Tracing multiscale mineral system processes through sulfur isotopography

Vikraman Selvaraja, BSc, BSc (Hons)

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Centre for Exploration Targeting
ARC Centre of Excellence in Core to Crust Fluid Systems
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Supervisor: Dr. Marco L. Fiorentini (Principal and Coordinating)
Dr. Campbell T. McCuaig
Dr. Laure Martin
Dr. Franco Pirajno
Abstract

The cycle of sulfur in the earth’s crust is a critical aspect of understanding the sources, pathways and processes governing the formation of many mineral systems. However, the source and transport processes of sulfur, and the thermodynamic conditions which govern them, remain cryptic in many Precambrian terranes. Understanding and clearly delineating the source and transport processes of sulfur gains an added importance in studying gold deposits, as it is well accepted in the literature that gold is transported in the earth’s crust in sulfide ligands.

This thesis seeks to plug this knowledge gap by utilising the mass-independent fractionation of sulfur (MIF-S) as a chemically conservative tracer of Archaean surficially derived sulfur in a variety of Archaean and Paleoproterozoic gold deposits in the West Australian Craton. My natural laboratories to evaluate the contrasting arguments around the source of sulfur and gold in gold deposits are the Paleoproterozoic Glenburgh orogenic gold deposit in the Glenburgh terrane (Chapter 2), 24 Archean orogenic gold deposits in the Yilgarn Craton (Chapter 3) and the Paulsens Archaean sediment hosted gold deposit (Chapter 4, 5).

In all the areas studied, I performed multiple sulfur isotope analysis using a variety of dissolution and in situ techniques and in the Paulsens deposit, this was complemented with trace element analysis of gold bearing and diagenetic pyrite, the study of mineralisation associated fluid inclusions and geochemical transport modelling. Each case study was carefully contextualised within the known regional and cratonic geology and geochronology to develop a clear mineral system based method of understanding the source and transport of sulfur and gold in that mineral system.

My results show that Archaean surficially derived sulfur with a MIF-S anomaly ($\Delta^{33}S$, $\Delta^{36}S$) are a major contributor of sulfur to gold mineralising systems in both the Archaean and the Paleoproterozoic across a wide variety of tectonic environments and through 700 Ma of geological time from 2.7 Ga to 2.0 Ga. Further, the MIF-S signature in all the case studies
presented in this work is invariably a $+\Delta^{33}\text{S}$ signature, which is thought to be derived from sulfur sequestered in Archaean carbonaceous sedimentary rocks. Thus, my work lends significant support to the theory that the gold in many gold mineralising systems is derived from carbonaceous sedimentary rocks, and is transported by a sulfide ligand. The work presented in this thesis thus demonstrates the utility of multiple sulfur isotope analysis and the MIF-S tracer in unravelling key questions in the study of source and transport pathway of fluids, metals and ligands in mineral systems at multiple scales.
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CHAPTER ONE

OVERVIEW and THESIS STRUCTURE

Introduction

The mineral systems framework for understanding the genetic processes leading to the formation of a mineral deposit has created a new context for research in economic geology. This approach to understanding mineralising processes observes that ore deposits are fundamentally small expressions of much larger earth processes that focus mass and energy flux at multiple scales. The mineral systems idea itself was defined by Wyborn et al. (1994) to involve “all the geological factors that control the generation and preservation of mineral deposits... the processes that are involved in mobilising ore component from a source, transporting and accumulating them in a more concentrated form, and then preserving them throughout the subsequent geological history”. This framework was then set out by McCuaig et al. (2010) to define the three fundamental elements in the generation of a mineral deposit, which were initially adopted from the petroleum industry: a source, a pathway and a trap (Fig. 1). The elements interact probabilistically, in that the odds of each stage occurring changes with the previous stage. The inherent complexity in mineral systems is thus accounted for, as the range of possible variations in geodynamic setting, architecture, fluid flow reservoirs, fluid flow drivers, pathways and depositional mechanics can all be seen as probabilistic functions that are interdependent in a scale biased manner.

The dominant paradigm in many economic geology studies is the ‘butterfly collecting’ approach of deposit scale studies of ore bodies. These were dominant in the past because there was a necessity to build up a knowledge base of the key geological characteristics of mineral deposits. However, this approach is less useful when the mineral systems framework is applied.
as it doesn’t ‘stack’ well with different datasets and often has binary predictive functions. The *mineral systems* framework, however, focuses on broad multi-scale geological processes ahead of ore deposit models. It is grounded in a more rigorous theoretical framework, relying on the understanding that probability theory is a much closer approximation to natural systems than binary outcomes.

Figure 1: A pictorial representation of the source-pathway-trap-sink model proposed in ore forming mineral systems. Adapted from McCuaig and Hronsky (2013).
Practical use of this framework in the study of mineral deposits thus requires that particular focus be placed on the drivers and boundary conditions of the overall mineral system at a variety of scales, from geodynamic setting to depositional mechanisms. It also requires that the work done be situated within a broad definition of terrane scale processes (McCuaig et al., 2010). The challenge, however, is that processes cannot be mapped, only the results thereof, which is where the use of geochemistry, specifically isotope geochemistry comes into its element. Stable isotope geochemistry can, due to its sensitivity to thermodynamic conditions, answer fundamental questions about the variation in the processes governing the movement of metals, fluids and ligands from the source through the pathway and into the site of deposition (Fig. 2). This capability thus opens the window for the development of new isotopic tools to be applied to the problem of understanding the lithospheric architecture, fluid reservoirs and pathways and local thermodynamic conditions which control the processes leading to the formation of an economic mineral deposit. It is in this context that I attempt to situate my work.

Advances in the understanding of stable isotope geochemistry accompanied with new analytical tools to acquire accurate and precise data have opened a completely new avenue of study in the application of stable isotope analysis as a tool in unravelling the processes that govern mineral systems. One of the elements to which stable isotope geochemistry has been applied to in the past due to its abundance in many mineral deposits is sulfur. Sulfur is the key ligand in the transport and deposition of metals in gold deposits (Pokrovski et al., 2015), thus connecting the three key elements of a mineral system (e.g. source, pathway and trap). Attempts to utilise the stable isotopes of sulfur to answer questions about the processes governing gold mineralising systems have previously been hampered by the fact that only one isotopic system ($\delta^{34}$S) was commonly studied. This approach is limited as it uses a system which has only one degree of freedom to evaluate data which are governed by two degrees of freedom (source and thermodynamic process).
The discovery of the variability in the other isotopes of sulfur $^{33}\text{S}$ and $^{36}\text{S}$ relative to $^{34}\text{S}$, as will be discussed further, opened additional degrees of freedom, which allow us to now postulate some new possibilities and close other dead ends in the investigation of gold mineralising systems. In this work, I bring to the fore the use of the Mass Independent Fractionation of Sulfur (MIF-S) as an isotopic tracer of processes relating to the formation of gold mineralisation. My work also tackles some of the larger scale questions in the global sulfur cycle from the Archaean through to the Palaeoproterozoic, the most fundamental of which are the constraints on the recycling of sulfur in the early earth’s crust. Essentially, I have used the mineral system framework as a window into the evolution of geological processes through time. In keeping with the spirit of the mineral system approach, my work is situated within the context of the Capricorn Distal Footprints project to create a new roadmap for mineral exploration under cover in the Capricorn Orogen of Western Australia (Hough et al., 2013). This project is a terrane scale investigation and my findings have been well integrated with other work, both geochemical and geophysical in the Capricorn Orogen as a whole.
Figure 2: A space-time diagram showing the key scale dependent features and processes in a mineral system. A deposit is formed when there is a favourable conjunction of the right factors ranging from the global to the deposit scale. My work spans the various scales of this model by looking at the processes that connect one specific ligand, sulfur, between the different reservoirs and through different processes during the dynamic operation of mineral systems. A key contrast with the petroleum systems is that the fluids are not trapped at the deposition site, but they are focused and then exit the system. Modified from Wyman et al. (2016).
Sulfur isotopography

Isotope Notation

Sulfur has four isotopes with the following abundances: $^{32}$S (95.02%), $^{33}$S (0.75%), $^{34}$S (4.21%), and $^{36}$S (0.02%), as reported in Seal (2006). Sulfur isotope geochemistry has usually been concerned with relative partitioning of the various isotopes of sulfur relative to each other due to equilibrium and kinetic effects (Thode et al., 1961; Seal, 2006). Due to the fact that heavier isotopes form more stable bonds, molecules containing different isotopes of the same element react at different rates depending on the nature of the reaction (O’Neil, 1986). These partitioning relationships have been determined to be due to their relative mass difference, thus creating the fundamental relationship between the 3 minor isotopes of sulfur that vary systematically between each other.

In simple terms, the variations in the $^{33}$S/$^{32}$S ratio of the sulfur bearing species will be half that of the $^{34}$S/$^{32}$S variation because the mass difference between $^{33}$S and $^{32}$S is half that of the difference between $^{34}$S and $^{32}$S. Thus the $^{36}$S/$^{32}$S variation would be twice that of the $^{34}$S/$^{32}$S variation. Due to the very small magnitudes of variation seen in isotopic fractionation, the convention of referring to isotopic fractionation in the $\delta$-notation was established. The $\delta$-notation is defined as:

$$\delta^xS = \left( \frac{\frac{xS}{^{32}S}_{sample} - \frac{xS}{^{32}S}_{reference}}{\frac{xS}{^{32}S}_{reference}} \right) \times 1000$$

Where $x = 33, 34$ or $36$. The reference material has been defined as the Vienna Canyon Diablo Troilite (V-CDT; Ding et al., 2001). All further sulfur isotope values referred to in this thesis will be quoted relative to V-CDT.
This linear fractionation trend, driven by thermodynamic processes, has come to be termed as mass-dependent fractionation (MDF; Hulston and Thode, 1965). For most of the period of scientific research into sulfur isotope fractionation and its applicability to geological systems, it was assumed that only mass-dependent fractionation was relevant to understanding the variation in the sulfur isotope composition of different Earth reservoirs. However, discoveries made by Farquhar et al. (2000) and later workers on the variation of $^{33}\text{S}/^{32}\text{S}$ and later $^{36}\text{S}/^{32}\text{S}$ ratios away from those predicted by a purely MDF process have caused a paradigm shift in the sulfur isotopography of geological systems. The addition of two more degrees of freedom to the analytical schema of sulfur isotopography has allowed us to begin to evaluate the different fractionation trends generated by different geological processes in an individual and constrained manner.

