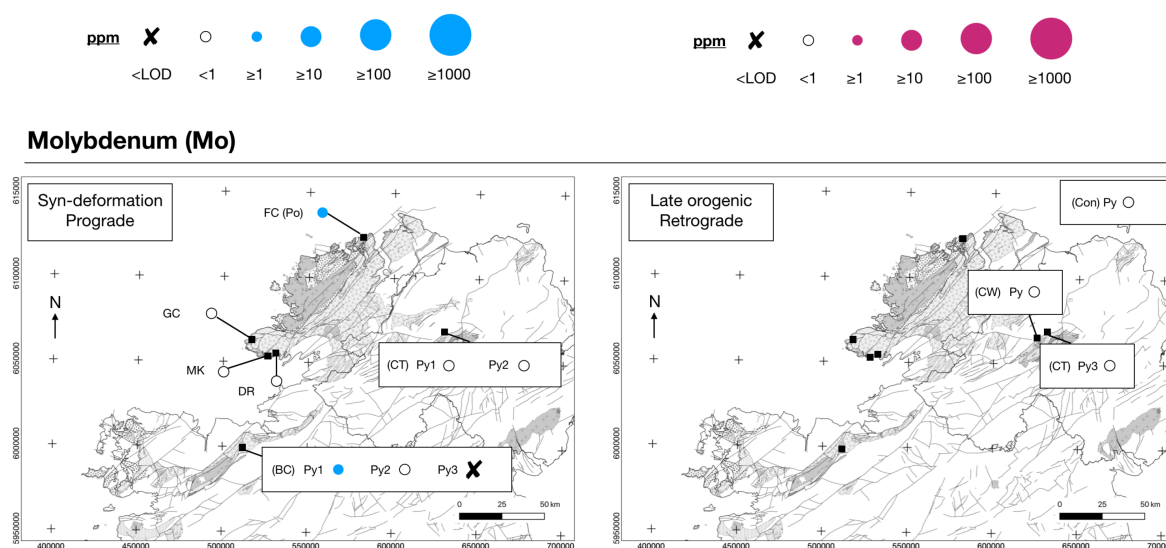
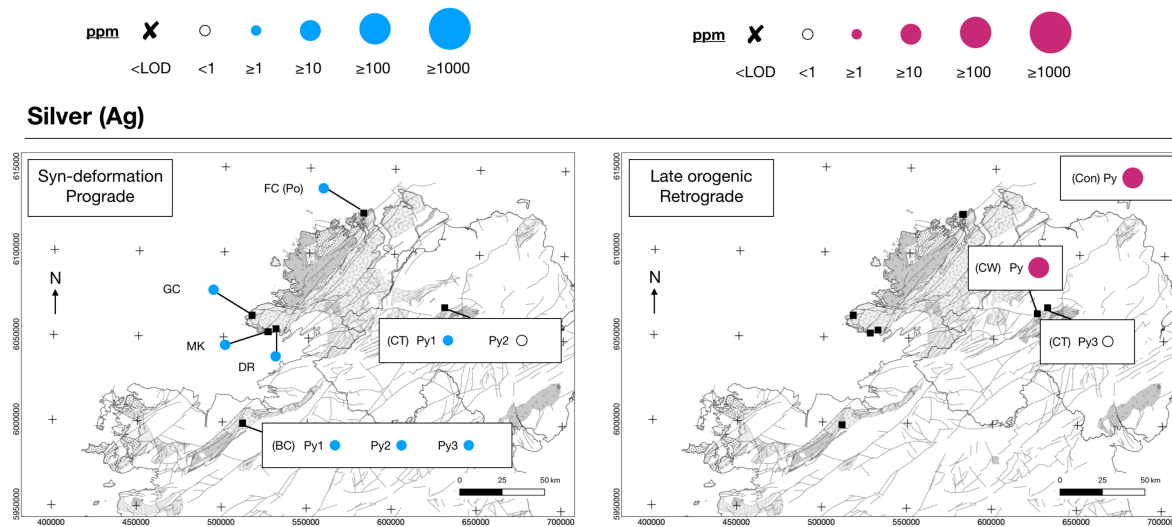


Figure 14.2. Proportional circle map for Mo median in pyrite (ppm) for 111 LA ICP-MS analyses reporting > limit of detection (n=520).

Identified pyrite phase (and chapter reference) (VG = visible Au, LT = lattice-bound Au)	Spearman rank correlation ($\rho \geq +0.5$)	Spearman rank correlation with Au ($\rho \geq +0.5$)	Mo ppm (median)	% +/-	n > LOD
● Cloonacool Py ₁ (C.6)	Tl	X	7.40	+1,621	37
● SL - Muckros (C.7)	Te	X	0.79	+83.7	13
● SL - Glencolumbkille (C.7)	Ga, Sn	X	0.56	+30.2	15
Median, all data			0.43	-	111
● SL - Derrylahan (C.7)	n/a	X	0.36	-16.3	2
● Cavanacaw Py-Ore (C.8) VG	W, Au, Hg, Tl	✓	0.28	-34.9	3
● Cononish Py-Ore (C.8) VG	Ga, Te, W	X	0.22	-48.8	19
● Curraghinalt Py ₃ (C.5) VG	W, Zn, Hg, Mn	X	0.18	-57.3	12
● Curraghinalt Py ₂ (C.5) LT	Mn, Cu, Bi	X	0.10	-76.0	6
● Curraghinalt Py ₁ (C.5)	Mn, Zn, Ga, Au	✓	0.08	-82.6	3
● Cloonacool Py ₂ (C.6) VG	n/a	n/a	0.04	-90.5	1
● Cloonacool Py ₃ (C.6)	n/a	n/a	n/a	n/a	0

Summary for tested pyrite including relative abundances and correlative elements.

14.1.v.Silver (Ag)



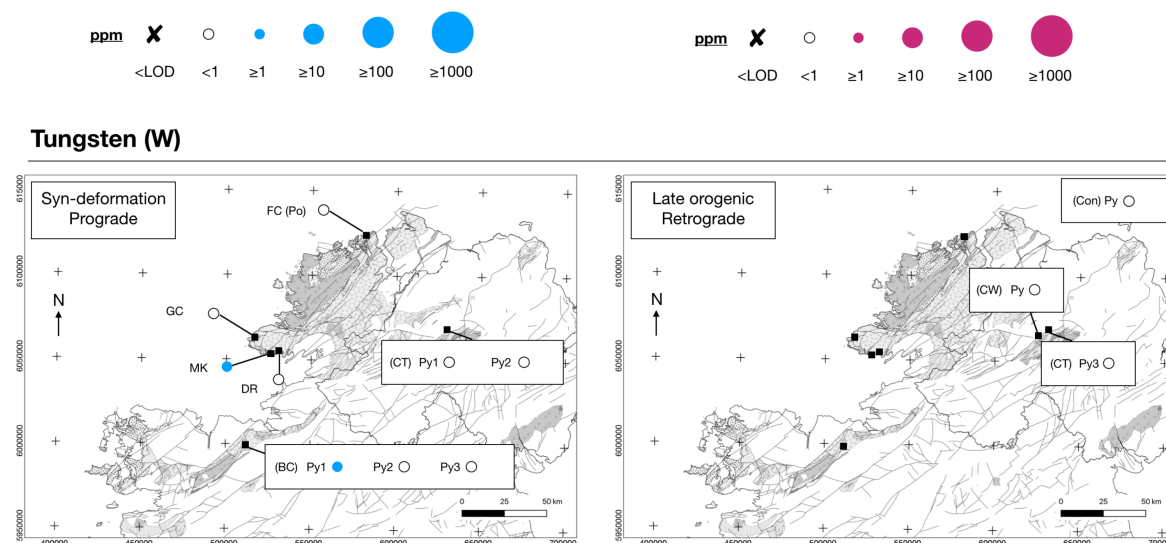
Proportional circle map for Ag median in pyrite (ppm) for 363 LA ICP-MS analyses reporting > limit of detection (n=520).

Identified pyrite phase (and chapter reference) (VG = visible Au, LT = lattice-bound Au)	Spearman rank correlation ($\rho \geq +0.5$)	Spearman rank correlation with Au ($\rho \geq +0.5$)	Ag ppm (median)	% +/-	n > LOD
● Cononish Py-Ore (C.8) VG	Te, Zn, Au, W, Sb, Cu, Sn, Hg, Pb	✓	14.0	+612	46
● Cavanacaw Py-Ore (C.8) VG	Sb, Co, Pb, Au, Hg	✓	13.0	+563	5
● Curraghinalt Py ₁ (C.5)	Sn, Ga, Hg, Zn	✗	5.12	+161	35
● Cloonacool Py ₁ (C.6)	Cu, Bi, Te, Pb, Sb	✗	2.80	+42.9	65
● SL - Derrylahan (C.7)	n/a	✗	2.55	+30.1	34
Median, all data			1.96	-	363
● SL - Muckros (C.7)	Hg, Ga, As, Cu, Pb, Tl	✗	1.90	-3.06	37
● Cloonacool Py ₂ (C.6) VG	Cu, Sb, Hg, Zn	✗	1.89	-3.57	24
● SL - Glencolumbkille (C.7)	Ga, Cu, Pb, Co	✗	1.48	-24.8	22
● Cloonacool Py ₃ (C.6)	Te, Hg, Cu, Pb	✗	1.38	-29.6	5
● Curraghinalt Py ₃ (C.5) VG	Pb, Au, Bi, As, Cu	✓	0.49	-75.3	64
● Curraghinalt Py ₂ (C.5) LT	W, Cu, Pb, Sb, Hg, Zn	✗	0.37	-81.4	26

Summary for tested pyrite including relative abundances and correlative elements.

14.1.vi. Tungsten (W)

 **Critical Raw Material for the European Union** (European Commission, 2017)



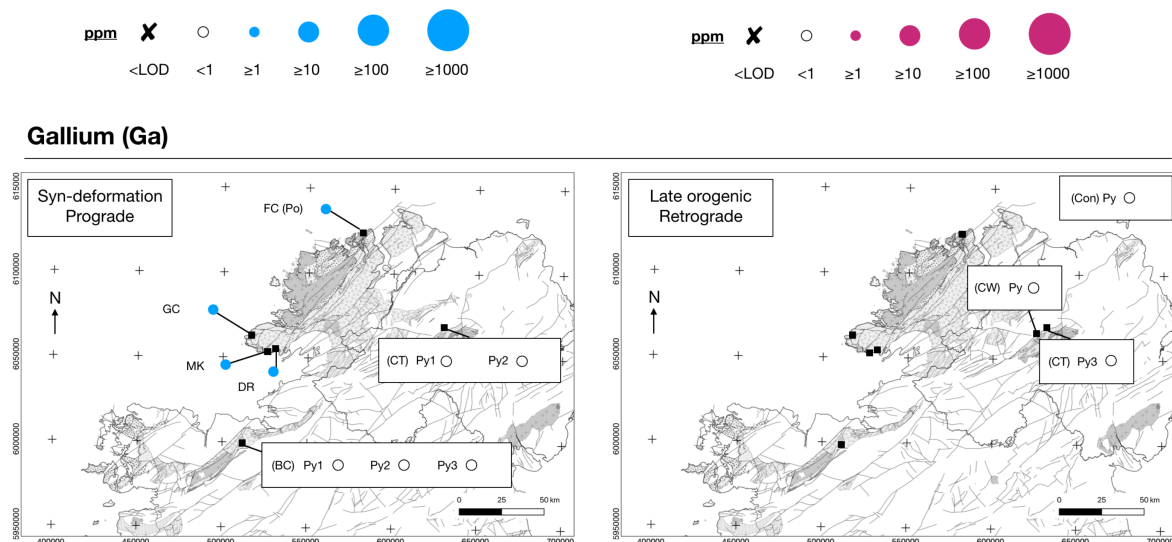
Proportional circle map for W median in pyrite (ppm) for 103 LA ICP-MS analyses reporting > limit of detection (n=520).

Identified pyrite phase (and chapter reference) (VG = visible Au, LT = lattice-bound Au)	Spearman rank correlation ($\rho \geq +0.5$)	Spearman rank correlation with Au ($\rho \geq +0.5$)	W ppm (median)	% +/-	n > LOD
● Cloonacool Py ₁ (C.6)	Sn, Sb, Cu	X	1.55	+308	40
● SL - Muckros (C.7)	n/a	X	1.40	+268	13
● Cloonacool Py ₂ (C.6) VG	n/a	n/a	0.80	+111	1
● Cloonacool Py ₃ (C.6)	n/a	n/a	0.40	+5.26	1
Median, all data			0.38	-	103
● SL - Glencolumbkille (C.7)	n/a	X	0.36	-5.26	5
● SL - Derrylahan (C.7)	Ga, Tl, Co, Ni, Zn, As	X	0.29	-23.7	14
● Curraghinalt Py ₂ (C.5) LT	Cu, Ag, Pb, Ga, Hg, Mn, Sb	X	0.19	-50.8	7
● Cavanacaw Py-Ore (C.8) VG	Ni, Te, Tl, Au, Hg, Cu, Ga, Mo, Bi	✓	0.14	-62.9	5
● Cononish Py-Ore (C.8) VG	Au, Ag, Te, Ni, Sb, As, Mo, Tl	✓	0.10	-73.7	9
● Curraghinalt Py ₃ (C.5) VG	Zn, Mo	X	0.05	-86.3	7
● Curraghinalt Py ₁ (C.5)	n/a	n/a	0.04	-88.9	1

Summary for tested pyrite including relative abundances and correlative elements.

14.1.vii. Gallium (Ga)

 **Critical Raw Material for the European Union** (European Commission, 2017)

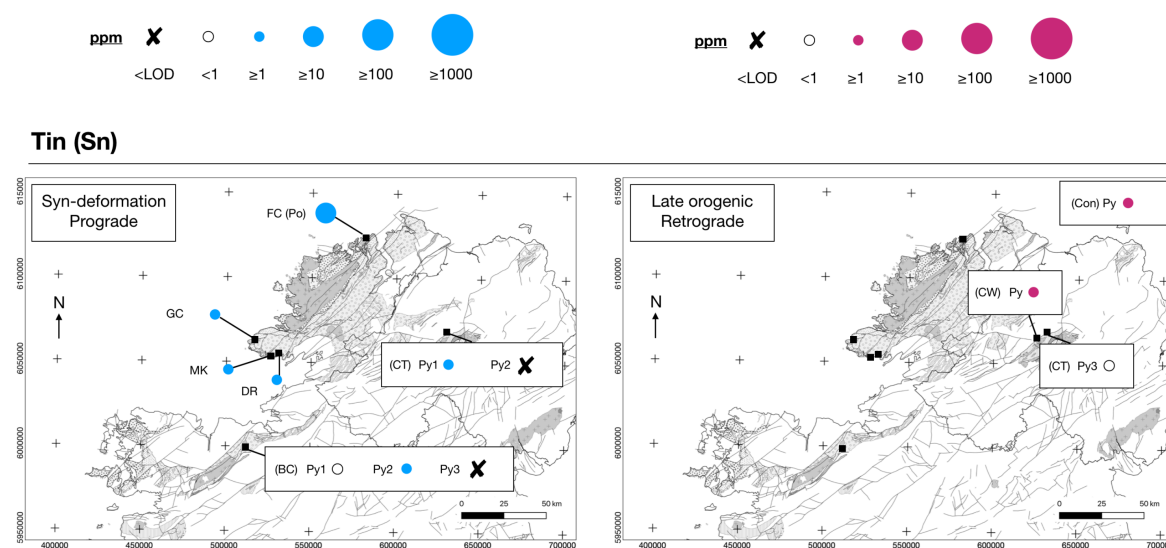


Proportional circle map for Ga median in pyrite (ppm) for 184 LA ICP-MS analyses reporting > limit of detection (n=520).

Identified pyrite phase (and chapter reference) (VG = visible Au, LT = lattice-bound Au)	Spearman rank correlation ($\rho \geq +0.5$)	Spearman rank correlation with Au ($\rho \geq +0.5$)	Ga ppm (median)	% +/-	n > LOD
● SL - Muckros (C.7)	Sn, Ag, Mn	X	1.50	+107	16
● SL - Glencolumbkille (C.7)	Ag, Mo, Sn, Hg	X	1.30	+78.6	14
● SL - Derrylahan (C.7)	W	X	1.00	+37.9	14
● Cloonacool Py ₂ (C.6) VG	Zn, Co	X	0.98	+35.2	8
● Curraghinalt Py ₁ (C.5)	Sn, Ag, Mn, Zn, Hg	X	0.91	+25.5	35
Median, all data			0.73	-	184
● Cononish Py-Ore (C.8) VG	Mo, Sn	X	0.59	-19.3	10
● Cloonacool Py ₁ (C.6)	Hg, Tl, Sb, Au	✓	0.43	-40.7	39
● Cloonacool Py ₃ (C.6)	n/a	n/a	0.34	-53.1	1
● Curraghinalt Py ₂ (C.5) LT	W, Cu, Hg, Mn, Bi, Zn, Tl	X	0.13	-82.8	12
● Cavanacaw Py-Ore (C.8) VG	Te, Au, Cu, W	✓	0.09	-87.7	5
● Curraghinalt Py ₃ (C.5) VG	Zn	X	0.03	-95.2	30

Summary for tested pyrite including relative abundances and correlative elements.

14.1.viii. Tin (Sn)

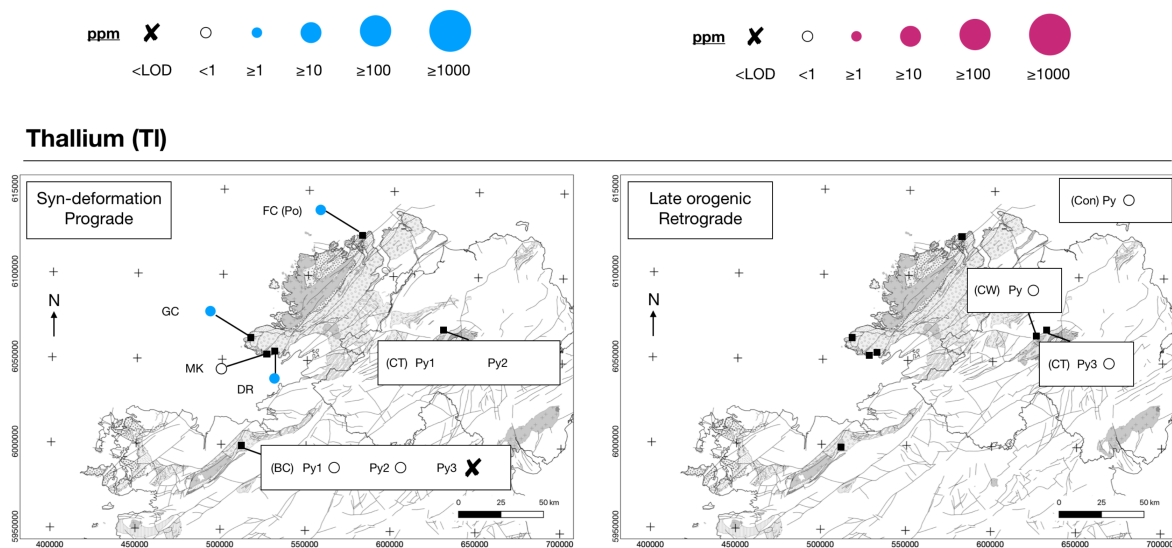


Proportional circle map for Sn median in pyrite (ppm) for 98 LA ICP-MS analyses reporting > limit of detection (n=520).

Identified pyrite phase (and chapter reference) (VG = visible Au, LT = lattice-bound Au)	Spearman rank correlation ($\rho \geq +0.5$)	Spearman rank correlation with Au ($\rho \geq +0.5$)	Sn ppm (median)	% +/-	n > LOD
● Cononish Py-Ore (C.8) VG	Mn, Hg, Ag, Te, Pb, Cu, Sb, Ga, Tl	X	6.15	+116	6
● Curraghinalt Py ₁ (C.5)	Ga, Ag, Hg, Mn	X	3.92	+37.4	32
● Cavanacaw Py-Ore (C.8) VG	Co, Cu, As, Sb, Au, Hg, Pb	✓	3.60	+26.3	3
● SL - Glencolumbkille (C.7)	Ga, Mo, Hg	X	3.60	+26.3	17
Median, all data			2.85	-	98
● SL - Derrylahan (C.7)	Ni	X	2.70	-5.26	4
● SL - Muckros (C.7)	Tl, Te, Ga, Mn, Se	X	2.50	-12.3	14
● Cloonacool Py ₂ (C.6) VG	n/a	n/a	1.09	-61.8	7
● Cloonacool Py ₁ (C.6)	Zn, Tl, Mn, W	X	0.46	-83.9	13
● Curraghinalt Py ₃ (C.5) VG	n/a	n/a	0.45	-84.2	2
● Curraghinalt Py ₂ (C.5) LT	n/a	n/a	n/a	n/a	0
● Cloonacool Py ₃ (C.6)	n/a	n/a	n/a	n/a	0

Summary for tested pyrite including relative abundances and correlative elements.