This paradigm shift was caused by the recognition that $^{33}\text{S}$ and $^{36}\text{S}$ do not fractionate relative to $^{32}\text{S}$ in the same mass difference dependent way that $^{34}\text{S}$ does in some sulfur bearing compounds in specific Archaean sedimentary units (Farquhar et al., 2000; Farquhar et al., 2003). These anomalous, seemingly mass independent variations are defined with their own nomenclature, $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ which is defined as follows:

$$\Delta^{33}\text{S} = \delta^{33}\text{S}_{\text{measured}} - \left[ \left( \frac{\delta^{34}\text{S}_{\text{measured}}}{1000} + 1 \right)^{0.515} - 1 \right] \times 1000$$

$$\Delta^{36}\text{S} = \delta^{36}\text{S}_{\text{measured}} - \left[ \left( \frac{\delta^{34}\text{S}_{\text{measured}}}{1000} + 1 \right)^{1.9} - 1 \right] \times 1000$$

**Mass Independent Fractionation of Sulfur**

Two possible mechanisms have been called upon to explain these anomalous fractionations, referred to herein as Mass Independent Fractionation of Sulfur (MIF-S). The two candidates are atmospheric photochemistry and a diagenetic process called thermochemical sulfate
reduction (TSR). Atmospheric photochemical excitation, the dominant theory in the scientific literature to explain the set of processes creating large MIF-S anomalies, stems from the observed correlation between the end of the temporal MIF-S record correlating with earlier research on earth surface oxidation (Sessions et al., 2009). This finding, made initially by Farquhar et al. (2000) and later refined by the expansion of the Time – Δ³³S record (Fig. 3) of sedimentary sulfur shows that the range of Δ³³S signatures found in sedimentary sulfur reservoirs varied significantly throughout the Archaean before dropping precipitously to near zero values at 2.33 Ga, where it remained for the rest of the Earth’s history.

Independent measures of the rise of oxygen in the Earth’s atmosphere, e.g. nitrogen isotopes, Fe oxidation states and bio-molecular markers in sedimentary sequences, also document a significant increase in the oxygen concentration of the atmosphere at this time. A thorough, experimentally supported theory which connects the generation of MIF-S anomalies and the presence of oxygen in the atmosphere was then developed by Farquhar et al. (2001) who demonstrated that the photodissociation of SO₂ under a variety of incident wavelengths of light generated a strong MIF signal at wavelengths between 190 – 220nm. This wavelength of light is absorbed by O₂ and O₃ in the modern atmosphere, supporting the thesis that the presence of MIF-S is a proxy of the surface oxidation on Earth, as oxygen molecules would not have existed in a low oxygen atmosphere. Further modelling by Pavlov and Kasting (2002) observed that at atmospheric oxygen concentrations above 10⁻⁵ present atmospheric level, the photochemical reactions creating MIF-S could no longer occur.
Figure 3: The evolution of the global sedimentary $\Delta^{33}$S record through time produced from the sulfur isotope through time database (http://www.cet.edu.au/research-projects/special-projects/gssid-global-sedimentary-sulfur-isotope-database). Analyses are coloured by the phases from which they were obtained, showing that most of the sulfur in the Archaean sedimentary record was preserved as sulfide. However, the higher sulfate content in modern sediments is a clear indicator of the higher oxidation state of the marine environment. It is also clear that sulfates dominantly show $-\Delta^{33}$S signatures in the Archaean.
TSR, another possible source of MIF-S, was suggested by Ohmoto et al. (2006) and followed up with experiments showing that some of the $\Delta^{33}S$ values seen in the geological record could be created by batch reactions between pure amino acid powders and sulfoxy anions (Lasaga et al., 2008). This work has however been shown to theoretically be based on flawed assumptions of adsorption reactions. In addition, it does not explain the observed $\Delta^{36}S$ variations in the geological record or the large magnitude of $\Delta^{33}S$ variations seen in Earth history (Johnston, 2011) and cannot explain the secular variation of the MIF-S record over geological time in the way that atmospheric photochemistry tied to the $pO_2^-$ concentration in the Archaean can.

The $\Delta^{33}S$ anomalies appear to be both positive and negative. These variations have been attributed to different photochemical preservation pathways (Pavlov and Kasting, 2002; Ono et al., 2003; Farquhar et al., 2013). The initial production of the different $\Delta^{33}S$ signatures are due to the differences in the products of the SO$_2$ photodissociation reactions generated by the low wavelength UV radiation in the Archaean atmosphere (Farquhar et al., 2001). The redox conditions in which these reactions occurred have also caused the $\Delta^{33}S$ and $\Delta^{36}S$ values to vary dramatically (Farquhar et al., 2001; Endo et al., 2016). Dominantly, the elemental sulfur products S$_0$, S$_2$ and S$_8$ preserve a strongly positive anomaly, whereas the SO$_2$ products preserve a strongly negative anomaly. The separate positive and negative $\Delta^{33}S$ signatures were then recorded in two separate crustal pathways: 1) the elemental sulfur settling into marginal basins and other siliciclastic sediment dominated environments where it reacts with H$_2$S to form positive anomaly enriched pyrite, and 2) the negatively anomalous SO$_2$ dissolving into seawater from which it forms chemical precipitant sulfate phases, e.g. barite and anhydrite (Farquhar et al., 2001; Ono et al., 2003; Farquhar et al., 2013). A small proportion of the seawater sulfate is also sequestered by biogenic processes into biogenic pyrite in sedimentary rocks. Thus, the documentation of positive or negative $\Delta^{33}S$ anomalies gives us a good tracer for sedimentary processes.
The second factor that makes MIF-S a highly effective tracer of geological processes is the fact that it is chemically conservative and mostly indelible. This is because its generation was linked to a specific period in Earth’s history and the photochemical processes that occurred at that time. Further, once the signature is created it cannot be removed by refractionation under thermodynamic processes, only diluted by the addition of sulfur with no MIF-S signatures or under rare metamorphic re-equilibration processes. Thus if a MIF-S signature is observed in rocks that did not form in the Archaean surface, the sulfur in that rock must have been sourced from an Archaean surficial reservoir. This makes it an excellent tracer of sulfur transport and, by extension, of a range of geological processes. This chemically conservative nature has been validated by the use of the MIF-S signature in tracing biogeochemical processes, particularly those to do with evolution of early life (McLoughlin et al., 2012; Wacey et al., 2011; Wacey et al., 2015).

**Boundaries of MIF-S**

The predicted slopes of 0.515 of $\delta^{33}\text{S}-\delta^{34}\text{S} (33\lambda)$ and 1.9 ($36\lambda$) of $\delta^{36}\text{S}-\delta^{34}\text{S}$ (Wing and Farquhar, 2015) are rooted in the differences in vibrational energies associated with isotopic substitution (Bigeleisen and Mayer, 1947). It was initially considered that all variation away from these theoretical slopes were documenting MIF-S processes, e.g. ones that were not being generated by the standard range of thermodynamic and biogeochemical processes. However, Jamieson et al. (2006) were the first to highlight that even in high temperature hydrothermal fluids, the $\lambda$ values appear to be slightly variable depending on the thermodynamic system being studied.

Further work by biogeochemists and microbiologists has shown that biological processes occurring in surficial sediments can cause significant shifts in the $\lambda$ value for both $^{33}\text{S}$ and $^{36}\text{S}$ (Fig. 4; Leavitt et al., 2014 and references therein; Zerkle et al., 2016). This range of possible $^{33}\lambda$ and $^{36}\lambda$ values can thus generate what appears to be small $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ signatures in natural
systems through non-mass independent reaction pathways. However, the range of these variations is predictable (Fig. 5A, B), based on the observed λ values in experiments (Leavitt et al., 2014) and the range of λ values closely matching the observed Proterozoic sedimentary rock records (Fig. 6A, B). In 6A and 6B respectively, 95% and 85% of analysed sedimentary sulfur younger than 2.33 Ga sits within the range of possible biogeochemically derived Δ^{33}S signatures. This supports the argument presented here that a clear difference between MIF-S derived Δ^{33}S and ^{33}λ variation derived Δ^{33}S signatures can be calculated based on the experimental evidence. It is possible that the analyses in both Δ^{33}S and Δ^{36}S space that do not fit the model are expressions of the fact that some stratospheric volcanic eruptions can place enough SO_2 into the upper parts of the atmosphere where O_2-O_3 shielding of UV rays is insufficient to prevent photochemical MIF-S from forming (Baroni et al., 2007). Additionally, biogenic processes which are occurring in a closed system can generate relatively high Δ^{33}S (up to 0.35‰) with little δ^{34}S fractionation (Ono et al., 2006). These minor shifts however are clearly insufficient to generate the very consistently large MIF-S signatures observed in the Archaean.

Thus it is possible to isolate the range of Δ^{33}S and Δ^{36}S values that are possible for a given δ^{34}S value in biogeochemical systems and hence define that values which fall outside of this range to be truly caused by mass independent fractionation. In this work we take these λ variability based estimates of the upper and lower bounds of non-MIF-S Δ^{33}S values as the threshold for which we define an analysis to show MIF-S sulfur. In simple terms, if a fractionation process for δ^{33}S – δ^{34}S (due to geobiological MDF) was operating at ^{33}λ = 0.508 instead of ^{33}λ = 0.515 and the measured δ^{34}S = +5‰, the measured δ^{33}S will give us +2.54‰, instead of +2.575‰, thus generating a MDF-Δ^{33}S of 0.035‰. Therefore, each 1.0‰ variation of δ^{34}S has a maximum potential to develop a Δ^{33}S of 0.007‰. Therefore, the generation of a large MDF-S–Δ^{33}S is only possible at significantly fractionated values of δ^{34}S as shown in Figure 6A, B.
Figure 4: Experimental and natural samples plotted as function of $^{33}\lambda$. Adapted from Johnston, 2011, Leavitt et al., (2014), Zerkle et al., (2016) and references therein.
Figure 5: A, B – Illustration of the relationship between $\delta^{34}\text{S}$ and $\delta^{33}\text{S}$ in different $\lambda$ environments.
Figure 6 – A, B – The upper and lower limits of the experimentally observed $\lambda$ fractionation slopes in $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ space over the usual range of natural $\delta^{34}\text{S}$ values. In the background, the database of post-Great Oxygenation Event (GOE; <2.33 Ga) sedimentary sulfur analyses from which analyses with a $\Delta^{33}\text{S}$ analytical error greater than 0.1‰ and a $\Delta^{36}\text{S}$ analytical error greater than 0.4‰ were trimmed out. Data are sourced from the sedimentary sulfur database maintained by the Centre for Exploration Targeting and reproduced as digital appendix to this thesis (http://www.cet.edu.au/research-projects/special-projects/gssid-global-sedimentary-sulfur-isotope-database).