14.1.ix. Thallium (Tl)

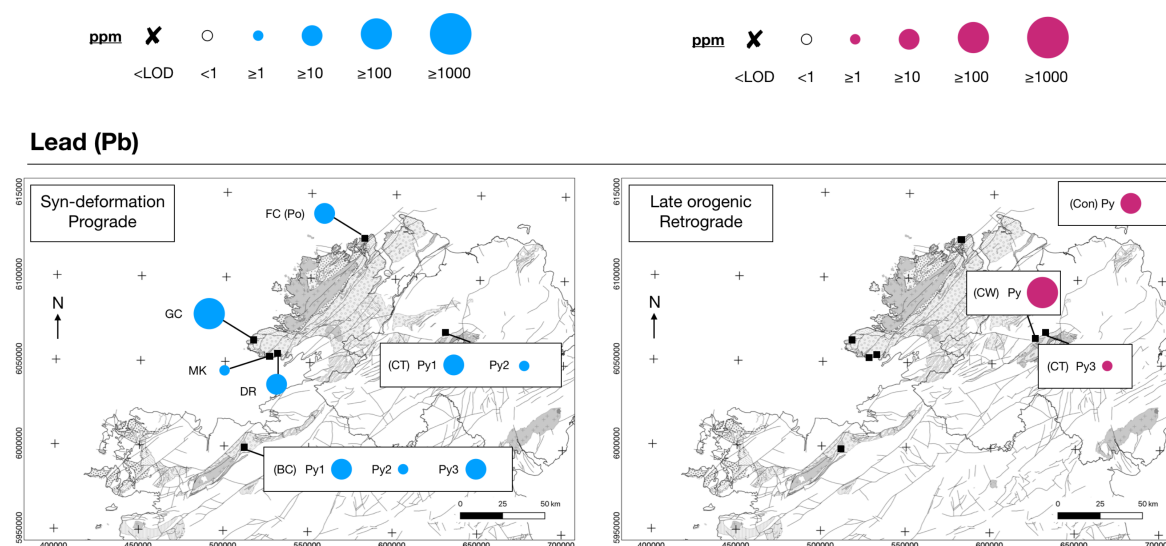


Proportional circle map for Tl median in pyrite (ppm) for 158 LA ICP-MS analyses reporting > limit of detection (n=520).

Identified pyrite phase (and chapter reference) (VG = visible Au, LT = lattice-bound Au)	Spearman rank correlation ($\rho \geq +0.5$)	Spearman rank correlation with Au ($\rho \geq +0.5$)	Tl ppm (median)	% +/-	n > LOD
● SL - Glencolumbkille (C.7)	Co, Pb, Cu, Zn	X	3.55	+617	36
● SL - Derrylahan (C.7)	W, Au, Hg	✓	1.10	+122	39
Median, all data			0.50	-	158
● Cononish Py-Ore (C.8) VG	Hg, Cu, Se, Pb, Sn, W	X	0.37	-26.3	20
● SL - Muckros (C.7)	Sn, Pb, Ag, Bi, Sb	X	0.36	-27.3	13
● Cavanacaw Py-Ore (C.8) VG	W, Ni, Mo, Bi	X	0.24	-51.9	4
● Cloonacool Py ₁ (C.6)	Zn, Mn, Sn, Hg, Ga, Mo	X	0.07	-86.2	22
● Curraghinalt Py ₂ (C.5) LT	Au, Ga	✓	0.03	-93.2	4
● Cloonacool Py ₂ (C.6) VG	n/a	X	0.03	-94.1	2
● Curraghinalt Py ₃ (C.5) VG	Cu	X	0.02	-96.1	16
● Curraghinalt Py ₁ (C.5)	n/a	n/a	0.02	-96.4	2
● Cloonacool Py ₃ (C.6)	n/a	n/a	0.00	0.0	0

Summary for tested pyrite including relative abundances and correlative elements.

14.1.x. Lead (Pb)



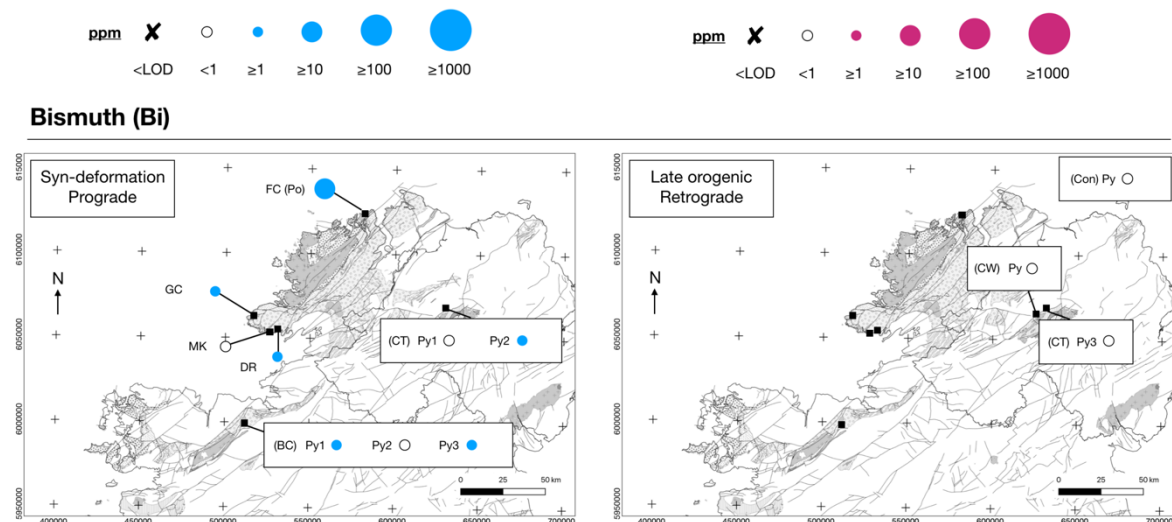
Proportional circle map for Pb median in pyrite (ppm) for 450 LA ICP-MS analyses reporting > limit of detection (n=520).

Identified pyrite phase (and chapter reference) (VG = visible Au, LT = lattice-bound Au)	Spearman rank correlation ($\rho \geq +0.5$)	Spearman rank correlation with Au ($\rho \geq +0.5$)	Pb ppm (median)	% +/-	n > LOD
● Cavanacaw Py-Ore (C.8) VG	Sb, Co, Ag, Cu, Mn, Sn	X	907	+5,622	6
● SL - Glencolumbkille (C.7)	Te, Tl, Ag, Co	X	306	+1,827	50
● SL - Derrylahan (C.7)	Sb	X	74.0	+367	49
● Cloonacool Py ₁ (C.6)	Sb, Bi, Ag, Te, Cu, Hg	X	26.4	+66.6	72
● Curraghinalt Py ₁ (C.5)	Sb, Au	✓	17.9	+12.9	35
● Cononish Py-Ore (C.8) VG	Sb, Zn, Hg, Cu, Sn, Bi, Ag, Mn, Au, Te, Tl	✓	17.2	+8.52	45
[Visible] : Median			15.9	-	450
● Cloonacool Py ₃ (C.6)	Co, Ni, Ag, Bi	X	12.6	-20.5	5
● Cloonacool Py ₂ (C.6) VG	n/a	X	8.60	-45.7	27
● SL - Muckros (C.7)	Cu, Tl, As, Bi, Ag, Au	✓	5.10	-67.8	42
● Curraghinalt Py ₂ (C.5) LT	W, Sb, Ag, Cu, Hg, Bi, Mn	X	4.85	-69.4	34
● Curraghinalt Py ₃ (C.5) VG	Bi, Mn, Ag, Sb, Cu, Se, As, Au	✓	1.10	-93.1	85

Summary for tested pyrite including relative abundances and correlative elements.

14.1.xi. Bismuth (Bi)

 **Critical Raw Material for the European Union** (European Commission, 2017)

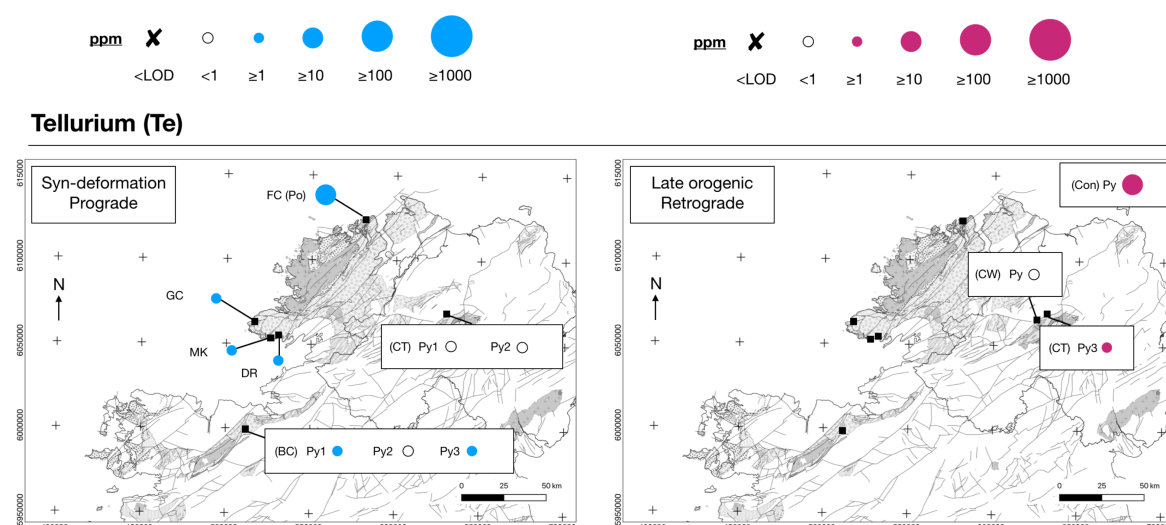


Proportional circle map for Bi median in pyrite (ppm) for 329 LA ICP-MS analyses reporting > limit of detection (n=520).

Identified pyrite phase (and chapter reference) (VG = visible Au, LT = lattice-bound Au)	Spearman rank correlation ($\rho \geq +0.5$)	Spearman rank correlation with Au ($\rho \geq +0.5$)	Bi ppm (median)	% +/-	n > LOD
● Cloonacool Py ₃ (C.6)	Co, Sb, Pb	✗	1.87	+111	5
● Cloonacool Py ₁ (C.6)	Te, Pb, Ag, Sb, Cu, Hg, Au	✓	1.32	+49.0	67
● SL - Glencolumbkille (C.7)	Cu	✗	1.29	+45.6	22
● Curraghinalt Py ₂ (C.5) LT	Mo, Hg, Cu, Ga, Pb	✗	1.22	+37.7	22
● SL - Derrylahan (C.7)	n/a	✗	1.16	+30.4	34
Median, all data			0.89	-	329
● Curraghinalt Py ₃ (C.5) VG	Pb, Se, Ag, Cu, Au, As, Sb	✓	0.86	-2.65	94
● SL - Muckros (C.7)	Au, Hg, As, Se, Pb, Cu, Te, Tl	✓	0.72	-19.3	26
● Cononish Py-Ore (C.8) VG	Mn, Pb	✗	0.63	-29.5	16
● Cloonacool Py ₂ (C.6) VG	Sb, Ni, Hg	✗	0.57	-35.7	24
● Cavanacaw Py-Ore (C.8) VG	W, Au, Hg, Tl	✓	0.13	-77.2	3
● Curraghinalt Py ₁ (C.5)	n/a	✗	0.04	-95.2	16

Summary for tested pyrite including relative abundances and correlative elements.

14.1.xii. Tellurium (Te)



Proportional circle map for Te median in pyrite (ppm) for 327 LA ICP-MS analyses reporting > limit of detection (n=520).

Identified pyrite phase (and chapter reference) (VG = visible Au, LT = lattice-bound Au)	Spearman rank correlation ($\rho \geq +0.5$)	Spearman rank correlation with Au ($\rho \geq +0.5$)	Te ppm (median)	% + / -	n > LOD
● Cononish Py-Ore (C.8) VG	Ag, Au, Zn, Sn, Sb, W, Cu, Pb, Mo	✓	55.0	+1,347	40
● SL - Muckros (C.7)	Sn, Mn, Se, Bi, Mo, Hg	✗	5.85	+53.9	16
● SL - Derrylahan (C.7)	n/a	✗	5.55	+46.1	14
● Curraghinalt Py ₃ (C.5) VG	Au	✓	5.21	+37.1	124
● SL - Glencolumbkille (C.7)	Pb	✗	4.60	+21.1	5
Median, all data			3.80	-	327
● Cloonacool Py ₁ (C.6)	Bi, Ag, Pb, Au, Sb, Cu, As, Hg	✓	1.75	-53.9	65
● Cloonacool Py ₃ (C.6)	Hg, Cu, Au, As, Ag, Sb	✓	1.24	-67.4	5
● Cloonacool Py ₂ (C.6) VG	Au	✓	0.99	-74.1	24
● Curraghinalt Py ₂ (C.5) LT	n/a	✗	0.78	-79.5	15
● Curraghinalt Py ₁ (C.5)	n/a	✗	0.41	-89.2	15
● Cavanacaw Py-Ore (C.8) VG	Cu, Ga, W, Ni	✗	0.24	-93.8	4

Summary for tested pyrite including relative abundances and correlative elements.

Appendix 3: LA ICP-MS spot analyses

Number	Phase tested	Mineral	Code	Mn (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Ga (ppm)	As (ppm)	Se (ppm)	Mo (ppm)	Ag (ppm)	Sn (ppm)	Sb (ppm)	Te (ppm)	W (ppm)	Au (ppm)	Hg (ppm)	Tl (ppm)	Pb (ppm)	Bi (ppm)
1	Curraghinalt Py1	Pyrite	py1_1	12.4	196	1930	64.5	6120	1.06	< LOD	< LOD	< LOD	7.25	20.4	1.92	0.32	< LOD	0.258	2.22	< LOD	39.8	0.037
2	Curraghinalt Py1	Pyrite	py1_2	11.9	79	1850	57.9	5440	1.29	< LOD	< LOD	< LOD	7.7	39.5	0.55	0.54	< LOD	0.217	2.09	< LOD	19.7	< LOD
3	Curraghinalt Py1	Pyrite	py1_3	9.3	97.5	2500	42.7	4640	1.02	< LOD	< LOD	< LOD	6.84	9.8	0.7	< LOD	0.042	0.219	1.94	< LOD	20.4	0.034
4	Curraghinalt Py1	Pyrite	py1_4	7.8	121.5	4270	36.4	4030	1.25	< LOD	< LOD	< LOD	5.99	14.4	0.75	0.34	< LOD	0.214	1.36	< LOD	20.6	0.033
5	Curraghinalt Py1	Pyrite	py1_5	5.7	70.7	2410	64	4770	1.34	< LOD	< LOD	< LOD	6.65	50	0.3	0.42	< LOD	0.119	1.85	< LOD	11.7	< LOD
6	Curraghinalt Py1	Pyrite	py1_6	4.1	96.8	1910	40.9	4170	1.04	< LOD	< LOD	< LOD	7.02	16.2	< LOD	0.27	< LOD	0.152	1.47	< LOD	6.56	< LOD
7	Curraghinalt Py1	Pyrite	py1_7	5.2	63	2260	51.6	4820	0.96	< LOD	< LOD	0.075	7.21	19.9	0.48	< LOD	< LOD	0.197	1.99	< LOD	13.6	< LOD
8	Curraghinalt Py1	Pyrite	py1_8	4.8	106	4670	29.1	3780	1.22	< LOD	< LOD	< LOD	4.96	1.79	0.85	< LOD	< LOD	0.221	1.42	< LOD	21.5	0.055
9	Curraghinalt Py1	Pyrite	py1_9	3.7	54.4	3190	68	3400	0.69	< LOD	< LOD	< LOD	1.74	1.08	0.23	0.37	< LOD	0.055	1.42	< LOD	3.15	< LOD
10	Curraghinalt Py1	Pyrite	py1_10	12.5	37.3	2410	347	21700	2.56	< LOD	< LOD	< LOD	13.8	199	0.47	0.53	< LOD	0.146	3.95	< LOD	10	< LOD
11	Curraghinalt Py1	Pyrite	py1_11	3.1	236	4130	21.9	3960	1.24	< LOD	< LOD	< LOD	4.48	4.11	0.55	0.58	< LOD	0.177	1.2	< LOD	15.7	< LOD
12	Curraghinalt Py1	Pyrite	py1_12	9.5	71.4	3700	135	13000	1.06	26	< LOD	< LOD	5.8	8.5	0.29	< LOD	< LOD	0.223	2.47	< LOD	11.9	< LOD
13	Curraghinalt Py1	Pyrite	py1_13	13.8	48.2	1460	280	18000	1.34	< LOD	< LOD	0.13	16	29	< LOD	0.41	< LOD	0.145	3.19	< LOD	13.7	< LOD
14	Curraghinalt Py1	Pyrite	py1_14	12.8	66.2	3640	36.1	18400	1.36	< LOD	< LOD	< LOD	8.4	11.5	0.34	< LOD	< LOD	0.26	3.08	< LOD	14.3	< LOD
15	Curraghinalt Py1	Pyrite	py1_15	7.8	106.7	1850	44.8	7700	1.22	< LOD	< LOD	0.04	6.47	3.72	< LOD	< LOD	< LOD	0.119	1.49	< LOD	5	< LOD
16	Curraghinalt Py1	Pyrite	py1_16	8.4	81.7	1576	111	12900	0.91	< LOD	< LOD	< LOD	4.37	3.54	0.66	0.42	< LOD	0.152	2.04	< LOD	15.3	< LOD
17	Curraghinalt Py1	Pyrite	py1_17	10.3	39	3660	172	14900	1.15	< LOD	< LOD	< LOD	9.4	20.5	0.31	0.53	< LOD	0.209	2.48	< LOD	18.5	< LOD
18	Curraghinalt Py1	Pyrite	py1_18	7.1	66.8	1618	50	6290	1.16	< LOD	< LOD	< LOD	8.09	8.8	< LOD	< LOD	< LOD	0.113	1.52	< LOD	3.3	< LOD
19	Curraghinalt Py1	Pyrite	py1_19	39	99.2	1589	48	13900	1.54	3.7	< LOD	< LOD	2.29	12	0.82	0.27	< LOD	0.078	2.61	< LOD	14.5	1.45
20	Curraghinalt Py1	Pyrite	py1_20	10.6	119.8	2060	33.6	5740	0.892	< LOD	46	< LOD	5.87	4.48	0.376	8.4	< LOD	0.173	11.7	< LOD	15.6	0.16
21	Curraghinalt Py1	Pyrite	py1_21	9	391	1397	9.2	7400	0.86	< LOD	< LOD	< LOD	1.24	< LOD	1.92	< LOD	< LOD	0.072	2.26	< LOD	12	0.037
22	Curraghinalt Py1	Pyrite	py1_22	5.8	403	3440	10.8	3900	0.64	33.2	< LOD	< LOD	1.3	< LOD	1.97	< LOD	< LOD	0.158	1.88	0.02	25.7	0.026
23	Curraghinalt Py1	Pyrite	py1_23	5.5	225	1617	12.3	4540	0.65	3.2	< LOD	< LOD	1.07	< LOD	1.99	< LOD	< LOD	0.048	1.4	0.016	11.8	< LOD
24	Curraghinalt Py1	Pyrite	py1_24	4.8	420	2910	13.3	1110	0.37	< LOD	< LOD	< LOD	0.78	0.186	< LOD	< LOD	< LOD	0.06	1.2	< LOD	3.31	< LOD
25	Curraghinalt Py1	Pyrite	py1_25	5	84.1	1710	160	4860	0.61	18.2	< LOD	< LOD	4.7	0.98	1.96	0.27	< LOD	0.14	1.18	< LOD	23	0.043
26	Curraghinalt Py1	Pyrite	py1_26	5.3	60.7	2320	370	6400	0.83	6.3	< LOD	< LOD	4.31	0.76	1.22	0.32	< LOD	0.135	1.48	< LOD	82	0.022
27	Curraghinalt Py1	Pyrite	py1_27	4.9	46.5	3340	188	5260	0.75	29.5	< LOD	< LOD	4.63	2.13	3.92	< LOD	< LOD	0.416	2.02	< LOD	44.9	0.096
28	Curraghinalt Py1	Pyrite	py1_28	4.3	69.6	2850	65	2560	0.387	8.3	< LOD	< LOD	2.34	1.62	5.43	< LOD	< LOD	0.192	0.92	< LOD	46.1	0.073
29	Curraghinalt Py1	Pyrite	py1_29	6.6	112.1	3150	42	4000	0.89	3.8	< LOD	< LOD	2.31	1.89	4.31	< LOD	< LOD	0.188	1.22	< LOD	29.4	0.035
30	Curraghinalt Py1	Pyrite	py1_30	4	127.9	3420	11.8	3860	0.66	490	< LOD	< LOD	2.25	0.31	2.05	< LOD	< LOD	0.25	1	< LOD	17.9	< LOD
31	Curraghinalt Py1	Pyrite	py1_31	4.4	274	2032	460	6000	0.8	15.6	< LOD	< LOD	6.7	0.47	5.3	< LOD	< LOD	0.24	1.79	< LOD	150	0.053
32	Curraghinalt Py1	Pyrite	py1_32	7.5	92.2	1985	29	5340	0.71	3.1	< LOD	< LOD	3.47	0.229	6.46	< LOD	< LOD	0.221	1.37	< LOD	41	0.055
33	Curraghinalt Py1	Pyrite	py1_33	4.7	100	2240	61	3510	0.51	11.9	< LOD	< LOD	2.19	0.25	4.7	< LOD	< LOD	0.236	0.76	< LOD	32.2	< LOD
34	Curraghinalt Py1	Pyrite	py1_34	6.3	14.6	4610	95	4610	0.79	59	< LOD	< LOD	7.03	2.4	3.03	< LOD	< LOD	0.362	1.64	< LOD	37.7	0.043
35	Curraghinalt Py1	Pyrite	py1_35	7.6	15.9	2700	49.6	5030	0.64	27.7	45	< LOD	5.12	1	1.42	< LOD	< LOD	0.307	1.73	< LOD	20.4	< LOD
36	Curraghinalt Py2	Pyrite	py2_1	5.3	328	384	0.8	< LOD	< LOD	6970	< LOD	< LOD	0.083	< LOD	< LOD	1.54	< LOD	0.306	0.53	< LOD	0.99	0.0165
37	Curraghinalt Py2	Pyrite	py2_2	6.9	284	611	0.38	< LOD	< LOD	10280	< LOD	< LOD	< LOD	< LOD	< LOD	2.44	< LOD	0.74	0.94	< LOD	< LOD	< LOD
38	Curraghinalt Py2	Pyrite	py2_3	3.9	10.6	25.3	0.96	< LOD	< LOD	14310	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	5.23	0.43	< LOD	0.253	< LOD
39	Curraghinalt Py2	Pyrite	py2_4	34200	48.1	133	9.5	60	< LOD	10100	< LOD	0.28	0.32	< LOD	< LOD	< LOD	0.25	2.15	2.1	< LOD	14.6	2.27
40	Curraghinalt Py2	Pyrite	py2_5	1290	7.1	15	1.05	< LOD	< LOD	16460	< LOD	< LOD	0.073	< LOD	< LOD	< LOD	0.094	4.9	0.81	< LOD	2.27	< LOD
41	Curraghinalt Py2	Pyrite	py2_6	166	26.4	18.2	2.47	< LOD	< LOD	19210	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	9.47	0.83	< LOD	0.71	< LOD
42	Curraghinalt Py2	Pyrite	py2_7	8100	43.2	32.6	8.2	< LOD	0.185	14560	< LOD	< LOD	0.6	< LOD	< LOD	0.46	< LOD	3.6	5.6	< LOD	43.3	0.256
43	Curraghinalt Py2	Pyrite	py2_8	4.5	70	146	0.51	< LOD	0.134	7930	< LOD	< LOD	0.07	< LOD	< LOD	0.96	0.076	0.99	0.54	< LOD	2.31	< LOD
44	Curraghinalt Py2	Pyrite	py2_9	6400	22.4	40	5.03	12.6	0.088	13200	< LOD	< LOD	0.47	< LOD	0.48	< LOD	0.187	6.5	0.5	< LOD	15.6	< LOD
45	Curraghinalt Py2	Pyrite	py2_10	21.1	26.1	13.6	8.5	< LOD	< LOD	17620	< LOD	0.096	3.05	< LOD	0.78	6.5	< LOD	3.09	10.5	< LOD	30.1	2.92
46	Curraghinalt Py2	Pyrite	py2_11	< LOD	3.04	10.2	1.78	< LOD	0.052	17670	< LOD	0.072	0.24	< LOD	< LOD	0.6	< LOD	3.97	1.06	< LOD	4.5	0.036
47	Curraghinalt Py2	Pyrite	py2_12	< LOD	29.7	58	0.71	< LOD	0.076	14000	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	3.62	0.45	< LOD	0.55	< LOD
48	Curraghinalt Py2	Pyrite	py2_13	3.8	534	690	4.6	< LOD	0.068	17700	< LOD	< LOD	0.63	< LOD	< LOD	1.03	< LOD	4.02	0.99	< LOD	42	4.7
49	Curraghinalt Py2	Pyrite	py2_14	< LOD	< LOD	1.73	1.43	< LOD	< LOD	2310	< LOD	< LOD	0.102	< LOD	0.43	< LOD	< LOD	0.83	0.57	< LOD	5.2	< LOD
50	Curraghinalt Py2	Pyrite	py2_15	6.1	215	133	8.7	< LOD	< LOD	10600	< LOD	< LOD	0.18	< LOD	< LOD	< LOD	< LOD	2.79	1.12	< LOD	39	3.3