**MIF-S in mineral systems**

Previous work on the use of the MIF-S as a tracer of geological process in mineral systems has been limited to deposit-district scale work, which addressed some fundamental questions on the sourcing of sulfur in Archaean VMS deposits (Jamieson et al., 2006; Sharman et al., 2014) and komatiite hosted nickel systems (Fiorentini et al., 2012a, b). Application of the MIF-S tracer to gold mineralising systems is even more limited, with only Xue et al. (2013) and Agangi et al. (2016) existing in the literature. Both of these publications were based on analysis performed with the less precise SHRIMP-SI (Sensitive High Resolution Ion Micro Probe – Stable Isotope), which has large errors on $\Delta^{33}\text{S}$ analyses, hence reducing its utility in clearly differentiating MIF-S from MDF-S processes. Additionally, the interpretations made by Xue et al. (2013) on the source of sulfur in some orogenic gold deposits were in direct opposition to the findings of Agangi et al. (2016). My work attempts to bridge these differing perspectives in the literature in a holistic manner. This began with the development of a new technique of *in situ* analysis of sulfide phases associated with mineralisation, specifically of pyrite, chalcopyrite, arsenopyrite, pyrrhotite and pentlandite (LaFlamme et al., 2016) and integrating these *in situ* analysis with well constrained microchemistry of the sulfide phases studied. This overcomes some of the methodological problems that existed in previous work.
MIF-S does not sit alone in the study of sulfur isotopes in mineral deposits, nor should it. The use of the MDF-S, i.e. that of variation in $\delta^{34}$S to understand the source and transport of mineralising fluid has a long and illustrious past starting with seminal papers by Thode et al. (1962) on the Sudbury Ni-Cu mineralisation. While $\delta^{34}$S has been used successfully in many mineralising environments, its main limitation has always been that it is easily reset and modified by thermodynamic processes. This is the main advantage of multiple sulfur isotope analysis, in that the $\Delta^{33}$S and $\Delta^{36}$S signatures are chemically conservative and thus can only be reset by dilution with non MIF-S. Combining the MDF-S and MIF-S datasets allows us to explore multiple geological problems with the same dataset, magnifying our ability to use ore deposits as a window into large scale Earth processes.

I believe that an under-explored way of tackling the fundamental question of sulfur and metal transport in mineralised systems is by utilising the MIF-S signature in a scale dependent way, which is in contrast to previous studies that focused on deposit-district scale studies. This scale dependence in mineral systems science is an important distinguishing feature of the mineral systems paradigm relative to the older genetic process driven method of studying ore deposits (McCuaig et al., 2010). Applying MIF-S as a tracer of fluid, sulfur and metal movement through the Earth at different scales allows us to answer a set of connected questions in the study of gold deposits. I hope that by the end of this work I will have convinced you of the thesis that MIF-S is useful as a multiscale tracer of sulfur and metals in the Earth.

**Thesis structure**

This thesis is structured as a series of papers (Fig. 2), each written to address how the combination of multiple sulfur isotope analysis, geological observations and mineral scale geochemical analysis can be used in a different way to address a fundamental question about the sulfur cycling on the Earth. The publications are structured by a series of smaller scale
studies of gold forming processes in the Capricorn Orogen and Yilgarn Craton of Western Australia. Structuring them in this scale dependent way allows us to think about how different regimes of fluid flow and mass transfer operate from the tectonic scale (Paper 1) to the processes of gold precipitation from a fluid at the scale of a single grain of pyrite (Paper 4). In all of these studies, the common connection is the ability of multiple sulfur isotope analyses to frame and answer questions that up to this point were tackled in indirect ways, such as using secondary proxies and relying on relative changes in chemical budgets. The mineral systems framework is considered in each paper individually as a guidebook to the approach of any specific terrane, but is validated by the thesis as a whole, in that processes of sulfur transport which may seem at first to have little connection with each other can be read as different expressions of the same set of thermodynamic boundary conditions operating at larger to smaller scales.

The first paper, ‘Anomalous sulfur isotopes trace volatile pathways in magmatic arcs’ is published in the journal Geology. This paper sits at the largest scale of consideration in my thesis, and utilises MIF-S as a tracer of sulfur cycling from subducting lithosphere through the mantle and into a magmatic arc. It addresses the poorly understood global sulfur cycle by tracing the path of MIF-S enriched sulfur from the subducting slab into an overlying magmatic arc. I studied the Glenburgh gold deposit in the Glenburgh arc of Western Australia as the first of my natural laboratories to trace the pathway of sulfur through the Earth’s mantle and crust. This was determined by studying the MIF-S signature of sulfide bearing samples related to the gold mineralisation at the Glenburgh deposit and of the surrounding felsic magmatic rocks. The results of this study suggest that sulfur and gold in magmatic arcs may be dominantly sourced from the devolatilisation of the downgoing slab.

Moving down an order of scale, to the cratonic scale, my next paper ‘Atmospheric sulfur in the Orogenic Gold Deposits of the Archaean Yilgarn Craton’ is accepted for publication in the
This paper addresses the highly debated topic of the sulfur and gold sources in Archaean orogenic gold deposits over an entire Archaean craton. I used the MIF-S signature derived from multiple sulfur isotope analysis of gold related samples from 24 orogenic gold deposits in the Archaean Yilgarn Craton to uniquely fingerprint for the first time the source of sulfur and gold in a craton-wide mineralising event. By conducting simple statistical analysis, comparing the orogenic gold mineralisation related MIF-S signatures to the established atmospheric sulfur record, I concluded that these deposits can be formed from fluids generated from crustal sources. I further postulate that the processes that lead to the formation of the truly gigantic orogenic gold deposits are likely to be different to those that form small deposits. In this paper, I also presented a thoroughly compiled and cleaned database of the primary atmospheric sulfur isotopic compositional signature through the Archaean and into the present. This database is current to all publications of multiple sulfur isotope datasets to January 2017 and contains 5146 analyses from 65 publications. The database will, upon the submission of this thesis be hosted publically for the usage of the scientific community as a whole and be continuously maintained by the Centre for Exploration Targeting at http://www.cet.edu.au/research-projects/special-projects/g ssid-global-sedimentary-sulfur-isotope-database.

My third paper, ‘Evidence of local sourcing of sulfur and gold in an Archaean sediment hosted gold deposit’, in review in Ore Geology Reviews, sits a further scale order down, looking at a single basin and discussing the dynamics of sulfur, fluid and metal transport using MIF-S as a tracer. This paper, set in the context of the Paulsens sediment hosted gold deposit of the Pilbara Craton steps into the highly uncertain and contentious area of the source of sulfur and gold in sediment hosted gold deposits e.g. The Nevada Carlin Trend deposits and those of the Youjiang Basin in China. I compared the Archaean Paulsens deposit to other modern sediment hosted gold deposits using a combination of thorough geological descriptions, the study of pyrite
textures and pyrite chemistry by a combination of micro-chemical techniques e.g. laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS), Nano Secondary Ion Mass Spectrometry (NanoSIMS) and electron probe micro-analysis (EPMA), concluding that Paulsens is a useful analogue for the more modern systems. This then allowed me to study the MIF-S signature in the gold bearing pyrites and to compare these signatures to that I analysed from diagenetic pyrites in the hosting stratigraphy several kilometres away from the deposit, suggesting that the sulfur and the gold in the deposit could have been derived from local sedimentary sources.

My final paper, ‘Conditions for the genesis of a low temperature sediment–hosted gold deposit’, in review at Mineralium Deposita, sits at the smallest scale horizon, the mineral scale. This paper also looks at the Paulsens deposit but uses measurements of multiple sulfur isotopes in pyrite and chalcopyrite to postulate some possibilities about the kind of fluid reactions and thermodynamic pathways that a locally sourced fluid would need to undergo in order to form a viable gold deposit. This is done through a combination of temperature estimates for the formation of the pyrite-Au mineralisation obtained via sulfur isotope fractionation calculations and paired fluid inclusion thermometry. Isotope fractionation modelling will then be used to explain what kinds of source rocks could devolatilise to form a gold bearing fluid which records a small shift in δ³⁴S sulfur through its precipitation process while preserving the same Δ³³S signature.

This introductory chapter will been adapted, with the addition of some case study data, to argue for a clearer definition of MIF-S in the application to mineral systems into a publication authored by Crystal LaFlamme.

Additionally, to enable the in situ analysis of multiple sulfur isotopes in sulfide phases using a Cameca 1280 Ion Probe, I worked closely with Crystal LaFlamme and others to create a suite
of suitable sulfide standards. This work is detailed in LaFlamme et al. (2016) of which I am a co-author. This work is available online.

My work on the utilising sulfur isotope analysis on the Cameca 1280 Ion Probe at the Centre for Microscopy and Chemical Analysis (CMCA – UWA) has also led to the publication of a paper on the genetic processes leading to the formation of Jinding Mississippi Valley Type Zn-Pb deposit in the Yunnan Province of China. I am a co-author of Deng et al. (2016) which is available online.

These papers, in their sequence, aim to present a series of case studies of the utility of MIF-S as a tracer for fluid, ligand and metal transport in the earth’s crust. I consider my work as part of the ever growing literature on the applicability of MIF-S and other individual, non-thermodynamic sources of isotope fractionation in the understanding of the fractal nature of mineral systems at multiple scales.

**Statement of Author Contributions**

The main body of this thesis comprises four chapters (Chapter 2 to Chapter 5). Chapter 2 utilizes multiple sulfur isotope analysis in the Palaeoproterozoic Glenburgh arc to demonstrate the recycling on sedimentary sulfur from a downgoing slab into magmas and mineral systems in the continental arc above it. Chapter 3 studies a range of orogenic gold deposits in the Yilgarn craton and on the basis of multiple sulfur isotope analysis, argues that the sulfur in these deposits and possibly the gold was sourced from Archaean sedimentary units, thus providing a key line of evidence for the metamorphic devolatilisation model of orogenic gold deposit formation. Chapter 4 looks at the Paulsens sediment hosted gold deposit, and on the basis of *in situ* multiple sulfur isotope analysis, pyrite texture and microchemistry, shows that the gold and sulfur in this deposit was most likely derived from the local host rock, the Archaean Hardey Formation. Chapter 5 uses a combination of multiple sulfur isotope analysis, fluid inclusion
microthermometry and quantitative geochemical and isotopic modelling to demonstrate the unique physico-chemical conditions of formation in a relatively low temperature sediment hosted gold deposit. Supplementary data for Chapter 2, 3, 4 and 5 are provided in the Appendices and Digital Appendices as appropriate. A substantive introduction, literature review and opening argument is provided in Chapter 1 and conclusions to the work and suggestions for future work are provided in Chapter 5.

Chapter 2 is the manuscript ‘Anomalous sulfur isotopes trace volatile pathways in magmatic arcs’ published in the journal *Geology* by Vikraman Selvaraja, Marco L. Fiorentini, Crystal K. LaFlamme, Boswell A. Wing and Thi-Hao Bui. The work presented in this chapter was initiated and performed by myself including sample collection, all scientific analysis, data processing, interpretation and writing. Marco Fiorentini, Crystal LaFlamme and Boswell Wing assisted in the intellectual development and editing of the manuscript. Boswell Wing and Thi-Hao Bui assisted in the application of the analytical techniques.

Chapter 3 is the manuscript ‘Atmospheric sulfur in the Orogenic Gold Deposits of the Archean Yilgarn Craton‘ published in the journal *Geology* by Vikraman Selvaraja, Stefano Caruso, Marco L. Fiorentini, Crystal K. LaFlamme and Thi-Hao Bui. The work presented in this chapter was initiated and performed by myself including sample collection, all scientific analysis, data processing, interpretation and writing. Stefano Caruso, Marco Fiorentini and Crystal LaFlamme assisted in the intellectual development and editing of the manuscript. Stefano Caruso also assisted in the preparation of some figures. Thi-Hao Bui assisted in the application of the analytical techniques.

Chapter 4 is the manuscript ‘Evidence of local sourcing of sulfur and gold in an Archaean sediment hosted gold deposit’, in review at *Ore Geology Reviews* by Vikraman Selvaraja, Marco L. Fiorentini, Heejin Jeon, Dany D. Savard, Crystal K. LaFlamme, Paul Guagliardo,
Stefano Caruso and Thi-Hao Bui. The work presented in this chapter was initiated and performed by myself including fieldwork, sample collection, scientific analysis, data processing, interpretation and writing. Marco Fiorentini and Crystal LaFlamme assisted in the intellectual development and editing of the manuscript. Heejin Jeon, Dany Savard, Paul Guagliardo, Stefano Caruso and Thi-Hao Bui assisted in the application of the analytical techniques.

Chapter 5 is the manuscript ‘P-T-X conditions and precipitation mechanism of gold mineralization at the Paulsens gold deposit’ in review at Mineralium Deposita by Vikraman Selvaraja, Katy A. Evans, Steffen G. Hagemann, Marco L. Fiorentini, Terence P. Mernagh and Paul Duuring. The work presented in this chapter was initiated and performed by myself including fieldwork, sample collection, scientific analysis, data processing, interpretation and writing. Katy Evans assisted in the preparation of the thermodynamic model and in the interpretations of the results of the model. Steffen Hagemann and Marco Fiorentini assisted in the intellectual development and editing of the manuscript. Terence Mernagh and Paul Duuring assisted in the application of the analytical techniques.

I, Marco Fiorentini, certify on behalf of myself and the other co-authors that the student statements regarding their contribution to each of the works listed above are correct

Vikraman Selvaraja
PhD Candidate
06/12/2017

Marco L. Fiorentini
Principal Supervisor
06/12/2017
Thesis Declaration

I, Vikraman Selvaraja, certify that:

1) This thesis has been substantially accomplished during enrolment in the degree.

2) This thesis does not contain material which has been accepted for the award of any other degree or diploma in my name, in any university or other tertiary institution.

3) No part of this work will, in the future, be used in a submission in my name, for any other degree or diploma in any university or other tertiary institution without the prior approval of The University of Western Australia and where applicable, any partner institution responsible for the joint-award of this degree.

4) This thesis does not contain any material previously published or written by another person, except where due reference has been made in the text.

5) The work(s) are not in any way a violation or infringement of any copyright, trademark, patent, or other rights whatsoever of any person.

Vikraman Selvaraja
PhD Candidate
06/12/2017

Marco L. Fiorentini
Principal Supervisor
06/12/2017
References


CHAPTER TWO

ANOMALOUS SULFUR ISOTOPES TRACE VOLATILE PATHWAYS IN MAGMATIC ARCS

This chapter is presented as it is published in the journal *Geology*. The supplementary data consists of a supplementary set of information regarding the geology of the Glenburgh arc, methods used in this study and the full data set obtained in this study and a modelling spreadsheet. The former is appended to the end of this chapter, and the latter is included as an excel file in the electronic appendices to this thesis called Chapter 2 – SM.
Anomalous sulfur isotopes trace volatile pathways in magmatic arcs

Vikraman Selvaraja¹,², Marco L. Fiorentini¹,², Crystal K. LaFlamme¹,², Boswell A. Wing³,⁴, and Thi-Hao Bui⁴
¹Centre for Exploration Targeting, School of Earth Sciences, University of Western Australia, 35 Stirling Highway, Crawley, WA 6009, Australia
²ARC Centre of Excellence in Core to Crust Fluid Systems, University of Western Australia, 35 Stirling Highway, Crawley, WA 6009, Australia
³Department of Geological Sciences, University of Colorado, Boulder, Colorado 80309, USA
⁴Department of Earth and Planetary Sciences, McGill University, 3450 University St., Montreal, QC H3A 0E8, Canada

ABSTRACT
The cycle of sulfur, an important volatile in Earth’s crust, is the driver of many significant processes such as biological evolution, climate change, and the formation of ore deposits. This study investigates the ancient cycle of volatiles by tracing the indelible signal of anomalous sulfur isotopes, expressed as $\Delta^{34}S \neq 0$, to illuminate the pathway of sulfur recycling through magmatic arcs. We selected the ca. 2.0 Ga Glenburgh gold deposit in the Glenburgh magmatic arc of Western Australia as a natural laboratory for this study. High-precision multiple sulfur isotope analyses of samples from the Glenburgh gold deposit and surrounding granitoid rocks yield the largest known sulfur isotope anomalies ($\Delta^{34}S$ up to +0.82%) in rocks <2.33 Ga globally. These data indicate that sulfur, and possibly gold, originated from multiple geochemical reservoirs in sedimentary rocks subducted beneath the magmatic arc, one of which is >2.33 Ga. Multiple sulfur isotope data are able to clarify a process that is cryptic to most other currently available data sets, showing that the cycling of volatiles and metals in arc settings occurs on very large scales, from the atmosphere–hydrosphere through to the lithosphere during crustal generation.

INTRODUCTION
The Earth’s crust represents a complex and dynamically evolving chemical interface between three convective fluid systems: the geosphere (core and mantle), the hydrosphere, and the atmosphere. The flux of volatiles and metals through the various parts of the endosphere is best recorded in magmatic arcs. These are loci where eruptions emit large quantities of sulfur-bearing gases into the atmosphere (Wallace, 2005) and where significant concentrations of precious metals are accumulated in sulfide-rich rocks (Richards, 2011). However, the origin of sulfur, other volatiles, and metals remains unclear, with competing hypotheses arguing for different sources, including the subducted crust or the overlying lithosphere (Richards, 2011).

This study addresses the sulfur cycle in magmatic arcs and focuses on the ca. 2 Ga Glenburgh sulfide-bearing gold deposit in Western Australia as a natural laboratory to trace the pathway of sulfur through the Earth’s mantle and crust. The Glenburgh deposit formed when the Glenburgh terrane collided with the Yilgarn craton resulting in a period of subduction and magmatism during the progressive closure of an ocean in the Paleoproterozoic (2.5–1.6 Ga; Sheppard et al., 2004). At the planetary scale, this is the period when an oxygenated atmosphere first evolved (Kump and Barley, 2007) during the amalgamation of the supercontinent Columbia (Rogers and Santosh, 2002).

THE GLENBURGH ARC
The Glenburgh gold deposit is hosted within <2.03 Ga metasedimentary rafts in the ca. 2.0 Ga Dalgaringa Supersuite granites, which intrude the Glenburgh terrane (Sheppard et al., 2004). The deposit is believed to have formed after 2.03 Ga (the maximum depositional age estimated from 29 detrital zircons extracted from our studied samples; Roche et al., 2017), synchronous with subduction and arc magmatism (Sheppard et al., 2004). In order to constrain the link between the sulfur cycle, precious metal transport, and the geodynamic evolution of the Glenburgh arc, 36 samples were obtained from the Glenburgh gold deposit and from nearby intercalated magmatic rocks of the Dalgaringa Supersuite and Halfway Gneiss to investigate their sulfur isotope signatures (see the GSA Data Repository¹). Analyses were performed at the Stable Isotope Laboratory at McGill University, Quebec, Canada. Mineralized samples were microdrilled to generate a pure sulfide powder, whereas the magmatic rocks were milled into a fine powder so as to facilitate extraction of the reduced sulfur disseminated in the mineralogy of the rocks. Due to the significant analytical difficulties in attempting to extract small quantities of sulfate from whole rock samples and the low likelihood of preservation of magmatic sulfate in 2.0 Ga rocks, a reduced sulfur extraction was favored instead. Both powder suites were dissolved and an Ag₂S compound was extracted (Canfield et al., 1986), which was then analyzed by gas fluorination mass spectrometry.

MASS-INDEPENDENT FRACTIONATION OF SULFUR ISOTOPES
We investigated two multiple sulfur isotope signatures: (1) the mass-dependent fractionation of sulfur isotopes (defined as $\delta^{16}S$), which is sensitive to physical processes that occur during the hydrothermal circulation of fluids, metamorphic recrystallization, and biological processes (Ohimoto, 1972); and (2) the mass-independent fractionation of sulfur isotopes (MIF-S; defined as $\Delta^{33}S$ and $\Delta^{34}S$) (Farquhar and Wing, 2003), which is a chemically conservative signature that fingerprints the source of sulfur through a wide range of geological processes (Bekker et al., 2009). Nonzero $\Delta^{33}S$ and $\Delta^{34}S$ values, reflected in the fractionation of $^{34}S/^{32}S$ and $^{33}S/^{32}S$ ratios away from the expected mass-dependent fractionation relationship based on $^{32}S/^{34}S$ ratios, were generated during photochemical processing of S-bearing gases in the oxygen-poor Archaean atmosphere, prior to the Great Oxygeneration Event (GOE) at 2.33 Ga (Farquhar and Wing, 2003; Johnston, 2011, and references therein; Luo et al., 2016). The photochemical products of these reactions led typically to positive $\Delta^{34}S$ values in sedimentary pyrite and negative $\Delta^{34}S$ in reservoirs derived from oceanic sulfate (Farquhar and Wing, 2003; Ono et al., 2003). Once formed in the Archaean, these nonzero MIF-S signatures could only have been diluted by processing through the surface and subsurface geologic environments. Therefore, anomalous MIF-S signatures are viable candidates to illuminate the pathway of sulfur from the Archaean to the Proterozoic through the Glenburgh arc.