Number	Phase tested	Mineral	Code	Mn (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Ga (ppm)	As (ppm)	Se (ppm)	Mo (ppm)	Ag (ppm)	Sn (ppm)	Sb (ppm)	Te (ppm)	W (ppm)	Au (ppm)	Hg (ppm)	Tl (ppm)	Pb (ppm)	Bi (ppm)
51	Curraghinalt Py2	Pyrite	py2_16	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	2240	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.32	0.78	< LOD	0.045	< LOD
52	Curraghinalt Py2	Pyrite	py2_17	< LOD	9.4	9.2	3.1	< LOD	< LOD	12310	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	3.76	0.46	< LOD	1.53	0.76
53	Curraghinalt Py2	Pyrite	py2_18	< LOD	0.28	< LOD	0.48	< LOD	< LOD	1459	< LOD	< LOD	0.066	< LOD	< LOD	< LOD	< LOD	0.894	0.55	< LOD	0.78	< LOD
54	Curraghinalt Py2	Pyrite	py2_19	3.5	< LOD	< LOD	< LOD	< LOD	0.085	1161	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.065	< LOD	0.44	< LOD	0.29	< LOD
55	Curraghinalt Py2	Pyrite	py2_20	24.4	510	3.5	137	< LOD	< LOD	2850	58	< LOD	0.41	< LOD	0.72	1.19	< LOD	0.096	1.54	0.027	35	11.7
56	Curraghinalt Py2	Pyrite	py2_21	< LOD	1310	867	< LOD	< LOD	< LOD	39400	< LOD	< LOD	1.21	< LOD	< LOD	< LOD	< LOD	13.65	2.11	< LOD	8.5	1.38
57	Curraghinalt Py2	Pyrite	py2_22	< LOD	1155	454	7.4	< LOD	< LOD	40200	< LOD	0.087	0.155	< LOD	< LOD	< LOD	< LOD	29.8	0.66	< LOD	0.49	0.108
58	Curraghinalt Py2	Pyrite	py2_23	18	461	660	18.8	310	0.89	32400	< LOD	< LOD	1.33	< LOD	1.31	0.78	< LOD	12.92	1.78	< LOD	18.3	7.5
59	Curraghinalt Py2	Pyrite	py2_24	9.6	123	620	14.2	4.9	0.176	19900	< LOD	< LOD	0.77	< LOD	0.99	0.78	< LOD	5.8	2.86	0.032	24.3	12
60	Curraghinalt Py2	Pyrite	py2_25	4.4	750	119	8.6	< LOD	< LOD	37200	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	39.1	0.89	< LOD	2.3	0.022
61	Curraghinalt Py2	Pyrite	py2_26	590	34.9	235	11.7	18.8	0.4	20800	< LOD	< LOD	0.318	< LOD	0.72	0.45	< LOD	12.1	1.24	0.044	12.2	21.7
62	Curraghinalt Py2	Pyrite	py2_27	5	226	1240	0.81	< LOD	< LOD	20200	< LOD	0.11	0.051	< LOD	< LOD	< LOD	< LOD	3.44	0.77	< LOD	0.36	0.19
63	Curraghinalt Py2	Pyrite	py2_28	4.8	90	1170	8.3	< LOD	0.116	20360	< LOD	< LOD	0.32	< LOD	< LOD	< LOD	< LOD	3.57	1.5	0.035	9.2	9.1
64	Curraghinalt Py2	Pyrite	py2_29	5.1	119	980	0.58	< LOD	< LOD	21380	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	3.95	0.82	< LOD	1.42	< LOD
65	Curraghinalt Py2	Pyrite	py2_30	13600	211	920	580	290	< LOD	6060	< LOD	0.12	3.2	< LOD	8.7	0.6	0.29	1.61	2.8	< LOD	3700	2.58
66	Curraghinalt Py2	Pyrite	py2_31	< LOD	820	1210	650	< LOD	< LOD	28700	< LOD	< LOD	2.4	< LOD	0.5	0.38	< LOD	12.1	1.03	< LOD	15.3	1.06
67	Curraghinalt Py2	Pyrite	py2_32	910	9.7	22.1	43	39	0.145	8520	< LOD	< LOD	1.17	< LOD	1.8	0.58	1.55	2.43	0.74	< LOD	220	0.158
68	Curraghinalt Py2	Pyrite	py2_33	4880	30.9	343	1.39	< LOD	< LOD	14680	< LOD	< LOD	0.167	< LOD	0.46	< LOD	< LOD	3.17	0.68	< LOD	4	< LOD
69	Curraghinalt Py2	Pyrite	py2_34	5.3	1686	807	8.01	< LOD	< LOD	38300	< LOD	< LOD	0.76	< LOD	< LOD	< LOD	< LOD	28.2	1.15	< LOD	6.6	0.88
70	Curraghinalt Py2	Pyrite	py2_35	5.9	1600	811	4.82	< LOD	< LOD	42700	< LOD	< LOD	0.43	< LOD	< LOD	0.46	< LOD	17.67	1.4	< LOD	3.03	0.5
71	Curraghinalt Py3	Pyrite	Spot1	< LOD	5.39	24.8	< LOD	< LOD	0.051	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	6.2	< LOD	< LOD	0.317	< LOD	< LOD	< LOD
72	Curraghinalt Py3	Pyrite	Spot2	< LOD	2.54	5.6	1	< LOD	0.034	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.5	< LOD	< LOD	0.307	< LOD	< LOD	< LOD
73	Curraghinalt Py3	Pyrite	Spot3	< LOD	6.49	94.5	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	3.19	< LOD	0.078	0.317	< LOD	< LOD	< LOD
74	Curraghinalt Py3	Pyrite	Spot4	< LOD	441	51.3	1.2	< LOD	< LOD	23.7	< LOD	< LOD	59.9	< LOD	0.734	232	< LOD	3.9	0.599	< LOD	9	109
75	Curraghinalt Py3	Pyrite	Spot5	< LOD	113	10.4	< LOD	< LOD	< LOD	3.05	< LOD	< LOD	< LOD	< LOD	< LOD	8.3	< LOD	< LOD	0.261	< LOD	< LOD	< LOD
76	Curraghinalt Py3	Pyrite	Spot6	3.8	140	7.93	< LOD	< LOD	< LOD	3.71	< LOD	< LOD	< LOD	< LOD	< LOD	1.02	< LOD	< LOD	0.268	< LOD	< LOD	< LOD
77	Curraghinalt Py3	Pyrite	Spot7	2.69	29.5	241	< LOD	< LOD	< LOD	3.63	< LOD	< LOD	< LOD	< LOD	< LOD	12.79	< LOD	< LOD	0.315	< LOD	< LOD	< LOD
78	Curraghinalt Py3	Pyrite	Spot8	2.61	203	3080	< LOD	< LOD	< LOD	6.62	< LOD	< LOD	< LOD	< LOD	< LOD	3.18	< LOD	< LOD	0.299	< LOD	0.094	0.113
79	Curraghinalt Py3	Pyrite	Spot9	< LOD	493	3610	< LOD	< LOD	< LOD	15.58	< LOD	< LOD	< LOD	< LOD	< LOD	1.51	< LOD	< LOD	0.236	< LOD	< LOD	< LOD
80	Curraghinalt Py3	Pyrite	Spot10	< LOD	< LOD	1106	< LOD	< LOD	< LOD	0.73	< LOD	< LOD	< LOD	< LOD	< LOD	0.3	< LOD	< LOD	0.54	< LOD	< LOD	0.0136
81	Curraghinalt Py3	Pyrite	Spot11	< LOD	82	1820	14.9	< LOD	0.024	1.61	< LOD	< LOD	0.36	< LOD	< LOD	10.6	< LOD	0.63	0.285	< LOD	0.421	3.8
82	Curraghinalt Py3	Pyrite	Spot12	< LOD	80.5	1408	< LOD	< LOD	< LOD	1.07	< LOD	< LOD	< LOD	< LOD	< LOD	0.37	< LOD	< LOD	0.426	< LOD	< LOD	0.0187
83	Curraghinalt Py3	Pyrite	Spot13	< LOD	173	20.6	139	< LOD	< LOD	1.82	< LOD	< LOD	0.4	< LOD	< LOD	35.5	< LOD	1.48	0.53	< LOD	0.63	18.5
84	Curraghinalt Py3	Pyrite	Spot14	< LOD	67	2060	< LOD	< LOD	< LOD	3.63	< LOD	< LOD	< LOD	< LOD	< LOD	1.33	< LOD	< LOD	0.362	< LOD	< LOD	< LOD
85	Curraghinalt Py3	Pyrite	Spot15	< LOD	< LOD	593	< LOD	< LOD	0.129	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.93	< LOD	0.023	0.295	< LOD	0.079	0.258
86	Curraghinalt Py3	Pyrite	Spot16	< LOD	20.1	183	< LOD	< LOD	< LOD	2.85	< LOD	< LOD	< LOD	< LOD	< LOD	8.87	< LOD	< LOD	0.283	< LOD	< LOD	0.0202
87	Curraghinalt Py3	Pyrite	Spot17	< LOD	74.9	89.4	< LOD	< LOD	< LOD	3.69	< LOD	< LOD	< LOD	< LOD	< LOD	21.7	< LOD	< LOD	0.5	< LOD	< LOD	0.03
88	Curraghinalt Py3	Pyrite	Spot18	< LOD	3.46	74	< LOD	< LOD	0.021	4.8	< LOD	< LOD	< LOD	< LOD	< LOD	0.71	< LOD	< LOD	0.331	< LOD	0.021	0.0149
89	Curraghinalt Py3	Pyrite	Spot19	< LOD	20.2	1100	< LOD	< LOD	0.037	6.08	< LOD	< LOD	< LOD	< LOD	< LOD	1.23	< LOD	< LOD	0.338	< LOD	< LOD	< LOD
90	Curraghinalt Py3	Pyrite	Spot20	< LOD	1.16	10.42	< LOD	< LOD	0.028	4.16	< LOD	< LOD	< LOD	< LOD	< LOD	40.2	< LOD	< LOD	0.496	< LOD	< LOD	< LOD
91	Curraghinalt Py3	Pyrite	Spot21	< LOD	33.7	46.5	1.9	< LOD	< LOD	4.39	< LOD	< LOD	< LOD	< LOD	< LOD	4.9	< LOD	< LOD	0.458	< LOD	0.026	< LOD
92	Curraghinalt Py3	Pyrite	Spot22	2.3	72.3	71.9	< LOD	< LOD	< LOD	2	< LOD	< LOD	< LOD	< LOD	< LOD	8.9	< LOD	< LOD	0.46	< LOD	< LOD	< LOD
93	Curraghinalt Py3	Pyrite	Spot23	< LOD	17.4	78.6	0.57	< LOD	0.043	5.16	< LOD	< LOD	< LOD	< LOD	< LOD	3.8	< LOD	< LOD	0.53	0.0081	< LOD	0.0194
94	Curraghinalt Py3	Pyrite	Spot24	< LOD	340	174	< LOD	< LOD	< LOD	4.15	< LOD	< LOD	< LOD	< LOD	< LOD	21.5	< LOD	< LOD	0.73	< LOD	< LOD	< LOD
95	Curraghinalt Py3	Pyrite	Spot25	< LOD	88	454	3.11	< LOD	0.101	3.25	< LOD	< LOD	0.26	< LOD	< LOD	280	< LOD	0.31	0.68	< LOD	1.1	280
96	Curraghinalt Py3	Pyrite	Spot26	< LOD	275	52	< LOD	< LOD	< LOD	3.81	< LOD	< LOD	< LOD	< LOD	< LOD	16.7	< LOD	< LOD	0.64	< LOD	0.034	< LOD
97	Curraghinalt Py3	Pyrite	Spot27	< LOD	414	19	0.51	< LOD	< LOD	4.83	< LOD	< LOD	< LOD	< LOD	< LOD	19.2	< LOD	< LOD	0.53	0.009	< LOD	< LOD
98	Curraghinalt Py3	Pyrite	Spot28	< LOD	6.2	< LOD	< LOD	< LOD	0.057	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.44	< LOD	0.033	0.02
99	Curraghinalt Py3	Pyrite	Spot29	< LOD	41	6.8	< LOD	< LOD	0.024	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.13	< LOD	< LOD	0.43	< LOD	0.032	0.057
100	Curraghinalt Py3	Pyrite	Spot30	2.5	3.49	9.2	< LOD	< LOD	< LOD	3.87	< LOD	< LOD	< LOD	< LOD	< LOD	8.6	< LOD	< LOD	0.43	< LOD	< LOD	< LOD