¹GSA Data Repository item 2017122, supplementary data, providing a more detailed description of the geology of the Glenburgh arc, methods used in this study, and the full data set obtained in this study, is available online at www.geosociety.org/datarepository/2017 or on request from editing@geosociety.org.
RESULTS

The analyzed samples yielded Δ34S values ranging from +0.22‰ to +0.82‰ (2σ uncertainties on Δ34S = ±0.02‰), Δ33S values from -0.91‰ to +0.27‰ (2σ uncertainties on Δ33S = ±0.2‰), and δ34S values between +1.8‰ and +11.6‰ (uncertainties on δ34S = ±0.2‰; Fig. 1; see the Data Repository). The Halfway Gneiss, the ca. 2.5 Ga basement rock that hosts the Dalgaringa Supersuite and the Glenburgh gold deposit, yielded sulfur contents below the extraction threshold (<50 ppm). The linear slope of the relationship between Δ34S and Δ33S in the sulfide-bearing samples and associated magmatic rocks of the ca. 2.0 Ga Dalgaringa Supersuite is -1.4, which fits well within the Archaean reference array of MIF-S measurements (Johnston, 2011). These results are unexpected as the Glenburgh sulfide-bearing gold mineralization and nearby magmatic rocks display MIF-S signatures that are the largest documented anomalies in rocks formed after the GOE (Johnston, 2011).

DISCUSSION

The presence of MIF-S anomalies in a Proterozoic magmatic arc opens up the question of how these signatures were introduced and preserved. It has been suggested that anomalous Δ34S fractionation may be generated by thermochemical sulfate reduction, where SO42- is reduced by amino acids to H2S (Ohmoto et al., 2006). However, the experimental simulations of that process (Oduro et al., 2011) are not able to reproduce the large deviations in both Δ34S and Δ33S that are observed in this study. Prior to the GOE, short-wavelength UV photochemical reactions created Δ34S anomalies in atmospheric sulfur colloids (Farquhar et al., 2000). These elemental sulfur colloids reacted to form sediment-hosted pyrite at the bottom of the water column in iron- and carbon-rich shales prior to 2.33 Ga (Ono et al., 2003). Thus, the positive Δ34S values recorded in the ca. 2.0 Ga Glenburgh gold deposit and surrounding Dalgaringa Supersuite suggest input from Archaean shale-hosted pyrite (cf. Ono et al., 2003).

The conundrum lies in the fact that the rocks that host the Glenburgh gold deposit are largely Proterozoic in age, and hence are not likely the original sources of MIF-S. The only Archaean unit in the observed stratigraphy is the ca. 2.5 Ga Halfway Gneiss. However, it is improbable that the Halfway Gneiss contributed to the sulfur isotope signature recorded in the Glenburgh gold deposit for two reasons: (1) it is only observed to have a very low sulfur content (<50 ppm); and (2) it is an orthogneiss with a juvenile granitic protolith (Cawood and Tyler, 2004; Johnson et al., 2013), and as such it is unlikely to contain any Archaean surface-derived sulfur. An alternate possibility is that detrital pyrite grains sourced from the Pilbara craton, mirroring the population of Pilbara-derived detrital Archaean zircons in the metasedimentary rocks that host the deposit (Roche et al., 2017), may have contributed some MIF-S to the deposit. We argue that this scenario is unlikely, as it would have involved the transport of detrital pyrite grains in an oxygenated atmosphere for hundreds of kilometers (Johnson et al., 2013) in large enough volumes to modify the sulfur budget of entire granitoid batholiths. In addition, the metasedimentary formations are only a minor part of the Glenburgh terrane (Johnson et al., 2013).

Our model to explain the observed anomalous positive MIF-S signature is based on the observation that the Glenburgh multiple sulfur isotope data could have been generated by mixing between three end-member sulfur reservoirs in δ34S-Δ34S space (Fig. 1). One end-member reservoir is most likely to be Archaean shale-derived sedimentary pyrite (δ34S = -1‰–2‰, Δ34S = 0‰–1.2‰; the “Archean Reference Array”, sensu Ono et al., 2003); another is sulfur derived from seawater sulfate at ca. 2.0 Ga (δ34S ~+20‰, Δ34S = 0‰; Scott et al., 2014); and the third, sulfur from a depleted mantle–subducted mafic crust reservoir (δ34S = -1.28‰, Δ34S = 0‰; Labidi et al., 2013). We argue that the first end-member reservoir is likely to have been derived from the metamorphic devolatilization of Archaean pyritic carbonate sedimentary rocks which were deposited on the passive margin of the Yilgarn craton during subduction below the Glenburgh terrane, generating arc magmatism and mineralizing fluids (Fig. 2). Although subduction is argued to have occurred at least 350 m.y. after the deposition of the Yilgarn passive margin, this circumstance is not unusual, as modern environments with much more active subduction than in the Paleoproterozoic are known to preserve passive margins for hundreds of millions of years prior to subduction (Levell et al., 2010). The contribution of possibly seawater-sourced sulfur could have been due to devolatilization of Paleoproterozoic seawater-derived sulfate minerals contained in the subducted slab (cf. Tomkins and Evans, 2015). The last possible reservoir could have been made up of either the depleteted mantle in the wedge overlying the subducted slab or and the subducted mafic crust itself: the two essentially have the same sulfur isotopic composition and cannot be discriminated in δ34S-Δ34S space (Fig. 1).

It is argued that mixing between the three putative sulfur isotope reservoirs occurred during subduction of dense mafic crust located at the margin of the Archaean Yilgarn craton (Mole et al., 2015). Metamorphic dehydration reactions drove the breakdown of Archaean pyrite, hosted in the sedimentary rocks overlying the subducting mafic crust, contemporaneously with the breakdown of ca. 2.0 Ga seawater-derived sulfate minerals. The resulting sulfur-rich hydrothermal fluids (Tomkins, 2010) metasomatized the mantle wedge, driving partial melting of the subcontinental mantle lithosphere. Subsequently, mantle-derived melts containing the mixed isotopic signature ascended through the crust, assimilating crustal material and undergoing fractional crystallization to form the buoyant andesitic magmas (cf. Richards, 2011), which crystallized as the large batholiths of the Dalgaringa Supersuite.

The transport of gold at high temperatures in the crust is thought to be enabled by its mobilization as a sulfide complex in fluids (Goldfarb and Groves, 2015). Thus, by identifying a strong source of sulfur in the Glenburgh arc from carbonate sedimentary rocks, as we have done, we argue that a possible source of gold in this arc environment is from the same subducted sedimentary rocks. This fits well with a previous suggestion that the ultimate source of gold in continental arc-hosted gold deposits are carbon-rich sedimentary rocks (Tomkins, 2010). We recognize that
an alternative interpretation is that sulfur and gold sources are decoupled and the rising sulfur-bearing fluids and melts could have stripped the gold from the mantle wedge or lower crust (Mungall, 2002).

Although our new data do not preclude a significant contribution of sulfur, metals, and volatiles from the mantle wedge and subducting oceanic lithosphere into continental arcs, they do allow a coherent hypothesis to explain why the observed concentrations of sulfur and associated gold mineralization in arc magmas are significantly higher than the known concentrations of these elements in the mantle wedge below arcs (de Hoog et al., 2001; Kump and Barley, 2007; Labidi et al., 2013; Goldfarb and Groves, 2015). While quantifying the magnitude of the relative contribution of the different sulfur reservoirs would only be speculative without any conclusive Archaean end member (Fig. 1), nonetheless the new data suggest that enough sulfur was added to the system through the devolatilization of sedimentary rocks to shift the sulfur isotopic composition of large granitic batholiths (Sheppard et al., 2004).

CONCLUSIONS

Chemically conservative isotopic tracers like $\Delta^{34}S$ values enable a better understanding of magmatic and tectonic processes that drive fluid and metal transfer from Archaean cratons into their reworked margins, where some of the largest ore deposits on Earth formed and are currently preserved (Mole et al., 2015). At the Glenburgh gold deposit, multiple sulfur isotope data show that mixing of sulfur from at least three reservoirs, including sedimentary rocks containing Archaean shale-derived pyrite, Paleoproterozoic seawater-derived sulfate, and, possibly, sulfide-bearing mantle–subducted mafic crust, records the onset of continent-continent collision between the Glenburgh terrane and the Yilgarn craton. Hence, multiple sulfur isotope data are able to image a process that is cryptic to most other currently available approaches, showing that arc settings have facilitated cycling of volatiles and metals, from the atmosphere-hydrosphere through to the lithosphere, for at least the last 2 b.y. of Earth history.

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Supplementary Data

Geological Background

The Glenburgh Terrane (Supp Fig. DR1), located immediately north of the Archaean Yilgarn Craton in Western Australia, is interpreted to be an exotic crustal fragment that was accreted onto the Pilbara Craton during the Ophthalmian Orogeny (2215–2145 Ma; Cawood and Tyler, 2004). This block, which later collided with the Archaean Yilgarn Craton to form the West Australian Craton during the Glenburgh Orogeny (2005–1950 Ma; Occhipinti et al., 2004; Sheppard et al., 2004), comprises: (i) a basement of heterogeneous orthogneisses (the 2.5 Ga Halfway Gneiss) with protolith ages as young as ca. 2430 Ma; (ii) an overlying package of continent-derived siliciclastic metasedimentary rocks (the 2240–2125 Ma Moogie Metamorphics); (iii) a ca. 2005–1970 Ma series of metagranitic gneisses (the Dalgaringa Supersuite), which are interpreted to have formed in a continental-margin volcanic arc; and (iv) arc-related metasedimentary rocks (the ca. 2000–1955 Ma Camel Hills Metamorphics) that overlie the Dalgaringa Supersuite and the deformed northern margin of the Yilgarn Craton (Roche, 2015).

Thirty-six samples were collected from the Dalgaringa Supersuite and Halfway Gneiss, which surround the supracrustal metasedimentary rafts that host the Glenburgh gold deposit. The Dalgaringa Supersuite is exposed in the southern part of the Gascoyne province, separated from the Yilgarn Craton by the Errabiddy Shear Zone, which is the boundary between the Glenburgh Terrane and the Yilgarn Craton (Johnson et al., 2013). The Dalgaringa Supersuite comprises massive, foliated, and gneissic andesitic rocks that have rare earth element (REE) concentrations typical of supra-subduction zone settings enriched in light REE and depleted in heavy REE relative...
Their whole-rock Sm–Nd and magmatic zircon Lu–Hf isotopic signatures indicate the incorporation of Neoarchaean granitic gneisses with isotopic compositions compatible with those of the ca. 2.5 Ga Halfway Gneiss (Sheppard et al., 2004). These geochemical data and other geological associations indicate that magmatism occurred in a continental arc, termed the Dalgaringa Supersuite, which formed along the southern margin of the Glenburgh Terrane. This magmatic event occurs synchronously with the collision of the Glenburgh Terrane and the Yilgarn Craton (Sheppard et al., 2004).

Supp Figure DR1. Geological map of the Glenburgh Terrane and adjoining Yilgarn Craton, Western Australia, with a simplified stratigraphic column of the region. Inset box reflects Supp. Figure DR2. The inferred paleo-subduction zone is defined on the ground by the Errabiddy Shear Zone.
The sulfide-bearing samples were collected from a biotite-quartz-plagioclase±garnet paragneiss that occurs as a sedimentary raft within the Dalgaringa Supersuite (Supp Fig. DR2; Roche, 2015). The gneissic banding is defined by alternating leucosomes, melanosomes and restitic layers. Leucosomes consist of quartz-plagioclase-K-feldspar-garnet-cordierite-tschermakite. The melanosomes mainly consist of biotite-quartz-garnet. The restitic layers are composed of hornblende-quartz-orthopyroxene-plagioclase-chlorite-tremolite-tschermakite.

Supp Figure DR2. Geological map of the Glenburgh mineral field, which is inset in Supp. Figure DR1. Sample locations are marked with their drill hole collar location in most cases.

The five samples of felsic magmatic rocks that were analysed are two samples of quartz-Kfeldspar-plagioclase-garnet metatexite migmatite, two of quartz-muscovite-cordierite-plagioclase-magnetite pegmatitic granite, and one of quartz-plagioclase-amphibole schistose tonalite. Finally, one
additional sample of the Halfway Gneiss was analysed; however, its sulfur concentration was below detection limit (<50 ppm). All samples are unmineralised but are part of the Dalgaringa Supersuite, and are located within 2–3 km of the mineralised zone. Nearby plutons of the same intrusive suite have a U-Pb zircon age of 2002 ± 3 Ma (Sheppard et al., 2004). The age of the mineralisation at the Glenburgh gold deposit is constrained by the youngest detrital zircon population within the metasedimentary rocks that host the Glenburgh deposit (2035 ± 12 Ma; Roche, 2015; Wingate et al., 2015), and by the timing of peak metamorphism (1991 ± 2 Ma; Roche, 2015; Wingate et al., 2015), which postdates mineralisation. Sulfide textures and Au:Ag ratios in electrum grains also support peak metamorphism postdating the formation of the deposit (Roche, 2015).

In the 30 mineralised samples that were analysed, gold and the sulfide phases are generally coexisting but not necessarily spatially associated at the grain scale. This is due to the high grade metamorphism (peak Pressure-Temperature conditions of 750–790°C and at least 5.5 kbar; Cawood and Tyler, 2004) that melted and remobilised mineralisation. The most common observed sulfide is pyrrhotite, which locally contains small chalcopyrite inclusions and is interstitially located along the grain boundaries of silicates. In rare instances, pyrite has crystallised around the rims or replaces pyrrhotite. This texture is interpreted to reflect a retrograde metamorphic process. The sulfide phases are not preferentially associated with either leucosomes or melanosomes (Roche, 2015). Globular pyrrhotite inclusions are also observed within garnet porphyroblasts, implying the presence of sulfides prior to peak metamorphism and the subsequent breakdown during prograde metamorphism (Roche, 2015).

Methods

The thirty-six samples were analysed for their sulfur isotopic composition in the Stable Isotope
Laboratory of the Department of Earth and Planetary Sciences at the McGill University, Montreal, Canada. Sulfide-bearing samples were microdrilled using a 1 mm diameter hand drill, and the sulfur in the resulting powder was extracted to Ag₂S through a Cr(II) reduction procedure (Canfield et al., 1986). Bulk rock samples where no visible sulfide phase existed were powdered and 10g of the powder was then extracted in the same manner as above. The resulting Ag₂S was fluorinated at 225°C in a Ni bomb under 20X stoichiometric excess F₂ for >9 hours. The SF₆ so produced was purified cryogenically and chromatographically and analysed on a Thermo Electron MAT 253 mass spectrometer for multiple sulfur isotope ratios in a dual-inlet mode. The δ³³S, δ³⁴S and δ³⁶S values are conventional δ notations with respect to ViennaCanyon Diablo Troilite (V-CDT) defined as δₓS = 1000 × [(ₓS/³²S)sample/(ₓS/³²S)V-CDT − 1], where x is 33, 36 or 34 (Ding et al., 2001). The Δ³³S value, a measure of mass-independent fractionation of S isotopes, is based on δ³³S* and δ³⁴S* values defined as Δ³³S = δ³³S* − [(δ³⁴S*/1000 + 1)⁰.⁵¹⁵ − 1] × 1000, where * = measured values (Farquhar and Wing, 2003). The Δ³⁶S value, also a measure of mass-independent fractionation of S isotopes is defined as Δ³⁶S = δ³⁶S* − [(δ³⁴S*/1000 + 1)¹.⁹ − 1] × 1000 (Farquhar and Wing, 2003). Repeat analyses through the entire analytical procedure of the IAEA S-1 standard return uncertainties (2σ) on δ³⁴S, Δ³³S and Δ³⁶S values better than 0.2‰, 0.014‰ and 0.2‰, respectively. Further inter-laboratory comparative analyses of IAEA standards confirm this degree of accuracy in analytical procedure (Wing and Farquhar, 2015). Analysis of an externally validated standard was recently performed in this laboratory using this exact procedure. The full results of the Sierra pyrite standard repeats (n = 8) are detailed in LaFlamme et al., (2016) and as summarized with their 2σ uncertainties as follows; δ³⁴S = +2.17 ± 0.28, Δ³³S = -0.02 ± 0.014 and Δ³⁶S = -0.18 ± 0.15.
Supp Figure DR3. Δ36S vs Δ33S data from this study. Error bars for Δ33S are smaller than the points in all cases. Fractionation of Δ36S can only be explained by photochemical reactions in the Archaean and not by thermochemical sulfate reduction experiments (Oduro et al., 2011). The Δ\textsuperscript{33}S - Δ\textsuperscript{36}S slope produced in this dataset sits comfortably within the range of 2σ measurement error of Δ\textsuperscript{36}S of the existing Archaean MIF slope (grey zone in the figure). Further, the work of Zerkle et al. (2012), showed that the Δ\textsuperscript{33}S - Δ\textsuperscript{36}S slope changes from 0.9 to 1.5 within a single stratigraphic package due to possible variations in atmospheric concentrations of pSO\textsubscript{2}. Thus we
do not believe any additional fractionation processes are recorded in our dataset, as far as can be interpreted from the $\Delta^{33}S - \Delta^{36}S$ data. The S-isotope composition for all putative sulfur sources in our model other than Archaean sedimentary derived sulfur in $\Delta^{33}S - \Delta^{36}S$ space would plot at the origin due to their $\Delta^{33}S$ and $\Delta^{36}S$ values being close to 0‰. Thus mixing between the multiple possible components from our model in $\delta^{34}S - \Delta^{33}S$ space (Fig. 1) would only show up in $\Delta^{33}S - \Delta^{36}S$ space as a linear trend between Archaean sedimentary sulfur and the other components.
Supplementary Figure DR4: The quantitative modelling we have performed, as suggests that all realistic $\Delta^{33}S$-$\delta^{34}S$-$\Delta^{36}S$ compositions observed in the Archaean sedimentary sulfide record that observes the constraint of being above the maximum observed $\Delta^{33}S$ value we see in our data.
(minimum, δ^{34}S = 2‰, Δ^{33}S = 1.2‰, Δ^{36}S = -1.2% and maximum, δ^{34}S = 12‰, Δ^{33}S = 7.2‰, Δ^{36}S = -7.2%), somewhere between 15-85% of the sulfur budget must have been sources from Archaean sedimentary sulfides. The model is run in 20% steps, thus reading from each end member, the line steps 20% away from one end member towards the other. As can be seen, the Δ^{33}S – δ^{34}S values in the sample set indicate that all the three components play a significant role in creating the observed values. The full model is attached in a spreadsheet.
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| VRC 618060 | Mineralised quartz biotite garnet gneiss | 3.70 | 6.36 | 0.2 | 11.57 | 0.426 | 0.014 | -0.56 | 0.2 | Pyrrhotite (minor chalcopyrite) | 0.1 | 4 |
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| VRC 818080 | Mineralised quartz biotite garnet gneiss | 4.00 | 6.36 | 0.2 | 11.31 | 0.723 | 0.014 | -0.81 | 0.2 | Pyrrhotite (minor chalcopyrite) | 1.2 | 4.8 |
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| VRC 668108 | Mineralised quartz biotite garnet | 4.08 | 7.23 | 0.2 | 13.38 | 0.365 | 0.014 | -0.40 | 0.2 | Pyrrhotite (minor chalcopyrite) | 10.6 | 4.7 |
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Additional references:


Wingate, M. T. D., Kirkland, C. L., Hartley, G. J., Hitchings, B. L., (editor.), 2015, Compilation of geochronology information 2015: [Western Australia]. Geological Survey of Western Australia

CHAPTER THREE

ATMOSPHERIC SULFUR IN THE OROGENIC GOLD DEPOSITS OF THE ARCHEAN YILGARN CRATON, AUSTRALIA

This chapter comprises a manuscript which has been accepted for publication in the journal *Geology*. The chapter is included as published in the journal. The supplementary material comprises an extended description of the methods and several other ways of visualising the data presented in this study, which has been appended to the end of this chapter and two excel spreadsheets which have been included in the electronic appendices to this thesis. The first spreadsheet, Chapter 3 – SM1, presents the full set of data collected in this study and the compilation of information on each individual gold deposit sourced from the OSNACA open source database and appropriate references for the constraining parameters of each gold deposit. The second spreadsheet, Chapter 3 – SM2, presents the full sulfur isotope database compiled as part of this thesis.
Atmospheric sulfur in the orogenic gold deposits of the Archean Yilgarn Craton, Australia

Vikraman Selvaraja1, Stefano Caruso1, Marco L. Fiorentini1, Crystal K. LaFlamme1, and Thi-Hao Bui2
1Centre for Exploration Targeting and ARC Centre of Excellence of Core to Crust Fluid Systems, University of Western Australia, 35 Stirling Highway, Crawley, 6009 WA, Australia
2Department of Earth and Planetary Sciences, McGill University, 3450 University Street, Montreal, H3A 0E8 Quebec, Canada

ABSTRACT
The origin of sulfur and gold in Archean orogenic gold systems should provide significant insights into the dynamics of fluid movement in the crust of the early Earth, but is poorly constrained and highly debated. Our natural laboratory to address this knowledge gap is the metal-endowed Yilgarn Craton (Western Australia), where we measured the multiple sulfur isotope signatures of representative sulfide-bearing auriferous samples from 24 Archean orogenic gold deposits varying in size and geological setting. Utilizing chemically conservative mass-independent fractionated sulfur (MIF-S) isotope signatures, we fingerprinted a major source of sulfur in these deposits. Contrary to previous studies, our data show that they display MIF-S isotope anomalies, with Δ34S values ranging from ~1.18‰ to +2.04‰; most of the studied deposits show a sulfur signature that is consistent with a crustally derived source. Unlike smaller deposits, which may form with sulfur derived from a single sedimentary sulfur source, therefore providing a coherent Archean atmospheric signal in their Δ34S-Δ36S slopes (~0.9–1.5), the formation of giant deposits may require sourcing from a wider range of sulfur reservoirs and using different processes, as reflected in their apparently random Δ34S-Δ36S slopes.