Number	Phase tested	Mineral	Code	Mn (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Ga (ppm)	As (ppm)	Se (ppm)	Mo (ppm)	Ag (ppm)	Sn (ppm)	Sb (ppm)	Te (ppm)	W (ppm)	Au (ppm)	Hg (ppm)	Tl (ppm)	Pb (ppm)	Bi (ppm)
101	Curraghinalt Py3	Pyrite	Spot31	< LOD	399	301	0.57	< LOD	< LOD	2.31	< LOD	< LOD	< LOD	< LOD	< LOD	1.37	< LOD	0.035	0.5	< LOD	< LOD	0.046
102	Curraghinalt Py3	Pyrite	Spot32	< LOD	109	2.69	< LOD	< LOD	0.029	3.31	< LOD	< LOD	< LOD	< LOD	< LOD	1.74	< LOD	< LOD	0.6	< LOD	< LOD	0.063
103	Curraghinalt Py3	Pyrite	Spot33	2.9	38.5	1134	3.13	< LOD	< LOD	94	< LOD	< LOD	19.7	< LOD	0.747	164	< LOD	2.41	1.11	0.0198	13.3	261
104	Curraghinalt Py3	Pyrite	Spot34	< LOD	212	1024	< LOD	< LOD	0.025	4.17	< LOD	< LOD	< LOD	< LOD	< LOD	12.1	< LOD	< LOD	0.392	< LOD	< LOD	< LOD
105	Curraghinalt Py3	Pyrite	Spot35	< LOD	46.1	3600	4.9	< LOD	< LOD	44.3	< LOD	< LOD	24.1	< LOD	0.524	50.8	< LOD	3.27	0.62	< LOD	6.14	34.4
106	Curraghinalt Py3	Pyrite	Spot36	< LOD	21.2	5310	2.8	< LOD	< LOD	8.07	< LOD	< LOD	0.125	< LOD	< LOD	3.24	< LOD	0.51	0.377	< LOD	0.334	2.44
107	Curraghinalt Py3	Pyrite	Spot37	< LOD	< LOD	1290	0.96	< LOD	0.043	0.96	< LOD	< LOD	0.12	< LOD	< LOD	2.36	< LOD	0.31	0.341	< LOD	0.113	1.3
108	Curraghinalt Py3	Pyrite	Spot 1	< LOD	180	140	0.74	< LOD	< LOD	1.54	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.29	< LOD	1.84	0.3
109	Curraghinalt Py3	Pyrite	Spot 2	< LOD	470	278	4.81	< LOD	< LOD	10.7	< LOD	< LOD	2.14	< LOD	0.446	6.37	< LOD	0.43	0.58	0.0141	4.38	3.64
110	Curraghinalt Py3	Pyrite	Spot 3	< LOD	182	155	0.59	< LOD	< LOD	2	< LOD	< LOD	< LOD	< LOD	< LOD	0.188	< LOD	< LOD	0.3	< LOD	< LOD	< LOD
111	Curraghinalt Py3	Pyrite	Spot 4	17400	97	194	8.8	287	0.83	35.2	< LOD	< LOD	7.6	< LOD	1.52	20.2	< LOD	1.15	10.8	< LOD	59.6	20.3
112	Curraghinalt Py3	Pyrite	Spot 5	< LOD	841	297	2.16	< LOD	0.028	7.3	< LOD	< LOD	2.27	< LOD	0.311	4.9	< LOD	0.53	0.44	< LOD	10.9	5.3
113	Curraghinalt Py3	Pyrite	Spot 6	3.1	322	184	2.3	< LOD	0.032	5.5	< LOD	< LOD	0.95	< LOD	0.203	2.53	< LOD	0.15	0.43	< LOD	< LOD	2.41
114	Curraghinalt Py3	Pyrite	Spot 7	< LOD	141	138	< LOD	< LOD	< LOD	1.39	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.343	< LOD	0.023	0.019
115	Curraghinalt Py3	Pyrite	Spot 8	< LOD	55.1	151	1.43	< LOD	< LOD	4.2	< LOD	< LOD	0.2	< LOD	< LOD	7	< LOD	0.03	0.433	< LOD	1.48	0.76
116	Curraghinalt Py3	Pyrite	Spot 9	< LOD	402	1117	< LOD	< LOD	0.036	3.3	< LOD	< LOD	0.9	< LOD	3.8	9.5	< LOD	3.4	0.314	< LOD	8.9	1.55
117	Curraghinalt Py3	Pyrite	Spot 10	< LOD	273	329	1.85	< LOD	< LOD	4.99	< LOD	< LOD	0.38	< LOD	< LOD	1.41	< LOD	0.112	0.359	< LOD	1.77	1.07
118	Curraghinalt Py3	Pyrite	Spot 11	< LOD	108	254	6.47	< LOD	0.031	13.9	< LOD	< LOD	1.38	< LOD	0.86	4.37	< LOD	0.318	0.58	0.056	17	10.5
119	Curraghinalt Py3	Pyrite	Spot 12	< LOD	313	364	1.96	< LOD	< LOD	4.69	< LOD	< LOD	0.54	< LOD	0.35	8.4	0.026	0.09	0.39	0.052	8.1	2.48
120	Curraghinalt Py3	Pyrite	Spot 13	< LOD	118	340	< LOD	< LOD	< LOD	1.07	< LOD	< LOD	< LOD	< LOD	< LOD	0.211	0.0144	< LOD	0.417	< LOD	< LOD	< LOD
121	Curraghinalt Py3	Pyrite	Spot 14	< LOD	315	2460	< LOD	< LOD	0.052	3	< LOD	< LOD	< LOD	< LOD	< LOD	7.13	< LOD	< LOD	0.38	< LOD	< LOD	< LOD
122	Curraghinalt Py3	Pyrite	Spot 15	< LOD	278	583	< LOD	< LOD	< LOD	2.28	< LOD	< LOD	< LOD	< LOD	< LOD	0.25	< LOD	< LOD	0.343	< LOD	< LOD	< LOD
123	Curraghinalt Py3	Pyrite	Spot 16	< LOD	16.5	128	2.6	< LOD	< LOD	8.1	< LOD	< LOD	2.36	< LOD	0.442	4.81	< LOD	0.508	0.53	0.0128	12.5	5.55
124	Curraghinalt Py3	Pyrite	Spot 17	< LOD	68.7	482	2.43	< LOD	< LOD	6.36	< LOD	< LOD	3	< LOD	0.293	8.8	< LOD	0.538	0.349	< LOD	36	9.7
125	Curraghinalt Py3	Pyrite	Spot 18	< LOD	269	123	1.01	< LOD	< LOD	0.89	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.042	0.47	< LOD	0.116	0.062
126	Curraghinalt Py3	Pyrite	Spot 19	< LOD	28.4	173	1.78	< LOD	< LOD	5.23	< LOD	< LOD	0.81	< LOD	0.197	7.81	< LOD	0.225	0.5	< LOD	4.17	2.5
127	Curraghinalt Py3	Pyrite	Spot 20	< LOD	40	78	3.73	< LOD	< LOD	10.2	< LOD	< LOD	1.4	< LOD	0.37	3.72	< LOD	0.307	1.52	0.0232	8.13	3.95
128	Curraghinalt Py3	Pyrite	Spot 21	< LOD	161	111.4	< LOD	< LOD	< LOD	0.78	< LOD	< LOD	< LOD	< LOD	< LOD	0.69	< LOD	< LOD	0.27	< LOD	< LOD	< LOD
129	Curraghinalt Py3	Pyrite	Spot 22	< LOD	156	14.2	< LOD	< LOD	< LOD	10.8	< LOD	< LOD	4.36	< LOD	0.86	9.02	< LOD	0.74	0.91	0.0193	20.5	8.2
130	Curraghinalt Py3	Pyrite	Spot 23	< LOD	101	76.1	0.65	< LOD	< LOD	0.72	< LOD	< LOD	0.066	< LOD	< LOD	1.12	< LOD	< LOD	0.28	< LOD	0.44	0.17
131	Curraghinalt Py3	Pyrite	Spot 24	< LOD	760	211	< LOD	< LOD	< LOD	12.5	< LOD	< LOD	1.46	< LOD	0.88	3.64	< LOD	0.339	0.88	0.0303	19.8	6.4
132	Curraghinalt Py3	Pyrite	Spot 25	< LOD	300	175	< LOD	< LOD	< LOD	2.53	< LOD	< LOD	< LOD	< LOD	< LOD	35.1	< LOD	< LOD	0.58	< LOD	0.155	< LOD
133	Curraghinalt Py3	Pyrite	Spot 26	< LOD	104	198	1.56	< LOD	< LOD	2.13	< LOD	< LOD	< LOD	< LOD	< LOD	0.35	< LOD	< LOD	0.52	< LOD	0.26	0.122
134	Curraghinalt Py3	Pyrite	Spot 27	< LOD	170	69	15.3	< LOD	< LOD	12.1	< LOD	0.062	6.6	< LOD	2.13	7.4	< LOD	1.01	1.17	0.026	25.5	9
135	Curraghinalt Py3	Pyrite	Spot 28	< LOD	65	44.5	2.5	< LOD	< LOD	2.71	< LOD	< LOD	0.67	< LOD	0.55	0.76	< LOD	0.089	0.56	< LOD	16	3.6
136	Curraghinalt Py3	Pyrite	Spot 29	< LOD	15.4	8.43	4.8	< LOD	< LOD	6.38	< LOD	0.058	0.489	< LOD	< LOD	2.54	< LOD	0.065	0.69	< LOD	1.17	2.46
137	Curraghinalt Py3	Pyrite	Spot 30	< LOD	880	242	< LOD	< LOD	< LOD	1.84	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.39	< LOD	< LOD	< LOD
138	Curraghinalt Py3	Pyrite	Spot 31	< LOD	710	188	1.6	< LOD	< LOD	5.68	< LOD	< LOD	0.081	< LOD	< LOD	1.17	< LOD	< LOD	0.58	< LOD	1.12	1.23
139	Curraghinalt Py3	Pyrite	Spot 32	< LOD	81	158.1	< LOD	< LOD	< LOD	2.68	< LOD	< LOD	< LOD	< LOD	< LOD	28.7	< LOD	< LOD	0.34	< LOD	< LOD	0.053
140	Curraghinalt Py3	Pyrite	Spot 33	3.6	162	188	< LOD	< LOD	< LOD	7.9	< LOD	0.147	0.88	< LOD	0.32	2.43	< LOD	0.141	0.45	< LOD	3.1	3.4
141	Curraghinalt Py3	Pyrite	Spot 34	1430	566	193	22.2	8.7	< LOD	51	< LOD	1.67	1.96	< LOD	1.84	10.4	< LOD	0.81	2.1	0.016	23.5	21.1
142	Curraghinalt Py3	Pyrite	Spot 35	< LOD	62	109	0.58	< LOD	< LOD	4.38	< LOD	< LOD	1.13	< LOD	< LOD	8.2	< LOD	1.2	< LOD	< LOD	0.63	0.58
143	Curraghinalt Py3	Pyrite	Spot 36	< LOD	295	447	< LOD	< LOD	< LOD	1.81	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.33	< LOD	0.017	< LOD
144	Curraghinalt Py3	Pyrite	Spot 37	5.3	72	178	< LOD	< LOD	< LOD	1.22	< LOD	< LOD	< LOD	< LOD	< LOD	0.7	< LOD	< LOD	0.46	< LOD	0.28	0.22
145	Curraghinalt Py3	Pyrite	Spot 38	< LOD	3.69	13.8	1.5	< LOD	0.027	1.08	< LOD	< LOD	0.175	< LOD	< LOD	0.53	< LOD	0.079	0.363	< LOD	1.37	0.89
146	Curraghinalt Py3	Pyrite	Spot 39	< LOD	1230	427	1.73	< LOD	< LOD	4.95	< LOD	0.22	0.045	< LOD	< LOD	1.66	< LOD	0.034	0.69	< LOD	0.94	1.07
147	Curraghinalt Py3	Pyrite	Spot 40	< LOD	810	341	0.55	< LOD	< LOD	4.42	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.33	< LOD	0.12	< LOD
148	Curraghinalt Py3	Pyrite	Spot 41	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
149	Curraghinalt Py3	Pyrite	Spot 42	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
150	Curraghinalt Py3	Pyrite	Spot 43	< LOD	257	132	3.2	< LOD	< LOD	2.48	< LOD	< LOD	< LOD	< LOD	< LOD	4.1	< LOD	0.39	< LOD	< LOD	1.34	3.19

Number	Phase tested	Mineral	Code	Mn (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Ga (ppm)	As (ppm)	Se (ppm)	Mo (ppm)	Ag (ppm)	Sn (ppm)	Sb (ppm)	Te (ppm)	W (ppm)	Au (ppm)	Hg (ppm)	Tl (ppm)	Pb (ppm)	Bi (ppm)
151	Curraghinalt Py3	Pyrite	Spot 44	4.8	12.2	5.49	3.6	1.17	< LOD	4.01	23.7	< LOD	0.89	< LOD	< LOD	5.13	< LOD	< LOD	3.28	< LOD	1.26	1.62
152	Curraghinalt Py3	Pyrite	Spot 45	144	18.1	7.8	6.1	< LOD	< LOD	5.82	101	< LOD	2.6	< LOD	0.47	7.5	< LOD	0.58	< LOD	< LOD	17	8.9
153	Curraghinalt Py3	Pyrite	Spot 46	< LOD	21.5	2.72	1.92	< LOD	< LOD	2.02	< LOD	< LOD	0.92	< LOD	< LOD	27	< LOD	0.28	39	< LOD	3	1.86
154	Curraghinalt Py3	Pyrite	Spot 47	5.4	18.8	48.9	1.8	2.2	< LOD	1.62	47	0.088	0.7	0.28	0.41	3.81	< LOD	1.5	1.9	< LOD	1.8	0.4
155	Curraghinalt Py3	Pyrite	Spot 48	< LOD	148	94.9	2.22	< LOD	< LOD	3.22	< LOD	< LOD	3.99	< LOD	0.74	10.9	< LOD	0.6	1	< LOD	49.7	17.3
156	Curraghinalt Py3	Pyrite	Spot 49	< LOD	284	152	2.82	2.3	0.056	1.63	< LOD	< LOD	0.116	< LOD	0.16	4.34	< LOD	0.039	1.22	< LOD	1.48	2.37
157	Curraghinalt Py3	Pyrite	Spot 50	1950	128	184	6.8	4.4	0.056	6.7	< LOD	0.59	0.33	< LOD	1.52	6.5	0.052	0.91	5	< LOD	27	3.56
158	Curraghinalt Py3	Pyrite	Spot 51	< LOD	220	387	< LOD	< LOD	< LOD	1.79	< LOD	0.042	0.14	< LOD	< LOD	< LOD	< LOD	0.116	0.67	< LOD	0.28	0.122
159	Curraghinalt Py3	Pyrite	Spot 52	< LOD	478	383	< LOD	< LOD	< LOD	3.87	< LOD	< LOD	0.049	< LOD	< LOD	4.05	< LOD	0.0153	< LOD	< LOD	< LOD	0.04
160	Curraghinalt Py3	Pyrite	Spot 53	< LOD	1290	341	0.64	< LOD	< LOD	10.84	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.3	0.0135	0.3	< LOD
161	Curraghinalt Py3	Pyrite	Spot 54	< LOD	162	74	1.4	23.3	< LOD	1.43	< LOD	1.01	0.053	< LOD	< LOD	1.25	0.052	0.025	< LOD	< LOD	0.106	0.103
162	Curraghinalt Py3	Pyrite	Spot 55	< LOD	20.5	119	4.4	89	< LOD	< LOD	< LOD	5.1	< LOD	0.62	< LOD	< LOD	< LOD	0.062	< LOD	< LOD	0.32	0.141
163	Curraghinalt Py3	Pyrite	Spot 56	< LOD	58.7	123	5.1	111	< LOD	< LOD	< LOD	6.4	< LOD	< LOD	< LOD	< LOD	0.38	0.121	< LOD	< LOD	0.63	0.097
164	Curraghinalt Py3	Pyrite	Spot 57	< LOD	89.9	43.2	0.62	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.38	< LOD	0.015	0.66	< LOD	0.033	0.0148
165	Curraghinalt Py3	Pyrite	Spot 58	< LOD	1510	321	2.59	< LOD	< LOD	5.48	< LOD	< LOD	2.23	< LOD	< LOD	2.31	< LOD	0.38	2.02	< LOD	1.6	2.32
166	Curraghinalt Py3	Pyrite	Spot 59	< LOD	685	472	0.58	< LOD	< LOD	4.78	< LOD	< LOD	0.081	< LOD	< LOD	6.9	< LOD	< LOD	0.38	< LOD	0.92	3.7
167	Curraghinalt Py3	Pyrite	Spot 60	54	950	763	2.7	< LOD	< LOD	9.24	< LOD	< LOD	0.48	< LOD	0.32	17.8	0.014	0.126	0.76	0.017	2.55	3.21
168	Curraghinalt Py3	Pyrite	Spot 1	< LOD	< LOD	501	< LOD	< LOD	< LOD	11.32	< LOD	< LOD	< LOD	< LOD	< LOD	66.3	< LOD	< LOD	0.78	< LOD	< LOD	< LOD
169	Curraghinalt Py3	Pyrite	Spot 2	< LOD	1.42	43.5	0.49	< LOD	< LOD	3.34	22	< LOD	0.09	< LOD	< LOD	5.67	< LOD	0.223	0.85	< LOD	0.045	0.156
170	Curraghinalt Py3	Pyrite	Spot 3	< LOD	3.43	4.57	< LOD	< LOD	0.029	3.77	< LOD	< LOD	< LOD	< LOD	< LOD	4.21	< LOD	< LOD	0.8	< LOD	< LOD	< LOD
171	Curraghinalt Py3	Pyrite	Spot 4	< LOD	80.6	22.4	< LOD	< LOD	< LOD	5.27	< LOD	< LOD	< LOD	< LOD	< LOD	21.1	< LOD	< LOD	0.91	< LOD	< LOD	< LOD
172	Curraghinalt Py3	Pyrite	Spot 5	3.2	20.7	96	< LOD	< LOD	< LOD	2.98	15	< LOD	21	< LOD	< LOD	50	< LOD	10.1	1.41	< LOD	0.052	0.038
173	Curraghinalt Py3	Pyrite	Spot 6	< LOD	2.79	1322	< LOD	< LOD	< LOD	27.5	< LOD	< LOD	5.79	< LOD	< LOD	10.3	< LOD	0.86	0.75	< LOD	4.41	2.83
174	Curraghinalt Py3	Pyrite	Spot 7	< LOD	7.4	14.4	51	< LOD	< LOD	48.5	< LOD	< LOD	86	< LOD	0.78	163	< LOD	13.1	1.32	0.036	12.5	34.8
175	Curraghinalt Py3	Pyrite	Spot 8	< LOD	158.3	4.31	< LOD	< LOD	< LOD	8.84	< LOD	< LOD	< LOD	< LOD	< LOD	1.03	< LOD	< LOD	0.51	< LOD	< LOD	< LOD
176	Curraghinalt Py3	Pyrite	Spot 9	< LOD	311	299	< LOD	< LOD	< LOD	5.48	< LOD	0.054	< LOD	< LOD	< LOD	0.6	< LOD	< LOD	0.41	< LOD	< LOD	0.0146
177	Curraghinalt Py3	Pyrite	Spot 10	< LOD	33.8	15.4	< LOD	< LOD	< LOD	2.99	< LOD	< LOD	0.056	< LOD	< LOD	9.15	< LOD	0.071	0.4	< LOD	0.189	0.101
178	Curraghinalt Py3	Pyrite	Spot 11	< LOD	50.9	7.44	< LOD	< LOD	0.036	3.51	< LOD	< LOD	0.148	< LOD	< LOD	8.28	< LOD	< LOD	0.58	< LOD	0.239	0.57
179	Curraghinalt Py3	Pyrite	Spot 12	< LOD	0.79	1.81	0.39	< LOD	< LOD	2.87	< LOD	< LOD	0.123	< LOD	< LOD	7.84	< LOD	0.32	0.51	< LOD	0.289	0.148
180	Curraghinalt Py3	Pyrite	Spot 13	< LOD	2.61	2.5	3.85	< LOD	0.041	4.89	< LOD	< LOD	0.417	< LOD	0.155	8.52	< LOD	0.99	0.64	< LOD	4.12	1.37
181	Curraghinalt Py3	Pyrite	Spot 14	< LOD	19	< LOD	< LOD	< LOD	< LOD	1.68	< LOD	< LOD	< LOD	< LOD	< LOD	4.15	< LOD	< LOD	0.67	< LOD	< LOD	0.0414
182	Curraghinalt Py3	Pyrite	Spot 15	< LOD	67.8	9.57	1.11	< LOD	< LOD	5.26	< LOD	< LOD	0.187	< LOD	< LOD	14.9	< LOD	0.69	0.83	< LOD	0.9	0.875
183	Curraghinalt Py3	Pyrite	Spot 16	< LOD	21.4	< LOD	0.67	< LOD	0.035	2.33	< LOD	< LOD	0.088	< LOD	< LOD	6.34	< LOD	0.21	0.82	< LOD	0.077	0.302
184	Curraghinalt Py3	Pyrite	Spot 17	< LOD	70.1	6	< LOD	< LOD	< LOD	2.18	< LOD	< LOD	< LOD	< LOD	< LOD	6.58	< LOD	0.033	0.71	< LOD	0.047	0.108
185	Curraghinalt Py3	Pyrite	Spot 18	< LOD	3.63	6.93	< LOD	< LOD	< LOD	3.54	< LOD	< LOD	0.072	< LOD	< LOD	17.84	< LOD	0.159	0.54	< LOD	0.4	0.177
186	Curraghinalt Py3	Pyrite	Spot 19	< LOD	78.5	57	0.63	< LOD	< LOD	3.76	< LOD	< LOD	0.164	< LOD	< LOD	6.18	< LOD	0.189	0.62	< LOD	0.147	0.21
187	Curraghinalt Py3	Pyrite	Spot 20	< LOD	1.65	4.36	1.24	< LOD	< LOD	2.49	< LOD	< LOD	0.395	< LOD	< LOD	15.4	< LOD	0.547	0.6	< LOD	1.18	5.42
188	Curraghinalt Py3	Pyrite	Spot 21	< LOD	2.4	< LOD	0.68	< LOD	< LOD	3.03	24	< LOD	0.092	< LOD	< LOD	15.6	< LOD	0.063	0.79	< LOD	0.027	0.041
189	Curraghinalt Py3	Pyrite	Spot 22	< LOD	1.59	< LOD	< LOD	< LOD	0.03	3.33	< LOD	< LOD	< LOD	< LOD	< LOD	13.3	< LOD	< LOD	0.71	< LOD	< LOD	0.058
190	Curraghinalt Py3	Pyrite	Spot 23	< LOD	7.2	< LOD	< LOD	< LOD	< LOD	9.3	< LOD	< LOD	0.35	< LOD	< LOD	2.66	< LOD	0.073	1.16	< LOD	2.7	0.85
191	Curraghinalt Py3	Pyrite	Spot 24	< LOD	< LOD	3.7	< LOD	< LOD	< LOD	3.43	< LOD	< LOD	< LOD	< LOD	< LOD	4.12	< LOD	< LOD	1.43	< LOD	< LOD	0.0265
192	Curraghinalt Py3	Pyrite	Spot 25	< LOD	3.5	5.7	< LOD	< LOD	< LOD	3.3	< LOD	< LOD	< LOD	< LOD	< LOD	1.93	< LOD	< LOD	1.12	< LOD	< LOD	< LOD
193	Curraghinalt Py3	Pyrite	Spot 26	< LOD	4.32	6.1	< LOD	< LOD	< LOD	1.69	17	< LOD	< LOD	< LOD	< LOD	2.32	< LOD	< LOD	1.44	< LOD	< LOD	< LOD
194	Curraghinalt Py3	Pyrite	Spot 27	< LOD	22.3	19.9	< LOD	< LOD	< LOD	2.15	< LOD	< LOD	< LOD	< LOD	< LOD	2.28	< LOD	< LOD	0.88	< LOD	< LOD	< LOD
195	Curraghinalt Py3	Pyrite	Spot 28	< LOD	1.45	< LOD	< LOD	< LOD	< LOD	2.97	< LOD	< LOD	< LOD	< LOD	< LOD	2.1	< LOD	< LOD	1.35	< LOD	< LOD	< LOD
196	Curraghinalt Py3	Pyrite	Spot 29	< LOD	15.2	47.6	< LOD	< LOD	< LOD	1.44	< LOD	< LOD	< LOD	< LOD	< LOD	1.37	< LOD	< LOD	1.32	< LOD	< LOD	< LOD
197	Curraghinalt Py3	Pyrite	Spot 30	< LOD	4.91	3.57	3.52	1.5	< LOD	11.6	< LOD	< LOD	0.73	< LOD	0.49	3.26	< LOD	0.084	1.33	0.0201	5.7	2.44
198	Curraghinalt Py3	Pyrite	Spot 31	< LOD	< LOD	61.9	< LOD	< LOD	< LOD	26.2	< LOD	< LOD	< LOD	< LOD	< LOD	11.6	< LOD	< LOD	1.2	< LOD	0.028	0.276
199	Curraghinalt Py3	Pyrite	Spot 32	< LOD	83.7	134.2	< LOD	< LOD	< LOD	3.67	< LOD	< LOD	< LOD	< LOD	< LOD	8.14	< LOD	< LOD	1.58	< LOD	< LOD	< LOD
200	Curraghinalt Py3	Pyrite	Spot 33	< LOD	1.23	577	< LOD	< LOD	< LOD	9.68	< LOD	< LOD	< LOD	< LOD	< LOD	24.1	< LOD	< LOD	1.05	< LOD	< LOD	< LOD

Number	Phase tested	Mineral	Code	Mn (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Ga (ppm)	As (ppm)	Se (ppm)	Mo (ppm)	Ag (ppm)	Sn (ppm)	Sb (ppm)	Te (ppm)	W (ppm)	Au (ppm)	Hg (ppm)	Tl (ppm)	Pb (ppm)	Bi (ppm)
201	Curraghinalt Py3	Pyrite	Spot 34	< LOD	4.42	855	< LOD	< LOD	< LOD	7.57	< LOD	< LOD	< LOD	< LOD	< LOD	28.7	< LOD	< LOD	0.83	< LOD	< LOD	< LOD
202	Curraghinalt Py3	Pyrite	Spot 35	< LOD	77.3	195	< LOD	< LOD	0.029	4.56	< LOD	< LOD	< LOD	< LOD	< LOD	3.08	< LOD	< LOD	0.62	< LOD	< LOD	< LOD
203	Curraghinalt Py3	Pyrite	Spot 36	< LOD	39.5	7.57	< LOD	< LOD	0.03	3.62	< LOD	< LOD	< LOD	< LOD	< LOD	3.46	< LOD	< LOD	0.79	< LOD	0.094	0.057
204	Curraghinalt Py3	Pyrite	Spot 37	< LOD	3.38	2.96	1.02	< LOD	< LOD	2.55	< LOD	< LOD	0.229	< LOD	< LOD	5.01	< LOD	0.385	1.1	< LOD	2.55	1.09
205	Curraghinalt Py3	Pyrite	Spot 38	< LOD	1.34	1.15	< LOD	< LOD	< LOD	3.92	< LOD	< LOD	< LOD	< LOD	< LOD	5.29	< LOD	0.028	0.93	< LOD	< LOD	0.073
206	Curraghinalt Py3	Pyrite	Spot 39	< LOD	0.99	4.44	< LOD	< LOD	< LOD	4.07	< LOD	< LOD	0.066	< LOD	< LOD	7.79	< LOD	0.073	0.86	< LOD	0.75	0.538
207	Curraghinalt Py3	Pyrite	Spot 40	< LOD	66	21.6	< LOD	< LOD	< LOD	3.21	< LOD	< LOD	< LOD	< LOD	< LOD	3	< LOD	< LOD	0.73	< LOD	< LOD	< LOD
208	Cloonacool Py1	Pyrite	Output_1_31	< LOD	69	350	3.2	5	< LOD	6760	25	0.09	0.51	< LOD	0.68	< LOD	< LOD	0.362	< LOD	< LOD	1.88	0.69
209	Cloonacool Py1	Pyrite	Output_1_32	< LOD	7410	369	1.15	3.7	< LOD	684	< LOD	< LOD	< LOD	< LOD	< LOD	0.88	< LOD	< LOD	< LOD	< LOD	0.49	0.149
210	Cloonacool Py1	Pyrite	Output_1_33	< LOD	31.6	71	4.7	< LOD	< LOD	11100	< LOD	< LOD	0.77	< LOD	1.61	0.66	< LOD	2.21	< LOD	< LOD	3.27	1
211	Cloonacool Py1	Pyrite	Output_1_34	< LOD	31.3	105.7	8.8	< LOD	< LOD	9350	< LOD	< LOD	2.52	< LOD	4.3	1.75	< LOD	1.92	< LOD	< LOD	10.1	1.77
212	Cloonacool Py1	Pyrite	Output_1_35	< LOD	82	115	2.24	< LOD	< LOD	6460	< LOD	< LOD	1.03	< LOD	1.56	2.23	< LOD	1.79	< LOD	< LOD	2.83	0.45
213	Cloonacool Py1	Pyrite	Output_1_36	< LOD	4.4	5.1	3.01	< LOD	< LOD	16080	< LOD	< LOD	0.36	< LOD	0.25	3.77	< LOD	11.8	< LOD	< LOD	2.06	0.089
214	Cloonacool Py1	Pyrite	Output_1_37	< LOD	276	1620	7.5	< LOD	0.46	4980	< LOD	< LOD	1.35	< LOD	1.71	1.05	< LOD	0.389	< LOD	0.022	14.4	1.46
215	Cloonacool Py1	Pyrite	Output_1_38	12.1	5670	2990	13.2	< LOD	276	20100	< LOD	< LOD	2.17	< LOD	6.83	1.65	0.15	1.5	< LOD	0.087	49.9	4.67
216	Cloonacool Py1	Pyrite	Output_1_39	< LOD	115	878	0.74	< LOD	< LOD	3020	< LOD	< LOD	< LOD	< LOD	0.72	< LOD	0.16	0.84	< LOD	< LOD	1.48	0.03
217	Cloonacool Py1	Pyrite	Output_1_40	12.6	478	1637	7.1	< LOD	< LOD	4800	< LOD	< LOD	1.97	< LOD	3.52	2.14	< LOD	0.53	0.66	< LOD	28	0.97
218	Cloonacool Py1	Pyrite	Output_1_1	47	18.7	198	8.3	5.9	0.087	26.8	< LOD	0.43	0.98	< LOD	2.67	0.51	< LOD	0.138	< LOD	< LOD	27	0.112
219	Cloonacool Py1	Pyrite	Output_1_2	18	193	9400	6.7	4.4	0.093	357	< LOD	7.4	0.85	0.36	3.2	1.95	2.5	0.126	0.42	< LOD	32.2	1.44
220	Cloonacool Py1	Pyrite	Output_1_3	< LOD	272	9200	220	< LOD	0.07	13500	21.9	< LOD	5.9	< LOD	0.162	0.73	< LOD	0.102	< LOD	< LOD	2.5	0.46
221	Cloonacool Py1	Pyrite	Output_1_4	< LOD	51	246	184	< LOD	1.26	9600	< LOD	< LOD	0.56	< LOD	24.7	1.85	< LOD	2.84	< LOD	0.05	124	1.9
222	Cloonacool Py1	Pyrite	Output_1_5	< LOD	790	5000	23.4	< LOD	0.285	2320	< LOD	235	2.11	0.24	17.5	2.71	0.26	0.76	0.86	0.182	153	2.13
223	Cloonacool Py1	Pyrite	Output_1_6	< LOD	72.6	418	4.7	4.1	0.116	370	< LOD	7.4	0.263	< LOD	3.03	1	< LOD	< LOD	0.42	< LOD	21.2	0.423
224	Cloonacool Py1	Pyrite	Output_1_7	< LOD	279	6840	8.8	< LOD	< LOD	449	< LOD	0.175	0.62	< LOD	0.291	0.97	< LOD	0.043	< LOD	< LOD	4.35	0.107
225	Cloonacool Py1	Pyrite	Output_1_8	< LOD	207	640	53.4	7	0.56	4500	< LOD	48	2.48	< LOD	23.4	4.22	2.48	1.28	0.94	0.198	89	3.01
226	Cloonacool Py1	Pyrite	Output_1_9	54	521	5080	37	920	0.094	235	10.1	< LOD	34	< LOD	0.9	5.6	0.214	0.4	< LOD	< LOD	6100	89
227	Cloonacool Py1	Pyrite	Output_1_10	< LOD	520	3260	10.9	< LOD	0.38	94	< LOD	< LOD	0.64	0.77	0.94	1.75	30	< LOD	< LOD	< LOD	12.5	1.1
228	Cloonacool Py1	Pyrite	Output_1_11	13	35.4	213	21.1	< LOD	0.081	11.3	< LOD	< LOD	2.95	< LOD	2.07	1.31	< LOD	0.205	< LOD	< LOD	50	1.69
229	Cloonacool Py1	Pyrite	Output_1_12	< LOD	89	900	1.97	< LOD	< LOD	27.1	< LOD	12.8	0.57	< LOD	0.46	0.63	0.089	0.09	< LOD	< LOD	9.7	0.043
230	Cloonacool Py1	Pyrite	Output_1_13	17.7	348	355	8.1	22.9	0.07	561	< LOD	< LOD	0.69	< LOD	0.46	1.22	0.108	0.042	< LOD	< LOD	16.3	0.424
231	Cloonacool Py1	Pyrite	Output_1_14	< LOD	128	1130	1.6	2.9	0.151	17.6	< LOD	2.7	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	1.38	< LOD
232	Cloonacool Py1	Pyrite	Output_1_15	< LOD	5.6	35	1.5	< LOD	< LOD	6.9	< LOD	0.39	0.174	< LOD	0.114	< LOD	0.14	< LOD	< LOD	< LOD	1.99	0.017
233	Cloonacool Py1	Pyrite	Output_1_16	< LOD	2.17	70.5	< LOD	< LOD	< LOD	26.8	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.108	< LOD
234	Cloonacool Py1	Pyrite	Output_1_17	< LOD	5500	10710	18	1550	< LOD	11300	11.7	< LOD	1.75	< LOD	0.32	2.6	< LOD	0.54	0.45	< LOD	3	0.78
235	Cloonacool Py1	Pyrite	Output_1_18	< LOD	1990	3480	< LOD	3.4	< LOD	124	< LOD	< LOD	< LOD	< LOD	< LOD	1.38	< LOD	< LOD	0.31	< LOD	2.4	< LOD
236	Cloonacool Py1	Pyrite	Output_1_19	14.8	1510	3840	< LOD	< LOD	< LOD	98	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.12	< LOD	0.89	0.021
237	Cloonacool Py1	Pyrite	Output_1_20	< LOD	13.3	78	20	< LOD	< LOD	37.4	< LOD	270	5.5	< LOD	4.9	2.73	< LOD	0.54	0.34	< LOD	104	0.65
238	Cloonacool Py1	Pyrite	Output_1_21	< LOD	109	355	6.5	5.5	< LOD	46.1	< LOD	< LOD	0.58	< LOD	3.36	1.1	< LOD	0.156	0.5	< LOD	27.7	0.66
239	Cloonacool Py1	Pyrite	Output_1_22	58	17	204	69	< LOD	0.207	48.5	< LOD	1.36	2.93	5.87	3.74	0.94	47.5	0.283	0.23	< LOD	22.9	0.065
240	Cloonacool Py1	Pyrite	Output_1_23	< LOD	4680	5170	< LOD	5.4	< LOD	184	< LOD	0.38	0.121	< LOD	0.29	1.21	< LOD	< LOD	< LOD	< LOD	3.3	< LOD
241	Cloonacool Py1	Pyrite	Output_1_24	< LOD	451	3470	1.39	5.4	0.041	27.1	< LOD	15	0.26	< LOD	0.243	0.46	< LOD	0.038	< LOD	< LOD	11.2	0.092
242	Cloonacool Py1	Pyrite	Output_1_25	< LOD	4.15	90	2	< LOD	0.043	53.6	< LOD	61	0.49	< LOD	0.48	0.42	0.049	0.052	< LOD	< LOD	15	0.038
243	Cloonacool Py1	Pyrite	Output_1_26	< LOD	26.8	389	< LOD	< LOD	< LOD	50.2	< LOD	47	< LOD	< LOD	1.54	0.35	0.23	< LOD	0.21	< LOD	11.8	0.098
244	Cloonacool Py1	Pyrite	Output_1_27	< LOD	1510	950	32	6	< LOD	199	< LOD	0.37	1.57	< LOD	8.2	2.26	< LOD	0.235	0.33	0.045	630	2.28
245	Cloonacool Py1	Pyrite	Output_1_28	< LOD	39.7	346	5.4	< LOD	< LOD	68.6	< LOD	12	0.52	< LOD	0.89	< LOD	0.072	< LOD	< LOD	< LOD	12.1	0.092
246	Cloonacool Py1	Pyrite	Output_1_29	6.4	508	717	54	3.4	0.49	29.2	< LOD	< LOD	1.23	< LOD	0.38	0.82	< LOD	0.041	< LOD	0.023	8.8	1.25
247	Cloonacool Py1	Pyrite	Output_1_30	8.5	49.7	346	1.09	< LOD	< LOD	6.5	< LOD	< LOD	0.196	< LOD	< LOD	0.38	< LOD	< LOD	0.15	< LOD	2.86	< LOD
248	Cloonacool Py1	Pyrite	Output_1_31	15	159	280	24	29	1.9	145	< LOD	1.6	6.7	< LOD	6.3	1.86	1.5	0.46	0.86	< LOD	39	2.81
249	Cloonacool Py1	Pyrite	Output_1_32	< LOD	403	695	37	2.5	0.61	2210	< LOD	7.6	6.31	< LOD	5.07	3.26	4.5	1.37	0.5	0.025	40.6	3.8
250	Cloonacool Py1	Pyrite	Output_1_33	< LOD	557	870	57	25	10.5	2320	< LOD	348	11.7	0.73	20	6.7	42	1.32	2.3	0.6	262	9.3

Number	Phase tested	Mineral	Code	Mn (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Ga (ppm)	As (ppm)	Se (ppm)	Mo (ppm)	Ag (ppm)	Sn (ppm)	Sb (ppm)	Te (ppm)	W (ppm)	Au (ppm)	Hg (ppm)	Tl (ppm)	Pb (ppm)	Bi (ppm)
251	Cloonacool Py1	Pyrite	Output_1_34	< LOD	416	468	170	3.4	0.31	4040	< LOD	0.068	10.3	< LOD	12.9	6.9	2.66	2.36	0.67	0.015	147	11.7
252	Cloonacool Py1	Pyrite	Output_1_35	22	415	573	17.4	< LOD	0.51	4030	< LOD	80	5.31	< LOD	7.3	3.84	4.1	0.85	0.37	0.055	67	8
253	Cloonacool Py1	Pyrite	Output_1_36	15	96	307	103	19.5	4.3	140	< LOD	185	16.5	0.33	13.2	3.5	8.4	1.96	0.56	0.183	126	5.21
254	Cloonacool Py1	Pyrite	Output_1_37	420	686	521	75	115	186	2490	< LOD	670	37.6	3.8	172	22	70	1.3	71	6	570	15.4
255	Cloonacool Py1	Pyrite	Output_1_38	10.7	453	438	34.2	4.3	0.99	840	< LOD	14.4	11.3	0.29	13.9	7.5	3.25	1.77	0.54	0.027	300	13.5
256	Cloonacool Py1	Pyrite	Output_1_39	< LOD	620	960	11.6	< LOD	0.042	1560	< LOD	< LOD	6.4	< LOD	1.82	3.8	0.45	0.6	0.35	< LOD	47	5.5
257	Cloonacool Py1	Pyrite	Output_1_40	< LOD	278	1050	22.5	3.8	1.33	1060	< LOD	17	15.3	0.18	14.6	10.4	0.45	1	0.48	0.051	76	9
258	Cloonacool Py1	Pyrite	Output_1_41	< LOD	145	273	31.1	< LOD	0.75	670	< LOD	< LOD	6.4	< LOD	2.97	4.09	2.23	0.82	< LOD	< LOD	80	7.1
259	Cloonacool Py1	Pyrite	Output_1_42	< LOD	241	460	17.9	< LOD	< LOD	4670	< LOD	< LOD	6.1	< LOD	5.61	7.9	< LOD	0.768	< LOD	< LOD	76	9.7
260	Cloonacool Py1	Pyrite	Output_1_43	52	398	639	33	28	26.8	1560	< LOD	310	11.3	2.5	24.1	5.8	39	0.51	4.1	0.89	123	7.9
261	Cloonacool Py1	Pyrite	Output_1_44	26	23.1	118	3.3	36	6.7	31	2	8.5	0.9	< LOD	4.4	0.45	1.6	0.044	< LOD	0.095	36	0.29
262	Cloonacool Py1	Pyrite	Output_1_45	< LOD	336	800	9	< LOD	< LOD	1090	< LOD	< LOD	2.8	< LOD	1.75	1.31	3.8	0.38	< LOD	< LOD	25.8	2.48
263	Cloonacool Py1	Pyrite	Output_1_46	< LOD	21.8	55	6	< LOD	< LOD	13.5	< LOD	< LOD	3.9	< LOD	2.49	0.89	0.55	0.131	< LOD	0.116	220	2.5
264	Cloonacool Py1	Pyrite	Output_1_47	< LOD	283	750	12.1	< LOD	0.31	1210	15	< LOD	4.33	< LOD	2.85	2.7	< LOD	0.51	< LOD	< LOD	46.7	3.45
265	Cloonacool Py1	Pyrite	Output_1_48	< LOD	59	175	9.2	< LOD	< LOD	98	2	0.23	3.8	< LOD	3.17	1.85	3.6	0.147	< LOD	< LOD	19.2	1.32
266	Cloonacool Py1	Pyrite	Output_1_49	5.8	26.8	115.1	18.7	< LOD	0.9	36.2	2	2.8	4.07	0.46	2.68	1.07	20.3	0.33	< LOD	< LOD	22.8	1.07
267	Cloonacool Py1	Pyrite	Output_1_50	8.5	37	96	91	4.1	0.33	39.9	9	0.23	16	< LOD	2.77	3.9	1.12	2	< LOD	< LOD	68	0.83
268	Cloonacool Py1	Pyrite	Output_1_51	< LOD	7	55	15.3	< LOD	< LOD	11.1	< LOD	< LOD	4.21	< LOD	1.14	0.86	0.27	0.39	< LOD	< LOD	16.3	0.099
269	Cloonacool Py1	Pyrite	Output_1_52	< LOD	17	118.4	132	< LOD	< LOD	66	< LOD	0.16	13.5	< LOD	1.18	1.7	1.13	1.75	< LOD	< LOD	44.1	1.7
270	Cloonacool Py1	Pyrite	Output_1_53	< LOD	27.8	163	16	2.8	< LOD	212	9	< LOD	5.8	< LOD	0.6	2.49	< LOD	0.69	< LOD	< LOD	23.9	1.8
271	Cloonacool Py1	Pyrite	Output_1_54	78	240	580	27	2.5	< LOD	3980	< LOD	< LOD	4.91	< LOD	8.2	4.8	< LOD	3.3	< LOD	< LOD	53.6	4.82
272	Cloonacool Py1	Pyrite	Output_1_55	< LOD	136	278	42	< LOD	0.43	480	6	< LOD	8.4	< LOD	3.5	2.73	< LOD	1.21	< LOD	< LOD	69	3.27
273	Cloonacool Py1	Pyrite	Output_1_56	< LOD	73	144	63	< LOD	0.118	94	19	< LOD	8.7	0.32	5.46	1.54	10.2	0.55	< LOD	0.022	41.7	1.49
274	Cloonacool Py1	Pyrite	Output_1_57	25	97	449	5.9	38	43	15.7	110	0.39	1.29	1.6	2	0.5	0.27	< LOD	2.1	0.63	8	0.26
275	Cloonacool Py1	Pyrite	Output_1_58	< LOD	265	184	60	< LOD	< LOD	110	2	0.103	8.9	< LOD	5.87	3.5	1.65	0.78	< LOD	0.082	83	2
276	Cloonacool Py1	Pyrite	Output_1_59	< LOD	600	689	49.6	< LOD	0.508	2180	< LOD	4.3	15.9	< LOD	12.9	6.6	0.9	1.19	< LOD	0.025	760	7.2
277	Cloonacool Py1	Pyrite	Output_1_60	< LOD	104	707	3.74	< LOD	0.139	13.1	< LOD	17.2	1.21	< LOD	2.14	0.98	2.34	0.059	< LOD	< LOD	32.1	0.8
278	Cloonacool Py1	Pyrite	Output_1_61	< LOD	23.5	94	27.2	< LOD	< LOD	11.2	< LOD	< LOD	4.88	< LOD	0.89	1.27	1.26	0.57	< LOD	< LOD	13.4	0.337
279	Cloonacool Py1	Pyrite	Output_1_62	< LOD	4.3	704	1.66	< LOD	< LOD	28.7	< LOD	< LOD	0.81	< LOD	0.57	0.76	< LOD	0.087	< LOD	< LOD	8.1	0.404
280	Cloonacool Py2	Pyrite	Output_1_1	< LOD	< LOD	1.82	42	4470	1	6	< LOD	< LOD	4.09	1.66	2.96	0.47	< LOD	0.18	1.21	< LOD	36	0.206
281	Cloonacool Py2	Pyrite	Output_1_2	< LOD	< LOD	3.91	133	4680	0.58	20.8	< LOD	< LOD	4.14	0.84	3.77	0.75	< LOD	0.29	1.22	< LOD	62.1	0.886
282	Cloonacool Py2	Pyrite	Output_1_3	< LOD	0.58	5.3	76	4090	0.97	6.1	< LOD	< LOD	4.79	0.68	2.87	0.7	< LOD	0.202	1.28	< LOD	89.9	0.56
283	Cloonacool Py2	Pyrite	Output_1_4	< LOD	< LOD	2.41	26.2	4980	0.99	< LOD	27	< LOD	6.38	3.24	1.18	0.64	< LOD	0.231	1.16	< LOD	68.9	0.072
284	Cloonacool Py2	Pyrite	Output_1_5	< LOD	2.39	2.21	4.1	< LOD	< LOD	8670	28	< LOD	0.56	< LOD	0.51	2.13	< LOD	0.75	0.61	< LOD	28.2	0.115
285	Cloonacool Py2	Pyrite	Output_1_6	< LOD	8.89	3.79	1.3	< LOD	< LOD	5000	56	< LOD	< LOD	< LOD	< LOD	0.82	< LOD	0.88	0.8	0.022	3.5	< LOD
286	Cloonacool Py2	Pyrite	Output_1_7	< LOD	4.24	3.97	1.88	< LOD	< LOD	6970	49	< LOD	0.248	< LOD	0.183	1.29	< LOD	1.42	0.45	< LOD	11.5	0.068
287	Cloonacool Py2	Pyrite	Output_1_8	< LOD	< LOD	< LOD	0.94	< LOD	< LOD	348	< LOD	< LOD	0.23	< LOD	0.168	< LOD	< LOD	0.05	0.47	< LOD	7.8	0.33
288	Cloonacool Py2	Pyrite	Output_1_9	< LOD	< LOD	< LOD	4	< LOD	< LOD	5270	49	< LOD	0.25	< LOD	1.46	0.97	< LOD	1.02	0.42	< LOD	21.2	0.136
289	Cloonacool Py2	Pyrite	Output_1_10	< LOD	1.61	4.46	1.11	< LOD	< LOD	7400	38	< LOD	0.23	< LOD	0.148	0.5	< LOD	0.83	0.59	< LOD	28	0.2
290	Cloonacool Py2	Pyrite	Output_1_11	< LOD	< LOD	5.2	102	3490	0.79	68	< LOD	< LOD	7.02	1.94	2.27	1.24	< LOD	0.429	0.96	< LOD	60.2	0.374
291	Cloonacool Py2	Pyrite	Output_1_12	< LOD	8.8	4.8	14.3	< LOD	< LOD	10120	< LOD	0.041	0.48	< LOD	1.01	0.75	< LOD	8.18	< LOD	< LOD	21.1	0.129
292	Cloonacool Py2	Pyrite	Output_1_13	< LOD	15.8	28.5	< LOD	< LOD	< LOD	11500	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	1.4	0.74	< LOD	0.088	< LOD
293	Cloonacool Py2	Pyrite	Output_1_14	< LOD	3.13	6.07	< LOD	< LOD	< LOD	10710	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.145	0.81	< LOD	< LOD	< LOD
294	Cloonacool Py2	Pyrite	Output_1_15	< LOD	23.3	50.7	< LOD	< LOD	< LOD	9090	< LOD	< LOD	< LOD	< LOD	0.257	< LOD	< LOD	0.776	0.4	< LOD	1.96	< LOD
295	Cloonacool Py2	Pyrite	Output_1_16	< LOD	17.4	35.1	< LOD	< LOD	< LOD	10280	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.234	0.57	< LOD	< LOD	< LOD
296	Cloonacool Py2	Pyrite	Output_1_17	< LOD	32.3	34.9	1.08	< LOD	< LOD	10080	< LOD	< LOD	0.125	< LOD	0.45	0.47	< LOD	0.926	0.62	< LOD	3.09	0.07
297	Cloonacool Py2	Pyrite	Output_1_18	< LOD	131	305	< LOD	< LOD	< LOD	5300	44.6	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.474	< LOD	< LOD	< LOD	< LOD
298	Cloonacool Py2	Pyrite	Output_1_19	< LOD	< LOD	6.4	197	5400	1.03	16.7	< LOD	< LOD	7.24	0.88	3.85	0.82	< LOD	0.5	3.12	< LOD	23.1	1.66
299	Cloonacool Py2	Pyrite	Output_1_20	< LOD	2.25	3.5	2.86	< LOD	< LOD	13020	< LOD	< LOD	0.54	< LOD	0.49	2.6	< LOD	5.13	1.29	< LOD	8.5	0.168
300	Cloonacool Py2	Pyrite	Output_1_21	< LOD	75.1	118	6.7	< LOD	< LOD	4660	< LOD	< LOD	1.99	< LOD	1.06	4.3	< LOD	0.57	0.93	< LOD	3.8	0.58