INTRODUCTION
The elusive source of sulfur in Archean orogenic gold deposits is a highly contested area of research, with different models of deposit formation calling on a variety of crustal and mantle sources to explain the anomalous (10–100× average crustal abundance) amounts of sulfur in these systems. Possible sources of sulfur in Archean orogenic gold deposits include supracrustal rocks (e.g., Phillips and Groves, 1983; Phillips and Powell, 2010; Tomkins, 2013), mid-crustal magmatic hydrothermal systems (e.g., Mueller et al., 2008; Xue et al., 2013), or even deeper reservoirs, such as subduction-related metamorphic fluids (Selvaraja et al., 2017), the lower crust, or the mantle (e.g., Hornsky et al., 2012). The identification of the source of sulfur in Archean orogenic gold deposits not only strengthens exploration strategies for undiscovered mineralized provinces, but also provides key insights into the important and poorly constrained sulfur cycle, which plays a critical role in the evolution of Earth’s Archean climate and biosphere. In addition, because gold is transported in hydrothermal fluids mostly as bisulfide and/or trisulfide complexes (Pokrovski et al., 2015), fingerprinting the source of sulfur in Archean orogenetic gold deposits may also aid in constraining the controversial source of this metal.

The identification of anomalous mass-independent fractionated sulfur isotope (MIF-S) signatures (defined as Δ34S and Δ36S; Wing and Farquhar, 2015), in addition to the standard thermodynamic fractionation of δ34S (mass-dependent fractionated sulfur; MDF-S), has led to new insights into the genesis of a wide range of Archean and Proterozoic mineral systems. These include volcanicogenetic massive sulfide exhalative deposits (e.g., Sharan et al., 2014), komatiite-hosted Ni-Cu deposits (Bekker et al., 2009; Fiorentini et al., 2012a; LaFlamme et al., 2016), intrusion-related Ni-Cu deposits (Fiorentini et al., 2012b), and orogenic gold deposits (Xue et al., 2013; Agangi et al., 2016; Selvaraja et al., 2017). The production of MIF-S signatures occurred prior to the 2.45–2.33 Ga Great Oxygenation Event (Farquhar et al., 2000, 2013; Johnston, 2011). These anomalous signatures are chemically conservative (Sharan et al., 2014), so it is argued that MIF-S may be diluted but is ultimately an indelible tracer that has the potential to track the presence of sulfur derived from Archean surficial reservoirs throughout the geological evolution of the planet.

MIF-S signatures in Archean orogenetic gold deposits have been previously studied at the deposit and district scales with contrasting interpretations. Xue et al. (2013) documented the occurrence of small MIF-S anomalous signatures from four ca. 2.7 Ga orogenic gold deposits in the St. Ives belt of the Yilgarn Craton (Western Australia). In arguing that there was no detectable MIF-S in those deposits, Xue et al. (2013) hypothesized that (1) supracrustal fluids only play a minor role in the genesis of Archean orogenic gold systems, and (2) gold and sulfur are derived from juvenile mantle–derived fluids. Agangi et al. (2016) documented larger MIF-S signatures from two ca. 3.0 Ga deposits in the Barberton greenstone belt of South Africa to argue against the hypothesis of Xue et al. (2013).

In this study we resolve this disparity in previous deposit- to regional-scale studies by using a much broader scale, the Yilgarn Craton, to present a new high-precision MIF-S data set from multiple orogenic gold deposits that formed contemporaneously across the entire lithospheric block. We show that Archean sedimentary environments provide a significant proportion of sulfur to most Archean orogenic gold systems and that the formation of giant deposits may require the sourcing of a wider range of sulfur reservoirs than for smaller systems.

SAMPLES AND GEOLOGICAL SETTING
We investigated the multiple sulfur isotope composition of sulfide phases, dominantly pyrrhotite and pyrite, that are coeval with gold mineralization, locally containing gold and/or being spatially and genetically associated with orogenic gold mineralization. We obtained (1) sulfide-bearing auriferous samples from the open source project Ore Sulfides Normalized to Average Crustal Abundance (OSNACA; http://www.cet.edu.au), and (2) catalogued samples of orogenic gold deposits from the University of Western Australia rock library. Full descriptions of all samples studied in this project and the geological background on the various deposits are available in the GSA Data Repository1.

This project presents a comprehensive set of mineralized samples from Archean orogenic gold deposits, with 62 samples from 24 orogenic gold deposits in terranes that host the vast...
majority of the gold resources of the Yilgarn Craton (Robert et al., 2005): the Kalgoorlie terrane, the Kurnalpi terrane, the Youanmi terrane, and the South West terrane (Fig. 1). The deposits are broadly representative of the various styles of Archean orogenic gold mineralization (e.g., host-rock variation, different structural settings, metamorphic grade, and alteration mineralogy) and range in size from the 21.6 t Au Marymia deposit to the 2500 t Au Mount Charlotte–Golden Mile deposits. They are hosted in different greenstone belts that display analogous internal stratigraphy, variably underlain by mafic-ultramafic successions that commonly formed from 3.0 to 2.8 Ga, interdigitated with metasedimentary layers ranging from black shales to conglomerates, predominantly deposited between 2.9 and 2.7 Ga, locally intruded and overlain by multiple 2.7–2.6 Ga episodes of felsic magmatism (Cassidy et al., 2006).

Gold mineralization is hosted in different rock types with variable structural setting, alteration, and ore mineralogy (Duuring et al., 2007; Goldfarb and Groves, 2015). However, it is generally accepted that these ores are a single group of epigenetic deposits that formed due to widespread hydrothermal activity at 2650–2630 Ma (Vielreicher et al., 2015) during the Neoarchean evolution of the Yilgarn Craton. All of these deposits are associated with large regional-scale structures and splays, which are common in Archean cratons worldwide (Robert et al., 2005). The metamorphic grades of the deposit host rocks range from greenschist to granulite facies, but mineralization is primarily restricted to the brittle-ductile transition zone (Robert et al., 2005).

RESULTS

High-precision multiple sulfur isotope analyses are reported in the Data Repository and are displayed in Figure 2. The $\Delta^{34}S$ values in the studied deposits range from $-1.19\%$ to $+2.04\%$ (see the Data Repository). The range of $\delta^{34}S$ data obtained in this study ($-8.91\%$ to $+5.69\%$) mirrors the findings of Hodkiewicz et al. (2008), validating our data set as being representative of orogenic gold deposits in the Yilgarn Craton. Furthermore, the $\delta^{34}S$ values are very consistent between multiple samples in each deposit with the exception of the Golden Mile deposit, which shows a range of $-8.5\%$.

The results in $\Delta^{33}S$-$\Delta^{34}S$ space are displayed in Figure 3. The average array of the relationship between $\Delta^{33}S$ and $\Delta^{34}S$ is $-0.78$ for all samples from all deposits, which is slightly outside the accepted Archean array of $-0.9$ to $-1.5$ (Johnston, 2011; Zerkle et al., 2012). The array of $-0.78$ has not been documented before in the Archean sedimentary literature, and it cannot be created by mixing an Archean MIF-S array with an MDF-S array ($-9$ to $-7$; Wacey et al., 2015). Furthermore, an average of all samples may not be representative because it obscures the differences between different deposits. Whereas the $\Delta^{33}S$-$\Delta^{34}S$ arrays for the samples from the giant Golden Mile and Plutonic deposits are $-0.37$ and $2.2$, respectively, plotting outside both the Archean MIF-S array and MDF-S array and displaying weak $R^2$ correlations ($0.7$ and $0.04$, respectively), samples from the smaller Marymia and Griffins Find deposits yield slopes of $-0.92$, with strong $R^2$ correlations ($0.92$ and $0.98$, respectively), coinciding with the Archean MIF-S array.

SEDIMENTARY SOURCE OF SULFUR

The multiple sulfur isotope data set reveals that almost all the Archean orogenic gold
deposits in the Yilgarn Craton contain sulfur derived from Archean surficial reservoirs. Compared with all the known multiple sulfur isotope data on orogenic gold systems, including data sets from Xue et al. (2013) and Agangi et al. (2016), it is apparent that most deposits show a consistent bias toward +33S anomalies in their sulfur budget (Fig. 2). This anomalous signature is mainly preserved in Archean carbonaceous sedimentary units worldwide (Farquhar et al., 2013). Thus, it would be reasonable to argue that orogenic gold deposits derive a portion of their sulfur from devolatilization of carbonaceous shales (Tomkins, 2010). This hypothesis also aligns well with the findings of Large et al. (2011) and Gregory et al. (2016) that carbonaceous shales, and specifically Archean carbonaceous shales, commonly have very high concentrations of gold. Taken together with the fact that gold transport in high-temperature fluids occur as a bisulfide-trisulfide complex (Pokrovski and Dubessy, 2015), this suggest that it is possible that supracrustal sedimentary rocks are central to the formation of orogenic gold deposits.

However, the magnitude of the +33S anomalies observed in the orogenic gold deposits from the Yilgarn Craton is only about half of the one observed in the published data of ca. 2711–2675 Ma Yilgarn sediments (see the Data Repository). There are several possible explanations for the observed magnitude of the +33S anomaly of the orogenic gold deposits: (1) it reflects a mixture between sulfur derived from supracrustal Archean magmatic rocks (Δ33S = −0.8‰), Fiorentini et al., 2012a) and intercalated sedimentary units that have variable but broadly positive Δ33S values; (2) it reflects mixing between mantle-derived sulfur (Δ33S = 0‰) and the aforementioned sedimentary units; or (3) the sulfur is derived from deeper, older and currently unidentified sedimentary units with a much smaller positive Δ33S anomaly, which mirrors the observed magnitude of the Δ33S anomaly of the orogenic gold deposits in the Yilgarn Craton.

A cursory glance at the stratigraphic column of the Eastern Goldfields (Cassidy et al., 2006) suggests that the deep stratigraphy of the Eastern Goldfields is poorly constrained. Previous models for supracrustal devolatilization to generate fluids that form orogenic gold deposits have generally called for both the magmatic and sedimentary rocks to devolatilize simultaneously (Phillips and Powell, 2010). Considering the significant unknowns discussed here, it is difficult to argue conclusively for a purely sedimentary sulfur source for orogenic gold deposits. Thus, the most probable reason for the observed higher +33S magnitude in gold deposits relative to the MIF-S signature of the known sedimentary sources is that there is a mix of sulfur sources, including sulfur derived from magmatic and sedimentary supracrustal rocks as well as from the mantle.