Number	Phase tested	Mineral	Code	Mn (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Ga (ppm)	As (ppm)	Se (ppm)	Mo (ppm)	Ag (ppm)	Sn (ppm)	Sb (ppm)	Te (ppm)	W (ppm)	Au (ppm)	Hg (ppm)	Tl (ppm)	Pb (ppm)	Bi (ppm)
301	Cloonacool Py2	Pyrite	Output_1_22	< LOD	8.9	28.3	54	< LOD	< LOD	10040	< LOD	< LOD	2.74	< LOD	2.66	3.55	< LOD	8.32	< LOD	< LOD	8.6	1.3
302	Cloonacool Py2	Pyrite	Output_1_23	< LOD	26.3	54	11.1	< LOD	< LOD	6890	< LOD	< LOD	1.79	< LOD	2.55	2.27	< LOD	3.01	0.92	< LOD	7.5	0.95
303	Cloonacool Py2	Pyrite	Output_1_24	< LOD	1.15	33	96	< LOD	< LOD	3230	< LOD	< LOD	1.32	< LOD	3	0.79	< LOD	0.67	1.59	< LOD	6.6	2.73
304	Cloonacool Py2	Pyrite	Output_1_25	< LOD	14.7	25.8	22.9	3740	0.96	510	< LOD	< LOD	5.12	1.09	4.43	1	< LOD	0.46	1.66	< LOD	6.8	1.37
305	Cloonacool Py2	Pyrite	Output_1_26	< LOD	127	346	12.4	< LOD	< LOD	4640	28	< LOD	2.72	< LOD	3.66	1.93	< LOD	1.34	0.94	< LOD	7.6	2.69
306	Cloonacool Py2	Pyrite	Output_1_27	< LOD	158	370	14.5	< LOD	1.57	4450	27	< LOD	2.93	< LOD	4.72	4.51	< LOD	0.93	0.76	0.036	9.1	2.31
307	Cloonacool Py2	Pyrite	Output_1_28	< LOD	85	255	12.4	2.7	< LOD	6230	< LOD	< LOD	3.3	< LOD	9.8	3.98	< LOD	1.15	1.55	< LOD	33	6.6
308	Cloonacool Py2	Pyrite	Output_1_29	< LOD	27.2	136	4.2	3.5	< LOD	151	< LOD	< LOD	1.44	< LOD	0.39	0.45	0.8	0.156	1.18	< LOD	1.6	0.62
309	Cloonacool Py2	Pyrite	Output_1_30	< LOD	8.4	30	6.5	< LOD	< LOD	11190	< LOD	< LOD	0.34	< LOD	2.53	2.1	< LOD	1.52	0.61	< LOD	7.8	1.73
310	Cloonacool Py3	Pyrite	Output_1_41	< LOD	27	16.3	8	104	< LOD	16960	< LOD	< LOD	1.38	< LOD	2.9	2.76	< LOD	6.42	1.84	< LOD	9.5	1.87
311	Cloonacool Py3	Pyrite	Output_1_42	< LOD	2.9	10.1	30	< LOD	< LOD	11060	24	< LOD	1.12	< LOD	1.87	1.24	< LOD	4.03	1.84	< LOD	11.2	1.56
312	Cloonacool Py3	Pyrite	Output_1_43	5	28	147	5.4	< LOD	< LOD	3210	< LOD	< LOD	1.49	< LOD	1.09	0.84	< LOD	0.52	1.19	< LOD	16.5	1.7
313	Cloonacool Py3	Pyrite	Output_1_44	< LOD	298	140	3	< LOD	< LOD	2350	< LOD	< LOD	0.94	< LOD	2.11	0.51	< LOD	0.221	1.08	< LOD	12.6	2.09
314	Cloonacool Py3	Pyrite	Output_1_45	< LOD	95	78	44	209	0.34	4990	29	< LOD	6.1	< LOD	15.1	4.7	0.4	2.22	2.13	< LOD	137	10.5
315	SL - Glencolumbkille	Pyrite	Output_1_31	< LOD	< LOD	68	33.4	160	< LOD	18	< LOD	< LOD	< LOD	< LOD	3.8	10.5	< LOD	< LOD	< LOD	0.87	1030	< LOD
316	SL - Glencolumbkille	Pyrite	Output_1_32	< LOD	21	328	46	< LOD	1.9	86	< LOD	0.56	< LOD	5.4	4.8	< LOD	< LOD	1.4	9.4	< LOD	1610	0.83
317	SL - Glencolumbkille	Pyrite	Output_1_33	< LOD	270	850	28.8	< LOD	1.2	241	< LOD	< LOD	< LOD	< LOD	4.5	< LOD	< LOD	< LOD	< LOD	< LOD	841	< LOD
318	SL - Glencolumbkille	Pyrite	Output_1_34	< LOD	500	2040	< LOD	< LOD	< LOD	444	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	208	14.9
319	SL - Glencolumbkille	Pyrite	Output_1_35	< LOD	1930	4110	1510	< LOD	< LOD	9.6	41	< LOD	4.8	< LOD	< LOD	< LOD	< LOD	< LOD	3.5	25.2	1650	35
320	SL - Glencolumbkille	Pyrite	Output_1_36	< LOD	2900	5050	900	< LOD	< LOD	13	86	< LOD	4	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	10.2	760	49
321	SL - Glencolumbkille	Pyrite	Output_1_37	< LOD	2240	3990	436	< LOD	< LOD	< LOD	27	0.27	8.3	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	63.4	1278	150
322	SL - Glencolumbkille	Pyrite	Output_1_38	< LOD	< LOD	< LOD	19	< LOD	< LOD	< LOD	20	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	793	< LOD
323	SL - Glencolumbkille	Pyrite	Output_1_39	< LOD	19	< LOD	15	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	617	< LOD
324	SL - Glencolumbkille	Pyrite	Output_1_40	< LOD	< LOD	< LOD	22	< LOD	1.16	< LOD	50	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	1	730	< LOD
325	SL - Glencolumbkille	Pyrite	Output_1_41	81	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	10	2.1	< LOD	< LOD	3	< LOD	< LOD	< LOD	< LOD	2.9	233	< LOD
326	SL - Glencolumbkille	Pyrite	Output_1_42	< LOD	< LOD	35	10.2	< LOD	< LOD	11	24	5	< LOD	< LOD	5.8	< LOD	< LOD	< LOD	< LOD	1.34	368	< LOD
327	SL - Glencolumbkille	Pyrite	Output_1_43	< LOD	< LOD	< LOD	15.3	110	< LOD	27	< LOD	1.8	< LOD	< LOD	11	< LOD	< LOD	< LOD	5	0.48	369	< LOD
328	SL - Glencolumbkille	Pyrite	Output_1_44	< LOD	3700	13500	324	< LOD	< LOD	< LOD	41	< LOD	1.5	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	9	312	3.81
329	SL - Glencolumbkille	Pyrite	Output_1_45	< LOD	3090	9710	463	< LOD	< LOD	< LOD	21	< LOD	< LOD	< LOD	2.2	< LOD	< LOD	< LOD	< LOD	22.1	547	3.65
330	SL - Glencolumbkille	Pyrite	Output_1_46	< LOD	4210	12900	282	< LOD	1.06	< LOD	48	< LOD	1.06	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	6.8	175	2.4
331	SL - Glencolumbkille	Pyrite	Output_1_47	< LOD	1620	3930	27.6	< LOD	< LOD	< LOD	< LOD	< LOD	1.3	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	362	454	0.66
332	SL - Glencolumbkille	Pyrite	Output_1_48	< LOD	1421	3360	17.1	< LOD	< LOD	< LOD	21	< LOD	1.1	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	158	1840	0.36
333	SL - Glencolumbkille	Pyrite	Output_1_49	< LOD	1600	3360	20.5	< LOD	< LOD	< LOD	43	< LOD	1.61	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	133	1610	0.77
334	SL - Glencolumbkille	Pyrite	Output_1_50	< LOD	4190	13700	622	< LOD	< LOD	< LOD	61	0.11	4.1	< LOD	5.7	< LOD	0.19	< LOD	< LOD	77	1370	0.79
335	SL - Glencolumbkille	Pyrite	Output_1_51	< LOD	387	383	147	< LOD	< LOD	< LOD	< LOD	1.8	< LOD	< LOD	3.3	< LOD	< LOD	< LOD	< LOD	4.8	110	0.64
336	SL - Glencolumbkille	Pyrite	Output_1_52	< LOD	369	325	134	< LOD	< LOD	< LOD	31	0.85	0.8	< LOD	< LOD	< LOD	< LOD	< LOD	3.2	29.5	475	1.27
337	SL - Glencolumbkille	Pyrite	Output_1_53	< LOD	445	430	101	< LOD	< LOD	< LOD	30	2.4	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	7.3	3.1	75	1.12
338	SL - Glencolumbkille	Pyrite	Output_1_54	< LOD	2240	5270	280	< LOD	< LOD	< LOD	117	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	30.8	443	9.2
339	SL - Glencolumbkille	Pyrite	Output_1_55	< LOD	1710	3440	17.9	< LOD	< LOD	< LOD	36	< LOD	< LOD	< LOD	2.1	< LOD	1.27	< LOD	< LOD	247	158	1.6
340	SL - Glencolumbkille	Pyrite	Output_1_56	< LOD	547	274	67	< LOD	< LOD	< LOD	84	< LOD	1.3	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	4	61	< LOD
341	SL - Glencolumbkille	Pyrite	Output_1_57	86	590	300	47	< LOD	15.5	< LOD	160	< LOD	1.6	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	5.3	303	14.6
342	SL - Glencolumbkille	Pyrite	Output_1_58	< LOD	365	299	100	< LOD	1.33	< LOD	60	< LOD	< LOD	< LOD	< LOD	< LOD	1.8	< LOD	< LOD	2.1	33	< LOD
343	SL - Glencolumbkille	Pyrite	Output_1_59	< LOD	2530	3330	257	< LOD	< LOD	< LOD	90	< LOD	1.71	< LOD	2.6	< LOD	0.28	< LOD	< LOD	35.5	1890	1.07
344	SL - Glencolumbkille	Pyrite	Output_1_60	< LOD	2590	3240	218	< LOD	< LOD	< LOD	39	< LOD	2.31	< LOD	< LOD	< LOD	0.36	< LOD	< LOD	45.5	1538	1.31
345	SL - Glencolumbkille	Pyrite	Output_1_51	< LOD	< LOD	< LOD	7.1	< LOD	< LOD	< LOD	< LOD	0.3	< LOD	2.4	3.9	4.6	< LOD	< LOD	< LOD	< LOD	95	< LOD
346	SL - Glencolumbkille	Pyrite	Output_1_52	51	25	< LOD	6.9	< LOD	1.26	< LOD	< LOD	< LOD	< LOD	3.7	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	44.2	< LOD
347	SL - Glencolumbkille	Pyrite	Output_1_53	< LOD	345	930	4.8	< LOD	< LOD	< LOD	79	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.25	79	0.48
348	SL - Glencolumbkille	Pyrite	Output_1_54	26	19	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	3.5	< LOD	< LOD	< LOD	< LOD	< LOD	0.2	3.2	< LOD
349	SL - Glencolumbkille	Pyrite	Output_1_55	< LOD	< LOD	< LOD	< LOD	< LOD	0.83	< LOD	< LOD	0.28	< LOD	4	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	7.2	< LOD
350	SL - Glencolumbkille	Pyrite	Output_1_56	< LOD	< LOD	< LOD	< LOD	< LOD	0.52	< LOD	< LOD	< LOD	< LOD	2.2	2	4	< LOD	< LOD	< LOD	< LOD	42	< LOD

Number	Phase tested	Mineral	Code	Mn (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Ga (ppm)	As (ppm)	Se (ppm)	Mo (ppm)	Ag (ppm)	Sn (ppm)	Sb (ppm)	Te (ppm)	W (ppm)	Au (ppm)	Hg (ppm)	Tl (ppm)	Pb (ppm)	Bi (ppm)
351	SL - Glencolumbkille	Pyrite	Output_1_57	< LOD	< LOD	< LOD	4.3	71	< LOD	< LOD	< LOD	0.44	1.05	2.8	2.3	< LOD	< LOD	< LOD	< LOD	< LOD	48.4	< LOD
352	SL - Glencolumbkille	Pyrite	Output_1_58	< LOD	< LOD	< LOD	< LOD	< LOD	1.84	< LOD	< LOD	< LOD	1.42	6.5	< LOD	< LOD	< LOD	< LOD	< LOD	0.47	31.1	< LOD
353	SL - Glencolumbkille	Pyrite	Output_1_59	< LOD	< LOD	< LOD	17.5	< LOD	< LOD	< LOD	< LOD	< LOD	0.56	< LOD	15.2	< LOD	< LOD	< LOD	< LOD	0.5	372	< LOD
354	SL - Glencolumbkille	Pyrite	Output_1_60	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	4	< LOD	< LOD	< LOD	< LOD	2.01	< LOD
355	SL - Glencolumbkille	Pyrite	Output_1_61	< LOD	< LOD	< LOD	9	< LOD	3.9	< LOD	< LOD	< LOD	1.6	4.3	11.1	< LOD	< LOD	< LOD	< LOD	0.73	308	< LOD
356	SL - Glencolumbkille	Pyrite	Output_1_62	< LOD	8	< LOD	3.2	100	< LOD	< LOD	< LOD	0.9	0.82	4.5	2.2	< LOD	< LOD	< LOD	< LOD	0.57	165	< LOD
357	SL - Glencolumbkille	Pyrite	Output_1_63	< LOD	13	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	1.45	2.8	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	2.2	< LOD
358	SL - Glencolumbkille	Pyrite	Output_1_64	< LOD	320	7100	20.8	< LOD	< LOD	< LOD	< LOD	< LOD	1.72	3.6	2	< LOD	< LOD	< LOD	< LOD	1.54	539	< LOD
359	SL - Glencolumbkille	Pyrite	Output_1_65	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	3.7	1.1	5.2	< LOD	< LOD	< LOD	< LOD	72	< LOD
360	SL - Glencolumbkille	Pyrite	Output_1_66	< LOD	< LOD	< LOD	9.6	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	3.9	4.2	< LOD	< LOD	< LOD	< LOD	0.54	431	< LOD
361	SL - Glencolumbkille	Pyrite	Output_1_67	< LOD	11.5	< LOD	< LOD	< LOD	< LOD	< LOD	73	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	15.3	< LOD
362	SL - Glencolumbkille	Pyrite	Output_1_68	< LOD	17	< LOD	< LOD	< LOD	0.96	< LOD	< LOD	< LOD	0.83	3	< LOD	< LOD	< LOD	< LOD	< LOD	0.59	45.4	< LOD
363	SL - Glencolumbkille	Pyrite	Output_1_69	< LOD	< LOD	< LOD	< LOD	< LOD	1.46	< LOD	< LOD	0.07	< LOD	2.9	< LOD	< LOD	< LOD	< LOD	3.8	0.8	86	< LOD
364	SL - Glencolumbkille	Pyrite	Output_1_70	< LOD	170	380	6.9	< LOD	1.58	< LOD	< LOD	0.43	< LOD	3.5	< LOD	< LOD	< LOD	< LOD	3.4	0.87	212	0.46
365	SL - Muckros	Pyrite	Output_1_61	< LOD	24.1	27	< LOD	< LOD	1.4	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	1.5	< LOD	< LOD	9.7	0.69
366	SL - Muckros	Pyrite	Output_1_62	< LOD	15	< LOD	< LOD	< LOD	< LOD	< LOD	70	< LOD	< LOD	< LOD	1.3	< LOD	1.1	< LOD	< LOD	< LOD	17.1	5.2
367	SL - Muckros	Pyrite	Output_1_63	45	20	24	< LOD	< LOD	< LOD	< LOD	102	< LOD	< LOD	< LOD	< LOD	< LOD	1.9	< LOD	< LOD	< LOD	2.4	1.45
368	SL - Muckros	Pyrite	Output_1_64	< LOD	< LOD	< LOD	4.7	< LOD	< LOD	< LOD	75	0.72	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
369	SL - Muckros	Pyrite	Output_1_65	< LOD	< LOD	43	< LOD	140	< LOD	< LOD	79	< LOD	1.5	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	3.2	0.53
370	SL - Muckros	Pyrite	Output_1_66	58	< LOD	< LOD	14	< LOD	< LOD	< LOD	170	< LOD	< LOD	8	< LOD	9	< LOD	< LOD	4.9	< LOD	< LOD	< LOD
371	SL - Muckros	Pyrite	Output_1_67	< LOD	< LOD	26	4.5	110	< LOD	< LOD	40	1.2	0.67	< LOD	< LOD	5.9	< LOD	< LOD	< LOD	< LOD	5.7	0.3
372	SL - Muckros	Pyrite	Output_1_68	40	36	64	12.5	< LOD	< LOD	< LOD	70	1.3	6.1	< LOD	< LOD	5.2	< LOD	< LOD	< LOD	< LOD	4.8	< LOD
373	SL - Muckros	Pyrite	Output_1_69	< LOD	40	82	19.6	< LOD	< LOD	< LOD	59	< LOD	5	< LOD	< LOD	5.8	< LOD	< LOD	< LOD	< LOD	5.1	0.87
374	SL - Muckros	Pyrite	Output_1_70	< LOD	45	75	47	< LOD	2.9	48	< LOD	0.79	11.9	< LOD	< LOD	< LOD	< LOD	< LOD	6.2	< LOD	20.2	3.4
375	SL - Muckros	Pyrite	Output_1_71	36	44	79	6	< LOD	< LOD	< LOD	< LOD	< LOD	1.41	< LOD	< LOD	8.4	1.7	< LOD	< LOD	< LOD	1.4	< LOD
376	SL - Muckros	Pyrite	Output_1_72	55	40	51	10	< LOD	< LOD	< LOD	58	< LOD	1.07	12	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	1.8	0.39
377	SL - Muckros	Pyrite	Output_1_73	63	12	< LOD	< LOD	< LOD	1.1	< LOD	< LOD	< LOD	0.95	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	1.1
378	SL - Muckros	Pyrite	Output_1_74	< LOD	13	69	6.3	< LOD	1.3	< LOD	< LOD	< LOD	1.81	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.56	< LOD
379	SL - Muckros	Pyrite	Output_1_75	< LOD	45	< LOD	13	< LOD	6.4	< LOD	200	< LOD	4.3	26	< LOD	< LOD	0.36	< LOD	< LOD	< LOD	11.6	< LOD
380	SL - Muckros	Pyrite	Output_1_76	110	66	60	36	< LOD	3.7	147	< LOD	< LOD	10.7	< LOD	< LOD	< LOD	< LOD	3	7	< LOD	36	7.7
381	SL - Muckros	Pyrite	Output_1_77	33	71	63	22	100	3	13.1	< LOD	< LOD	6.7	< LOD	< LOD	< LOD	< LOD	2.7	< LOD	< LOD	23.8	0.72
382	SL - Muckros	Pyrite	Output_1_78	< LOD	31	54	< LOD	< LOD	< LOD	< LOD	110	< LOD	2.6	< LOD	< LOD	10	< LOD	1.9	< LOD	0.36	5.1	< LOD
383	SL - Muckros	Pyrite	Output_1_79	< LOD	53	32	4.1	< LOD	< LOD	13.6	< LOD	< LOD	1.9	6	< LOD	11	1	< LOD	< LOD	< LOD	21.7	0.71
384	SL - Muckros	Pyrite	Output_1_80	< LOD	40.7	120	4.7	< LOD	< LOD	< LOD	< LOD	< LOD	2.3	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	3.9	< LOD
385	SL - Muckros	Pyrite	Output_1_81	< LOD	17	< LOD	17	130	1.1	< LOD	< LOD	< LOD	5.3	< LOD	< LOD	< LOD	6	< LOD	< LOD	< LOD	9.4	< LOD
386	SL - Muckros	Pyrite	Output_1_82	< LOD	185	177	66	< LOD	4.6	46	< LOD	< LOD	14.2	< LOD	< LOD	< LOD	3.8	< LOD	< LOD	1.6	36	1.14
387	SL - Muckros	Pyrite	Output_1_83	67	95	44	30	< LOD	< LOD	45	< LOD	< LOD	5.7	< LOD	< LOD	20	< LOD	< LOD	< LOD	< LOD	19.1	4.2
388	SL - Muckros	Pyrite	Output_1_84	< LOD	36	111	28	< LOD	2.4	38	< LOD	< LOD	11.1	< LOD	< LOD	< LOD	0.21	1.6	< LOD	< LOD	24.3	2.5
389	SL - Muckros	Pyrite	Output_1_85	< LOD	39	69	13.6	< LOD	< LOD	< LOD	94	< LOD	1.2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	2.3	< LOD
390	SL - Muckros	Pyrite	Output_1_86	< LOD	15	45	12.2	< LOD	< LOD	< LOD	70	0.86	1.9	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	3.7	< LOD
391	SL - Muckros	Pyrite	Output_1_87	56	18	47	< LOD	< LOD	2	< LOD	170	< LOD	5.6	< LOD	< LOD	12	1.4	< LOD	< LOD	< LOD	9	0.69
392	SL - Muckros	Pyrite	Output_1_88	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.84	< LOD	2.6	< LOD	4.6	< LOD	< LOD	2.7	< LOD	2.9	< LOD
393	SL - Muckros	Pyrite	Output_1_89	< LOD	< LOD	< LOD	7.2	< LOD	1.6	< LOD	30	< LOD	5.7	< LOD	< LOD	< LOD	1.1	< LOD	3.6	< LOD	2.5	0.37
394	SL - Muckros	Pyrite	Output_1_90	< LOD	< LOD	18	10.9	< LOD	< LOD	10	50	< LOD	2.1	< LOD	< LOD	< LOD	2.1	< LOD	< LOD	< LOD	1.65	< LOD
395	SL - Muckros	Pyrite	Output_1_1	< LOD	334	1030	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.72	< LOD	< LOD	3.1	< LOD	< LOD	< LOD	< LOD	1.33	< LOD
396	SL - Muckros	Pyrite	Output_1_2	< LOD	313	958	8	< LOD	< LOD	< LOD	< LOD	< LOD	1.17	< LOD	1.6	< LOD	< LOD	< LOD	< LOD	0.56	15.1	1.27
397	SL - Muckros	Pyrite	Output_1_3	30	450	540	31	80	0.97	< LOD	< LOD	< LOD	6	2.5	1.6	< LOD	0.55	< LOD	< LOD	< LOD	61	8.6
398	SL - Muckros	Pyrite	Output_1_4	< LOD	59	101	5.4	< LOD	0.41	< LOD	< LOD	< LOD	1.48	1.7	1.01	< LOD	< LOD	< LOD	1.4	0.28	4.2	0.48
399	SL - Muckros	Pyrite	Output_1_5	< LOD	298	814	8.5	< LOD	< LOD	< LOD	< LOD	< LOD	0.9	1.65	< LOD	< LOD	< LOD	< LOD	< LOD	0.27	2.8	< LOD
400	SL - Muckros	Pyrite	Output_1_6	< LOD	142	286	6.4	< LOD	< LOD	< LOD	< LOD	0.44	1.26	< LOD	< LOD	3.6	< LOD	< LOD	< LOD	< LOD	5	0.31

Number	Phase tested	Mineral	Code	Mn (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Ga (ppm)	As (ppm)	Se (ppm)	Mo (ppm)	Ag (ppm)	Sn (ppm)	Sb (ppm)	Te (ppm)	W (ppm)	Au (ppm)	Hg (ppm)	Tl (ppm)	Pb (ppm)	Bi (ppm)
401	SL - Muckros	Pyrite	Output_1_7	< LOD	197	466	10.7	< LOD	< LOD	< LOD	< LOD	< LOD	0.62	< LOD	< LOD	3	< LOD	< LOD	< LOD	0.32	2.09	0.31
402	SL - Muckros	Pyrite	Output_1_8	< LOD	328	586	13.7	< LOD	< LOD	< LOD	< LOD	0.28	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.39	6.3	0.4
403	SL - Muckros	Pyrite	Output_1_9	< LOD	238	751	20.6	< LOD	< LOD	< LOD	< LOD	0.15	1.46	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.91	4.7	< LOD
404	SL - Muckros	Pyrite	Output_1_10	< LOD	< LOD	273	930	206	< LOD	< LOD	< LOD	< LOD	13	2.5	< LOD	5.2	< LOD	< LOD	< LOD	0.41	42	0.41
405	SL - Muckros	Pyrite	Output_1_11	< LOD	459	1240	34.7	< LOD	< LOD	< LOD	< LOD	< LOD	0.91	< LOD	0.95	< LOD	< LOD	< LOD	< LOD	0.35	24.4	1.49
406	SL - Muckros	Pyrite	Output_1_12	< LOD	327	1049	17.4	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	47	< LOD
407	SL - Muckros	Pyrite	Output_1_13	< LOD	< LOD	< LOD	< LOD	< LOD	9	< LOD	< LOD	< LOD	< LOD	3.1	< LOD	6.2	1.6	< LOD	< LOD	< LOD	2.07	< LOD
408	SL - Muckros	Pyrite	Output_1_14	< LOD	< LOD	< LOD	4.5	< LOD	< LOD	< LOD	< LOD	0.2	< LOD	2.4	< LOD	< LOD	< LOD	< LOD	< LOD	0.36	< LOD	< LOD
409	SL - Muckros	Pyrite	Output_1_15	< LOD	13	28	< LOD	< LOD	< LOD	< LOD	< LOD	1.01	< LOD	< LOD	< LOD	2.7	< LOD	< LOD	3	0.61	31	< LOD
410	SL - Muckros	Pyrite	Output_1_16	< LOD	< LOD	31	5	< LOD	< LOD	< LOD	< LOD	0.41	< LOD	1.8	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	1.6	< LOD
411	SL - Muckros	Pyrite	Output_1_17	34	< LOD	< LOD	< LOD	< LOD	1.08	< LOD	< LOD	1.01	0.67	2.3	< LOD	< LOD	< LOD	1.47	< LOD	< LOD	< LOD	< LOD
412	SL - Muckros	Pyrite	Output_1_18	< LOD	< LOD	14	< LOD	< LOD	0.76	< LOD	< LOD	< LOD	1.3	< LOD	1.4	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
413	SL - Muckros	Pyrite	Output_1_19	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	2	< LOD	< LOD	< LOD	< LOD	< LOD	0.28	< LOD	0.24
414	SL - Muckros	Pyrite	Output_1_20	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.78	< LOD	1.9	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
415	SL - Derrylahan	Pyrite	Output_1_1	< LOD	28	300	15.5	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	1	397	< LOD
416	SL - Derrylahan	Pyrite	Output_1_2	< LOD	115	206	46	< LOD	12.9	< LOD	< LOD	< LOD	1.6	< LOD	< LOD	13	< LOD	7.5	< LOD	< LOD	232	1.9
417	SL - Derrylahan	Pyrite	Output_1_3	< LOD	317	549	< LOD	< LOD	< LOD	< LOD	26	< LOD	< LOD	< LOD	< LOD	< LOD	1.04	< LOD	< LOD	1.4	55	< LOD
418	SL - Derrylahan	Pyrite	Output_1_4	< LOD	252	349	12.7	142	< LOD	9.4	36	< LOD	< LOD	< LOD	< LOD	4.1	0.57	< LOD	< LOD	< LOD	94	< LOD
419	SL - Derrylahan	Pyrite	Output_1_5	350	285	710	55	230	< LOD	< LOD	175	< LOD	1.33	< LOD	< LOD	< LOD	0.45	< LOD	< LOD	3.4	164	0.5
420	SL - Derrylahan	Pyrite	Output_1_6	< LOD	249	562	< LOD	< LOD	5.5	< LOD	< LOD	< LOD	2.4	< LOD	< LOD	< LOD	2.4	< LOD	< LOD	4.1	133	1.9
421	SL - Derrylahan	Pyrite	Output_1_7	< LOD	239	840	17.9	125	< LOD	< LOD	52	< LOD	2.9	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	3.9	30.8	< LOD
422	SL - Derrylahan	Pyrite	Output_1_8	< LOD	550	1290	38	< LOD	< LOD	< LOD	56	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	7.4	54	0.56
423	SL - Derrylahan	Pyrite	Output_1_9	< LOD	84	314	6.7	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.21	< LOD	< LOD	1.2	< LOD	1.25
424	SL - Derrylahan	Pyrite	Output_1_10	< LOD	117	403	< LOD	< LOD	< LOD	< LOD	36	< LOD	< LOD	< LOD	< LOD	< LOD	0.38	< LOD	< LOD	1.1	47.1	6.2
425	SL - Derrylahan	Pyrite	Output_1_11	< LOD	158	421	7.1	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	5.3	36.5	1.52
426	SL - Derrylahan	Pyrite	Output_1_12	< LOD	315	700	15.3	< LOD	< LOD	< LOD	21	< LOD	2.06	< LOD	< LOD	5.2	0.34	< LOD	< LOD	5.6	76	2.28
427	SL - Derrylahan	Pyrite	Output_1_13	25	263	291	44	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	2.3	4.8	1.3
428	SL - Derrylahan	Pyrite	Output_1_14	< LOD	191	491	124	< LOD	11.2	< LOD	< LOD	< LOD	1.77	< LOD	2.3	< LOD	< LOD	< LOD	< LOD	6.5	176	1.11
429	SL - Derrylahan	Pyrite	Output_1_15	< LOD	143	1350	178	140	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	2.9	3.1	2.42
430	SL - Derrylahan	Pyrite	Output_1_16	< LOD	178	294	8.4	< LOD	< LOD	< LOD	< LOD	< LOD	2.31	< LOD	< LOD	4.5	< LOD	< LOD	< LOD	1.6	38.6	3.82
431	SL - Derrylahan	Pyrite	Output_1_17	< LOD	391	910	8.5	< LOD	0.82	< LOD	< LOD	< LOD	2.7	3.1	< LOD	< LOD	< LOD	< LOD	3.1	1.8	141	0.9
432	SL - Derrylahan	Pyrite	Output_1_18	< LOD	229	515	4.9	< LOD	1.1	< LOD	23	0.37	2.11	< LOD	< LOD	< LOD	0.9	< LOD	< LOD	1.4	62	0.76
433	SL - Derrylahan	Pyrite	Output_1_19	< LOD	98	407	14.6	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	6.1	< LOD	< LOD	< LOD	1.6	74	0.24
434	SL - Derrylahan	Pyrite	Output_1_20	< LOD	252	760	8.4	< LOD	0.93	< LOD	< LOD	< LOD	1.96	< LOD	< LOD	5.7	< LOD	< LOD	< LOD	1.3	54.3	1.09
435	SL - Derrylahan	Pyrite	Output_1_21	< LOD	20	< LOD	38	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	1.52	1200	0.79
436	SL - Derrylahan	Pyrite	Output_1_22	41	< LOD	< LOD	35	< LOD	1.4	< LOD	< LOD	< LOD	1.09	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	1.2	1090	0.78
437	SL - Derrylahan	Pyrite	Output_1_23	< LOD	150	412	7.3	< LOD	< LOD	< LOD	< LOD	< LOD	1.62	< LOD	< LOD	5.1	< LOD	< LOD	3	0.79	28.6	0.55
438	SL - Derrylahan	Pyrite	Output_1_24	< LOD	107	515	13.8	< LOD	< LOD	< LOD	< LOD	< LOD	4.7	< LOD	< LOD	6.5	< LOD	< LOD	< LOD	0.9	113	1.72
439	SL - Derrylahan	Pyrite	Output_1_25	< LOD	< LOD	28	39	< LOD	1	< LOD	< LOD	< LOD	1.8	< LOD	< LOD	11.8	< LOD	< LOD	< LOD	1.4	910	< LOD
440	SL - Derrylahan	Pyrite	Output_1_26	< LOD	203	540	16	< LOD	< LOD	< LOD	< LOD	< LOD	3.1	< LOD	< LOD	6	< LOD	< LOD	< LOD	< LOD	104	0.52
441	SL - Derrylahan	Pyrite	Output_1_27	< LOD	232	500	5.5	< LOD	< LOD	< LOD	< LOD	< LOD	1.32	< LOD	< LOD	3.8	< LOD	< LOD	< LOD	< LOD	42.7	0.61
442	SL - Derrylahan	Pyrite	Output_1_28	< LOD	196	655	12	< LOD	< LOD	< LOD	< LOD	< LOD	2.8	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.79	107	1.89
443	SL - Derrylahan	Pyrite	Output_1_29	< LOD	< LOD	< LOD	32	< LOD	< LOD	< LOD	< LOD	< LOD	1.03	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	1030	< LOD
444	SL - Derrylahan	Pyrite	Output_1_30	< LOD	259	453	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.79	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	24.5	< LOD
445	SL - Derrylahan	Pyrite	Output_1_21	< LOD	181	352	73.8	< LOD	0.81	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.031	< LOD	< LOD	< LOD	6.8	< LOD
446	SL - Derrylahan	Pyrite	Output_1_22	< LOD	185	420	4.7	< LOD	1	< LOD	< LOD	< LOD	2.8	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	53	< LOD
447	SL - Derrylahan	Pyrite	Output_1_23	< LOD	186	810	8	< LOD	< LOD	< LOD	< LOD	< LOD	2.35	< LOD	0.81	< LOD	< LOD	< LOD	< LOD	< LOD	11	< LOD
448	SL - Derrylahan	Pyrite	Output_1_24	< LOD	< LOD	< LOD	65	< LOD	0.39	< LOD	< LOD	0.35	3.7	< LOD	3.3	< LOD	< LOD	< LOD	< LOD	0.76	1010	0.65
449	SL - Derrylahan	Pyrite	Output_1_25	< LOD	< LOD	42	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.98	< LOD	1	< LOD	< LOD	< LOD	< LOD	0.25	0.97	< LOD
450	SL - Derrylahan	Pyrite	Output_1_26	< LOD	259	840	31	< LOD	< LOD	< LOD	< LOD	< LOD	5.5	< LOD	0.88	< LOD	< LOD	< LOD	< LOD	0.52	61	1.72

Number	Phase tested	Mineral	Code	Mn (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Ga (ppm)	As (ppm)	Se (ppm)	Mo (ppm)	Ag (ppm)	Sn (ppm)	Sb (ppm)	Te (ppm)	W (ppm)	Au (ppm)	Hg (ppm)	Tl (ppm)	Pb (ppm)	Bi (ppm)
451	SL - Derrylahan	Pyrite	Output_1_27	< LOD	208	1260	25.2	< LOD	< LOD	< LOD	< LOD	< LOD	8.8	< LOD	1.67	< LOD	< LOD	< LOD	< LOD	0.3	38.1	0.91
452	SL - Derrylahan	Pyrite	Output_1_28	390	19	17	< LOD	300	6.1	< LOD	< LOD	< LOD	5.3	< LOD	3.8	< LOD	< LOD	< LOD	< LOD	0.35	168	< LOD
453	SL - Derrylahan	Pyrite	Output_1_29	< LOD	280	600	11	< LOD	0.42	< LOD	< LOD	< LOD	7.2	< LOD	0.98	5.4	< LOD	< LOD	< LOD	< LOD	35.1	2.12
454	SL - Derrylahan	Pyrite	Output_1_30	< LOD	< LOD	23	4.7	< LOD	0.62	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.1	< LOD	< LOD	0.31	59	< LOD
455	SL - Derrylahan	Pyrite	Output_1_31	< LOD	7	< LOD	43	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	9.6	3.4	< LOD	< LOD	< LOD	0.53	1930	< LOD
456	SL - Derrylahan	Pyrite	Output_1_32	42	83	442	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	5.7	< LOD	2.6	< LOD	0.24	0.76	< LOD	0.41	72	0.27
457	SL - Derrylahan	Pyrite	Output_1_33	< LOD	< LOD	< LOD	62	< LOD	< LOD	9	1800	< LOD	6.5	< LOD	4.5	< LOD	0.13	< LOD	4.4	0.91	2030	0.48
458	SL - Derrylahan	Pyrite	Output_1_34	< LOD	372	960	41.9	< LOD	< LOD	< LOD	< LOD	< LOD	6.6	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.51	163	2.08
459	SL - Derrylahan	Pyrite	Output_1_35	25	183	440	14	< LOD	< LOD	< LOD	< LOD	< LOD	1.92	< LOD	4.2	< LOD	< LOD	< LOD	< LOD	0.49	142	1.98
460	SL - Derrylahan	Pyrite	Output_1_36	51	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	1.6	5.1	10.1	< LOD	0.92	< LOD	0.55	16.7	< LOD
461	SL - Derrylahan	Pyrite	Output_1_37	< LOD	61	397	11.3	< LOD	< LOD	< LOD	< LOD	< LOD	2.8	3.7	4.9	< LOD	< LOD	< LOD	< LOD	< LOD	12.5	0.55
462	SL - Derrylahan	Pyrite	Output_1_38	< LOD	< LOD	320	22	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	2.3	8.6	< LOD	< LOD	0.9	< LOD	0.72	1320	< LOD
463	SL - Derrylahan	Pyrite	Output_1_39	69	58	490	330	70	< LOD	< LOD	< LOD	< LOD	4.7	< LOD	8.5	< LOD	0.029	< LOD	< LOD	0.78	177	5.4
464	SL - Derrylahan	Pyrite	Output_1_40	22	125	491	15.4	< LOD	< LOD	6	< LOD	< LOD	8	< LOD	2.2	< LOD	0.22	< LOD	< LOD	0.81	191	1.2
465	Falcarragh Po	Pyrrhotite	Output_1_21	< LOD	540	1490	< LOD	< LOD	24	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	7.3	103	13.7
466	Falcarragh Po	Pyrrhotite	Output_1_22	< LOD	780	1950	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	27	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	108	17.7
467	Falcarragh Po	Pyrrhotite	Output_1_23	< LOD	650	2760	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	57	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	173	62
468	Falcarragh Po	Pyrrhotite	Output_1_24	< LOD	592	1590	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	16.1	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	11.3	12.4
469	Falcarragh Po	Pyrrhotite	Output_1_25	< LOD	558	1890	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	63	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
470	Falcarragh Po	Pyrrhotite	Output_1_26	< LOD	556	1640	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	19.7	< LOD	< LOD	< LOD	< LOD	< LOD	2.6	42	11.4
471	Falcarragh Po	Pyrrhotite	Output_1_27	540	547	2570	< LOD	< LOD	115	< LOD	< LOD	< LOD	8.6	30	13.2	< LOD	13	< LOD	< LOD	4	161	5
472	Falcarragh Po	Pyrrhotite	Output_1_28	< LOD	511	3050	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	14.4	5.4
473	Falcarragh Po	Pyrrhotite	Output_1_29	< LOD	603	2140	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	28	< LOD	< LOD	2.7	< LOD	< LOD	2.5	12.5	5.3
474	Falcarragh Po	Pyrrhotite	Output_1_30	< LOD	528	1910	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	5.2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
475	Falcarragh Po	Pyrrhotite	Output_1_31	< LOD	544	2530	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	29.6	< LOD
476	Falcarragh Po	Pyrrhotite	Output_1_32	< LOD	615	1290	42	< LOD	< LOD	< LOD	< LOD	< LOD	8.1	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	12.8	3.2
477	Falcarragh Po	Pyrrhotite	Output_1_33	< LOD	623	1700	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	14	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
478	Falcarragh Po	Pyrrhotite	Output_1_34	< LOD	538	1308	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	4.6	2.56
479	Falcarragh Po	Pyrrhotite	Output_1_35	< LOD	538	1710	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	19	< LOD	< LOD	< LOD	< LOD	13.3	1.94
480	Falcarragh Po	Pyrrhotite	Output_1_36	< LOD	542	1540	< LOD	< LOD	< LOD	< LOD	< LOD	1.6	< LOD	32	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	46	15.5
481	Falcarragh Po	Pyrrhotite	Output_1_37	< LOD	600	1660	< LOD	< LOD	< LOD	< LOD	< LOD	8	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	24.2	< LOD
482	Falcarragh Po	Pyrrhotite	Output_1_38	< LOD	450	2390	< LOD	< LOD	< LOD	< LOD	< LOD	2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	370	38
483	Falcarragh Po	Pyrrhotite	Output_1_39	< LOD	630	2850	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
484	Falcarragh Po	Pyrrhotite	Output_1_40	< LOD	639	2160	< LOD	< LOD	< LOD	< LOD	< LOD	1.7	< LOD	40	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	51	< LOD
485	Falcarragh Po	Pyrrhotite	Output_1_41	< LOD	712	2100	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	2.3	33.8	8.6
486	Falcarragh Po	Pyrrhotite	Output_1_42	< LOD	631	2420	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	3.7	13.1	5.1
487	Falcarragh Po	Pyrrhotite	Output_1_43	510	586	2810	< LOD	< LOD	19	< LOD	< LOD	< LOD	< LOD	35	< LOD	< LOD	< LOD	< LOD	< LOD	2.6	15.9	< LOD
488	Falcarragh Po	Pyrrhotite	Output_1_44	< LOD	632	1940	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	2.7	< LOD	< LOD
489	Falcarragh Po	Pyrrhotite	Output_1_45	< LOD	571	2230	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	39	< LOD	< LOD	< LOD	< LOD	< LOD	2.5	< LOD	< LOD
490	Falcarragh Po	Pyrrhotite	Output_1_46	< LOD	573	2020	< LOD	< LOD	< LOD	< LOD	< LOD	6.9	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	59	18.9
491	Falcarragh Po	Pyrrhotite	Output_1_47	< LOD	577	1690	< LOD	< LOD	< LOD	< LOD	< LOD	3.9	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
492	Falcarragh Po	Pyrrhotite	Output_1_48	< LOD	474	3140	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	19.8
493	Falcarragh Po	Pyrrhotite	Output_1_49	< LOD	559	2620	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	11.7	141	< LOD
494	Falcarragh Po	Pyrrhotite	Output_1_50	< LOD	680	1650	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
495	Falcarragh Po	Pyrrhotite	Output_1_1	910	450	2820	< LOD	< LOD	33	< LOD	< LOD	< LOD	< LOD	< LOD	8.9	32	< LOD	6.9	< LOD	1.7	52	14.8
496	Falcarragh Po	Pyrrhotite	Output_1_2	< LOD	432	2330	< LOD	23000	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	11.1	4.7
497	Falcarragh Po	Pyrrhotite	Output_1_3	< LOD	432	3130	< LOD	< LOD	45	< LOD	< LOD	< LOD	7.6	< LOD	< LOD	84	< LOD	12.4	< LOD	2.7	113	91
498	Falcarragh Po	Pyrrhotite	Output_1_4	< LOD	348	2510	< LOD	< LOD	2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
499	Falcarragh Po	Pyrrhotite	Output_1_5	< LOD	456	2860	< LOD	< LOD	3.7	< LOD	< LOD	0.61	6.8	< LOD	< LOD	< LOD	< LOD	7.3	< LOD	< LOD	49.5	14.9
500	Falcarragh Po	Pyrrhotite	Output_1_6	< LOD	433	2490	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	10.2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	2.4	69	22.4

Number	Phase tested	Mineral	Code	Mn (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Ga (ppm)	As (ppm)	Se (ppm)	Mo (ppm)	Ag (ppm)	Sn (ppm)	Sb (ppm)	Te (ppm)	W (ppm)	Au (ppm)	Hg (ppm)	Tl (ppm)	Pb (ppm)	Bi (ppm)
501	Falcarragh Po	Pyrrhotite	Output_1_7	< LOD	367	2920	< LOD	< LOD	4.1	< LOD	< LOD	< LOD	7.3	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	2700	25
502	Falcarragh Po	Pyrrhotite	Output_1_8	< LOD	412	2980	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.98
503	Falcarragh Po	Pyrrhotite	Output_1_9	< LOD	366	3480	< LOD	< LOD	< LOD	< LOD	< LOD	0.00129	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	11.7	6.8
504	Falcarragh Po	Pyrrhotite	Output_1_10	< LOD	515	4060	< LOD	< LOD	< LOD	< LOD	< LOD	0.19	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	9.4	4.6
505	Falcarragh Po	Pyrrhotite	Output_1_11	< LOD	470	3000	< LOD	< LOD	11.2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	8.4	2.2
506	Falcarragh Po	Pyrrhotite	Output_1_12	< LOD	551	1450	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.25	< LOD	< LOD	1.5	15.5	14.5
507	Falcarragh Po	Pyrrhotite	Output_1_13	< LOD	527	3420	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
508	Falcarragh Po	Pyrrhotite	Output_1_14	< LOD	523	3090	< LOD	< LOD	4.4	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	14.8	18.6
509	Falcarragh Po	Pyrrhotite	Output_1_15	< LOD	474	3300	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	12.9	28	0.39	< LOD	< LOD	2	17.4	9.5
510	Falcarragh Po	Pyrrhotite	Output_1_16	< LOD	600	3640	< LOD	< LOD	6.5	< LOD	< LOD	< LOD	6.7	< LOD	13.9	< LOD	< LOD	< LOD	< LOD	< LOD	31	14.3
511	Falcarragh Po	Pyrrhotite	Output_1_17	< LOD	679	2960	< LOD	1700	3.9	< LOD	< LOD	< LOD	6.1	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	3.9	111	17.6
512	Falcarragh Po	Pyrrhotite	Output_1_18	< LOD	524	3250	< LOD	< LOD	9.5	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.22	< LOD	< LOD	< LOD	< LOD	5.7
513	Falcarragh Po	Pyrrhotite	Output_1_19	< LOD	570	2860	36	< LOD	< LOD	< LOD	< LOD	1.4	4.4	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
514	Falcarragh Po	Pyrrhotite	Output_1_20	< LOD	726	3090	< LOD	< LOD	3.6	< LOD	< LOD	< LOD	4.9	< LOD	7.7	< LOD	< LOD	< LOD	< LOD	< LOD	12.5	9.7
515	Cononish PyOre	Pyrite	Con1	160	34	41	1500	< LOD	1	16	< LOD	2	90	< LOD	29	440	< LOD	8.2	< LOD	< LOD	99000	< LOD
516	Cononish PyOre	Pyrite	Con2	17	< LOD	78	8.7	< LOD	0.56	5.5	< LOD	< LOD	0.89	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.21	6.7	< LOD
517	Cononish PyOre	Pyrite	Con3	31	9.2	610	42	< LOD	< LOD	15	< LOD	< LOD	680	7.4	8.3	630	0.9	150	< LOD	< LOD	98	< LOD
518	Cononish PyOre	Pyrite	Con4	34	6	< LOD	47	< LOD	< LOD	< LOD	< LOD	15.3	206	< LOD	6.1	253	< LOD	14.7	12.1	0.29	147	< LOD
519	Cononish PyOre	Pyrite	Con5	28	33	27	77	< LOD	< LOD	17	< LOD	0.11	6	< LOD	8.7	7.9	0.06	0.68	< LOD	0.56	45.4	< LOD
520	Cononish PyOre	Pyrite	Con6	< LOD	7	322	14800	100	0.74	< LOD	2000	< LOD	740	60	35	980	< LOD	6.6	5	0.43	278	< LOD
521	Cononish PyOre	Pyrite	Con7	75	56	48	34000	< LOD	0.07	38	< LOD	< LOD	49000	12	45	32900	< LOD	73	< LOD	1.5	389	< LOD
522	Cononish PyOre	Pyrite	Con8	12	< LOD	< LOD	22	< LOD	< LOD	41	< LOD	0.05	380	4	3.7	320	< LOD	12.1	1.7	0.22	20.3	< LOD
523	Cononish PyOre	Pyrite	Con9	14	< LOD	17	13.5	< LOD	< LOD	27	< LOD	0.04	2.1	< LOD	2.1	< LOD	< LOD	< LOD	1.7	< LOD	4.2	< LOD
524	Cononish PyOre	Pyrite	Con10	19	< LOD	< LOD	1940	< LOD	0.55	< LOD	< LOD	0.019	146	4	10.1	172	< LOD	45	4.5	< LOD	54	< LOD
525	Cononish PyOre	Pyrite	Con11	25	12.6	22	26000	< LOD	0.61	9	< LOD	0.39	158	< LOD	14.4	250	< LOD	2.4	< LOD	1.02	116	< LOD
526	Cononish PyOre	Pyrite	Con12	60	< LOD	< LOD	26	< LOD	0.56	5	< LOD	< LOD	1.8	< LOD	1.2	7.2	0.013	< LOD	< LOD	< LOD	36	3.7
527	Cononish PyOre	Pyrite	Con13	< LOD	< LOD	< LOD	10.2	< LOD	< LOD	21	< LOD	< LOD	1.8	< LOD	2.2	< LOD	< LOD	< LOD	< LOD	0.26	9.2	0.61
528	Cononish PyOre	Pyrite	Con14	< LOD	< LOD	< LOD	19	< LOD	< LOD	< LOD	< LOD	< LOD	4.5	4.9	1.4	5.1	< LOD	< LOD	< LOD	< LOD	7	0.18
529	Cononish PyOre	Pyrite	Con15	< LOD	< LOD	< LOD	18	< LOD	< LOD	< LOD	< LOD	0.12	7.3	< LOD	4	9.6	< LOD	2.4	< LOD	< LOD	26.5	< LOD
530	Cononish PyOre	Pyrite	Con16	< LOD	< LOD	25	10100	< LOD	< LOD	< LOD	630	0.11	1480	< LOD	8	430	< LOD	550	< LOD	< LOD	21.2	0.4
531	Cononish PyOre	Pyrite	Con17	< LOD	18	< LOD	< LOD	< LOD	< LOD	< LOD	580	< LOD	82	< LOD	< LOD	58	0.1	12.9	< LOD	0.46	3.6	< LOD
532	Cononish PyOre	Pyrite	Con18	< LOD	28	< LOD	4600	< LOD	< LOD	18	< LOD	< LOD	3400	< LOD	16.1	2100	< LOD	1900	< LOD	< LOD	104	1.49
533	Cononish PyOre	Pyrite	Con19	< LOD	42	350	42000	360	1.3	< LOD	< LOD	0.62	26700	< LOD	12	450	0.35	46000	30	1.4	37.3	0.35
534	Cononish PyOre	Pyrite	Con20	< LOD	4	31	25	< LOD	< LOD	19.4	360	0.82	19700	< LOD	3	7800	0.32	2300	< LOD	< LOD	24.6	< LOD
535	Cononish PyOre	Pyrite	Con21	8	63	95	30000	< LOD	< LOD	17	< LOD	0.33	5400	< LOD	24.3	11300	< LOD	50	< LOD	0.65	66	1.2
536	Cononish PyOre	Pyrite	Con22	< LOD	< LOD	55	82	< LOD	< LOD	23	300	0.66	25800	< LOD	12.9	17500	< LOD	144	< LOD	0.32	44.7	1.69
537	Cononish PyOre	Pyrite	Con23	9	23	17	42	80	< LOD	< LOD	1100	< LOD	14	< LOD	2.9	24	< LOD	2.8	< LOD	0.35	7.4	< LOD
538	Cononish PyOre	Pyrite	Con24	31	138	< LOD	< LOD	< LOD	< LOD	< LOD	600	0.31	2.1	< LOD	1.7	9.4	< LOD	0.87	< LOD	0.36	17.2	< LOD
539	Cononish PyOre	Pyrite	Con25	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	800	0.051	2.4	< LOD	1.6	< LOD	< LOD	< LOD	1.6	< LOD	1.9	< LOD
540	Cononish PyOre	Pyrite	Con26	< LOD	< LOD	113	440	< LOD	< LOD	14	< LOD	< LOD	1640	< LOD	3	1240	0.22	24	< LOD	< LOD	12.4	0.173
541	Cononish PyOre	Pyrite	Con27	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	19	< LOD	< LOD	1.47	< LOD	1	< LOD	< LOD	1	< LOD	0.37	2.3	< LOD
542	Cononish PyOre	Pyrite	Con28	73	< LOD	15	17	< LOD	< LOD	19	< LOD	< LOD	4.8	< LOD	1.8	5.5	< LOD	0.96	< LOD	< LOD	8	< LOD
543	Cononish PyOre	Pyrite	Con29	< LOD	30	44	9.5	70	< LOD	< LOD	2100	< LOD	61	< LOD	2.7	86	0.013	1.2	2.5	< LOD	5.2	< LOD
544	Cononish PyOre	Pyrite	Con30	< LOD	540	53	6	< LOD	< LOD	< LOD	< LOD	< LOD	1.3	< LOD	1.1	4.6	< LOD	0.79	< LOD	0.46	< LOD	< LOD
545	Cononish PyOre	Pyrite	Con31	< LOD	58	< LOD	6.4	53	< LOD	< LOD	< LOD	< LOD	0.73	< LOD	< LOD	5.8	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
546	Cononish PyOre	Pyrite	Con32	< LOD	8	92	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	1200	< LOD	2.5	500	< LOD	< LOD	< LOD	< LOD	0.9	< LOD
547	Cononish PyOre	Pyrite	Con33	< LOD	68	208	321	< LOD	< LOD	< LOD	< LOD	0.22	38	< LOD	8	50	< LOD	5.7	< LOD	< LOD	39.1	0.66
548	Cononish PyOre	Pyrite	Con34	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.54	< LOD	< LOD	3.7	< LOD	1	< LOD	< LOD	1.04	< LOD
549	Cononish PyOre	Pyrite	Con35	8	< LOD	245	13.3	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	1.01	7.4	0.07	< LOD	< LOD	< LOD	2.77	< LOD
550	Cononish PyOre	Pyrite	Con36	16	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	1.16	< LOD	0.69	< LOD	< LOD	0.65	< LOD	< LOD	< LOD	< LOD

Number	Phase tested	Mineral	Code	Mn (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Ga (ppm)	As (ppm)	Se (ppm)	Mo (ppm)	Ag (ppm)	Sn (ppm)	Sb (ppm)	Te (ppm)	W (ppm)	Au (ppm)	Hg (ppm)	Tl (ppm)	Pb (ppm)	Bi (ppm)
551	Cononish PyOre	Pyrite	Con37	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	310	< LOD	< LOD	< LOD	1.42	< LOD	< LOD	< LOD	< LOD	< LOD	1.52	< LOD
552	Cononish PyOre	Pyrite	Con38	2	7	< LOD	5.6	< LOD	< LOD	< LOD	< LOD	< LOD	1.8	< LOD	1.85	< LOD	< LOD	0.78	< LOD	< LOD	2.09	< LOD
553	Cononish PyOre	Pyrite	Con39	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	570	0.33	1.11	< LOD	0.87	< LOD	< LOD	< LOD	< LOD	0.3	0.59	< LOD
554	Cononish PyOre	Pyrite	Con40	48	67	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	2.44	2.5	< LOD	1.08	< LOD	< LOD	< LOD	< LOD
555	Cononish PyOre	Pyrite	Con41	33	8	< LOD	1310	< LOD	0.13	< LOD	1000	0.1	60	< LOD	4.4	52	< LOD	7.6	< LOD	< LOD	35.2	1.78
556	Cononish PyOre	Pyrite	Con42	< LOD	49	402	11900	< LOD	< LOD	< LOD	1500	< LOD	670	< LOD	16.2	510	< LOD	1.5	< LOD	< LOD	29.3	0.83
557	Cononish PyOre	Pyrite	Con43	< LOD	< LOD	327	29	< LOD	< LOD	< LOD	< LOD	< LOD	3.9	< LOD	2.2	7.1	< LOD	< LOD	< LOD	< LOD	4.7	< LOD
558	Cononish PyOre	Pyrite	Con44	25	69	540	1110	< LOD	< LOD	< LOD	< LOD	< LOD	4.3	< LOD	2.6	8.2	< LOD	< LOD	< LOD	0.36	30.3	0.48
559	Cononish PyOre	Pyrite	Con45	31	< LOD	170	23	< LOD	< LOD	17	560	< LOD	1.8	< LOD	3.1	< LOD	< LOD	< LOD	< LOD	< LOD	7.5	< LOD
560	Cononish PyOre	Pyrite	Con46	< LOD	< LOD	238	31	< LOD	< LOD	10	600	< LOD	13.9	< LOD	1	91	< LOD	0.7	< LOD	< LOD	4.2	< LOD
561	Cononish PyOre	Pyrite	Con47	8	8	327	108	< LOD	< LOD	< LOD	360	0.14	24	< LOD	4.8	23	< LOD	2.3	< LOD	< LOD	23.9	0.64
562	Cononish PyOre	Pyrite	Con48	15	< LOD	221	12	< LOD	< LOD	< LOD	< LOD	< LOD	1.7	< LOD	2.8	19	< LOD	1.04	< LOD	0.28	2.06	< LOD
563	Cononish PyOre	Pyrite	Con49	4	< LOD	401	< LOD	< LOD	< LOD	41	< LOD	< LOD	< LOD	< LOD	1.9	17.2	< LOD	< LOD	< LOD	0.48	< LOD	0.16
564	Cononish PyOre	Pyrite	Con50	< LOD	< LOD	< LOD	< LOD	< LOD	0.94	< LOD	< LOD	< LOD	1.5	< LOD	1.09	3.1	< LOD	1.14	< LOD	< LOD	7.8	0.11
565	Cavanacaw PyOre	Pyrite	S3Spot1	< LOD	45.6	11.5	40.8	< LOD	0.089	2300	< LOD	< LOD	35.4	< LOD	60.6	0.21	0.034	4.28	14.3	0.152	43000	< LOD
566	Cavanacaw PyOre	Pyrite	S3Spot2	< LOD	32.9	39.4	54.3	< LOD	0.082	12200	< LOD	0.14	23.6	< LOD	59.3	0.26	0.144	8.07	15.3	0.324	1520	0.024
567	Cavanacaw PyOre	Pyrite	S3Spot3	15	3.2	20.7	44	34	25	311	< LOD	29	13	7.5	32	72	6.2	13	23.6	9	294	1.9
568	Cavanacaw PyOre	Pyrite	S3Spot5	< LOD	0.6	1.3	9.1	< LOD	< LOD	206.6	12	< LOD	< LOD	0.27	2.63	< LOD	< LOD	1.71	12.6	< LOD	80	< LOD
569	Cavanacaw PyOre	Pyrite	S3Spot8	11.1	20	13.6	86	28	1.8	349	< LOD	0.28	12	3.6	36.8	< LOD	0.141	1.49	6	0.11	9500	0.13
570	Cavanacaw PyOre	Pyrite	S3Spot10	3.9	< LOD	< LOD	4.3	< LOD	0.081	7130	18	< LOD	0.35	< LOD	1.28	0.18	0.087	0.64	6.26	< LOD	44	< LOD
571	CT wallrock	Pyrite	Wrock01	66	310	363	n/a	4.1	0.88	990	3.45	0.038	8.1	1.1	1.22	34	0.15	2.7	4.9	0.014	27	41
572	CT wallrock	Pyrite	Wrock02	35	274	1050	n/a	5.6	2.2	101	2.7	0.055	5	0.22	0.28	12.2	0.17	1.79	1.4	0.113	15.5	15.7
573	CT wallrock	Pyrite	Wrock03	3.65	180	890	n/a	1.45	0.0345	19.3	2.75	0.0215	37	0.135	0.055	36.7	0.031	11.7	0.325	0.0105	7.2	9.8
574	CT wallrock	Pyrite	Wrock04	4.4	209	360	n/a	2	0.0385	350	2.55	0.047	6	0.125	1.27	18.1	0.0305	3.85	1.4	0.0115	37.9	20
575	CT wallrock	Pyrite	Wrock05	4.4	257	218	n/a	4.7	0.036	2890	2.6	0.031	0.135	0.12	0.055	4.63	0.041	1.23	0.69	0.012	0.83	1.04
576	CT wallrock	Pyrite	Wrock06	4.6	8	88	n/a	2.35	0.036	2350	2.35	0.0435	0.12	0.145	0.232	2.95	0.065	0.323	0.85	0.014	9.2	2.44
577	CT wallrock	Pyrite	Wrock07	4.65	550	1950	n/a	2.3	0.046	3970	4.85	0.055	0.21	0.18	0.07	7.2	0.05	1.37	1.62	0.013	3.35	8.6
578	CT wallrock	Pyrite	Wrock08	3.95	91	237	n/a	6	0.0295	533	3.45	0.034	0.115	0.145	0.11	0.63	0.055	0.09	0.74	0.0105	0.54	0.31
579	CT wallrock	Pyrite	Wrock09	4	71	120	n/a	8.6	0.086	3030	9	0.0285	0.145	0.165	0.055	1.42	0.0195	0.055	0.385	0.008	1.2	1.7
580	CT wallrock	Pyrite	Wrock10	4.1	18.9	239	n/a	1.6	0.028	241	11	0.029	0.36	0.165	0.96	2	0.02	0.308	0.39	0.008	14.9	3.99