The sulfur budgets of the 3.0 Ga orogenic gold deposits studied by Agangi et al. (2016) show a much more restricted range of Δ33S values in relation to the ca. 2.65 Ga orogenic gold deposits of the Yilgarn Craton from this study and from Xue et al. (2013), as shown in Figure 2. We argue that the data from Agangi et al. (2016) reflect the relatively restricted range of available Δ33S in the 3.3–3.05 Ga global sedimentary reservoirs (inset in Fig. 2), whereas the data from the 2.65 Ga deposits reflect the much larger range of Δ33S values in the global sedimentary record at the time. This time-dependent signal may thus be an additional line of evidence that sediments represent a major source of sulfur in Archean orogenic gold deposits. It could also be argued that there is a secular evolution in the nature of orogenic gold ore-forming processes associated with the varying availability of sulfur from sedimentary sources and the fluctuating architecture of the underlying craton related to continental growth processes. This is an idea that can be further evaluated by studying the MIF-S compositions of orogenic gold deposits from various time slices of the Archean.

FRACTIONATION OF Δ36S

The small Marymia (21.6 t Au) and Griffins Find (2.5 t Au) deposits display a Δ36S/Δ33S array of −0.92, which coincides with the Archean MIF-S reference array (Johnston, 2011). This suggests that their sulfur source has an isotopic signature consistent with an Archean sedimentary reservoir. However, in the much larger Plutonic (350 t Au) and Golden Mile (2500 t Au) deposits, the Δ36S/Δ33S array does not fit the Archean MIF-S, MDF-S, or mixing arrays (Fig. 3). This discrepancy may reflect sourcing from multiple reservoirs, including sulfur that fractionated from oxidized (S2–) to reduced (S0), which would result in the Δ33S-Δ36S array along the MIF-S line from the top left to the bottom right quadrants in Figure 3. However, this fractionation would not explain the dispersion of the data toward the top right quadrant (Fig. 3). We suggest that one possible cause of this enigmatic fractionation pattern is the influence of S0, a speciation of sulfur that is not present in low-temperature environments, but becomes dominant at temperatures >250 °C and pressures >0.5 GPa, where the recycling of sulfur in hydrothermal environments occurs (Pokrovski and Dubessy, 2015). This possibility needs further experimental validation.

CONCLUSIONS

Our findings are consistent with high-temperature metamorphic devolatilization models for the formation of orogenic gold deposits that have been suggested previously (e.g., Phillips and Groves, 1983; Phillips and Powell, 2010). These models call on a metamorphic fluid generated by crustal dewatering to explain the presence of widespread hydrothermal activity and contemporaneous formation of gold deposits in the Yilgarn Craton during the Neoarchean (Phillips and Powell, 2010, and references therein). Metamorphism and deformation of interlayered mafic-ultramafic units and pyritic shales in the greenstone belts (Cassidy et al., 2006) could easily generate the +33S enriched sulfur and possibly the Au-rich fluids (Tomkins, 2010) required to form multiple broadly coeval orogenic gold deposits across the craton. The truly giant systems, however, probably need major contributions of sulfur and metals from deeper mantle and/or magmatic fluids for their formation.

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Methods

The MIF-S anomalous signatures can be either positive or negative, and are expressed as $\Delta^{33}\text{S} = \delta^{33}\text{S} - [(\delta^{34}\text{S}/1000 + 1)^{0.515} - 1] \times 1000$ and $\Delta^{36}\text{S} = \delta^{36}\text{S} - [(\delta^{34}\text{S}/1000 + 1)^{1.9} - 1] \times 1000$ (all data presented in this study is in ‰ relative to V-CDT; Ding et al., 2001). The calculation of the MIF-S anomalous signature is done by analysing the $\Delta^{33}\text{S}$ values of sulfur and the $\Delta^{36}\text{S}$ - $\Delta^{33}\text{S}$ slope: $\Delta^{33}\text{S}$ values which are more than 0.007‰ per mil variation in $\delta^{34}\text{S}$ of the same sample away from 0‰ and which fall in the $\Delta^{33}\text{S}$-$\Delta^{36}\text{S}$ array ~ -0.9 are most likely generated by Archaean atmospheric processes (Jamieson et al., 2006; Johnston, 2011; Caruso et al., in prep). High precision quadruple sulfur isotope analyses were conducted at the GEOTOP Stable Isotope Laboratory, McGill University using the dissolution-fluorination technique (Canfield et al., 1986). Sulfides in the samples were micro-drilled using a 1 mm diameter drill bit and the resulting pure sulfide powders were analysed using the Cr(II) reduction procedure (Canfield et al., 1986). Repeat analyses through the entire analytical procedure return uncertainties (2σ) on $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values better than 0.2‰, 0.02‰ and 0.1‰, respectively. For more detailed information on analytical methods see Wing and Farquhar (2015).
Supplementary Figure 1: Data sourced from the references in the Sulfur Isotope Database (Table DR2) appended to this publication, and currently maintained online at http://www.cet.edu.au/research-projects/special-projects/gssid-global-sedimentary-sulfur-isotope-database. All samples are thought to represent the primary atmospheric signal and are collected from sedimentary rocks.
Supplementary Figure 2: Relationship between total gold tonnage of the deposits studied and their sulfur isotope compositions in $\delta^{34}$S-$\Delta^{33}$S space. It is clear that regardless of the host rock type of the deposit, MIF-S is present in most deposits and further there is a weak relationship between the magnitude of the $\Delta^{33}$S signature, where smaller deposits have larger $\Delta^{33}$S ranges, and the total gold tonnage in the studied deposits. Samples hosted in quartz veins distal from any buffering host rock are defined as ‘Hydrothermal’.
Supplementary Figure 3: $\Delta^{33}\text{S} - \Delta^{36}\text{S}$ values of the deposits studied, coloured by their total gold tonnage. It is clear that the larger deposits (in lighter colours) have $\Delta^{33}\text{S} - \Delta^{36}\text{S}$ ratios which deviate from the -0.9 to -1.5 slope which is characteristic of the Archean photochemical fractionation pattern (MIF-S; Johnston, 2011). It remains unclear what is driving this process, and further investigation of this in more Archean orogenic gold deposits may outline the processes controlling this and the relationship of those processes to the size of the resource endowment.

References


CHAPTER FOUR

EVIDENCE OF LOCAL SOURCING OF SULFUR AND GOLD
IN AN ARCHAEOAN SEDIMENT–HOSTED GOLD DEPOSIT

This chapter is presented as the published manuscript in *Ore Geology Reviews*. There are a further two spreadsheets of supplementary material which are included in the electronic appendices to this thesis. The first, Chapter 4 – SM1, is the entirety of the laser ablation inductively coupled mass spectrometry data collected for this study, and the second, Chapter 4 – SM2, is the total secondary ion mass spectrometry multiple sulfur isotope data collected for this study.
Evidence of local sourcing of sulfur and gold in an Archaean sediment-hosted gold deposit

Vikraman Selvaraja\textsuperscript{a,b,⁎}, Marco. L. Fiorentini\textsuperscript{a,b}, Heejin Jeon\textsuperscript{c}, Dany D. Savard\textsuperscript{d}, Crystal K. LaFlamme\textsuperscript{a,b}, Paul Guagliardo\textsuperscript{c}, Stefano Caruso\textsuperscript{a,b}, Thi-Hao Bui\textsuperscript{e}

\textsuperscript{a} Centre for Exploration Targeting, School of Earth Sciences, University of Western Australia, 35 Stirling Highway, Crawley 6009, WA, Australia
\textsuperscript{b} ARC Centre of Excellence of Core to Crust Fluid Systems, School of Earth Sciences, University of Western Australia, 35 Stirling Highway, Crawley 6009, WA, Australia
\textsuperscript{c} Centre for Microscopy, Characterisation and Analysis, University of Western Australia, 35 Stirling Highway, Crawley 6009, WA, Australia
\textsuperscript{d} LabMaTer, Universite du Quebec a Chicoutimi, 555 Boulevard Universite, Chicoutimi QC G7H 2B1, Canada
\textsuperscript{e} Department of Earth and Planetary Sciences, McGill University, 3450 University Avenue, Montreal QC H3A 0E8, Canada

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\textbf{A B S T R A C T}

Determining the source of sulfur in an ore deposit is key to understanding the nature of the ore forming processes. The Neoarchaean Paulsens sediment-hosted gold deposit (∼1 Moz @ 7.6 g/t) located in the Pilbara Craton of Western Australia exhibits many of the characteristics of Phanerozoic shale hosted gold deposits (e.g. Huijiabao Trend, Northern Carlin Trend and Sukhoi Log), in that 1) black shales are the dominant host rock, 2) gold is hosted in pyrite as both free gold and dissolved gold in the lattice of the pyrite, and 3) multiple generations of pyrite have formed due to a variety of geological processes. In this contribution we utilised Secondary Ion Mass Spectrometer (SIMS) to measure the in-situ quadrupole ($^{32}$S, $^{33}$S, $^{34}$S and $^{36}$S) sulfur isotope compositions of the different generations of pyrite. Our results indicate that the both diagenetic and hydrothermal pyrite generations display similar and anomalous $\Delta$34S signatures (up to +0.4‰). Further, the $\Delta$33S-$\Delta$34S arrays in the hydrothermal pyrite generations lie on a slope which is similar to that of the diagenetic pyrite. These data support the hypothesis that the sulfur in the ore zones came from the host Hardey Formation black shales.

We also performed trace element analyses of syn-sedimentary and early diagenetic pyrite from the Hardey Formation using Nano Secondary Ion Mass Spectrometry (NanoSIMS), Electron Probe Microanalysis (EPMA) and Laser Ablation-inductively coupled plasma-mass spectrometry (LA-ICPMS), all of which show that the syn-sedimentary and early diagenetic pyrite contain high concentrations of many trace elements (As, Ni, Co, Ca, Ag, Se, Te, Bi), including up to 1.5 ppm Au. These metals contents are also abundant in the several generations of mineralised hydrothermal pyrite and form clear patterns of growth associated with couple dissolution precipitation reactions. These findings clearly indicate that the fluid that transported the Au must have also been enriched in the base and precious metals that are contained in the early, syn-diagenesis pyrite.

Data from this study clearly support the hypothesis that in some sediment-hosted gold systems, all the sulfur and gold required to form the deposit are sourced from the local sedimentary package. By using the presence of anomalous mass independent sulfur isotope signatures as chemically conservative and indelible tracers, it is possible to fingerprint the source of sulfur in a wide range of mineral systems, thus enhancing predictive exploration strategies at the regional to camp scales.

1. Introduction

The source of sulfur and gold in sediment-hosted gold deposits is poorly constrained and different reservoirs have been called on in different ore-forming environments. This is partly due to the fact that this class of deposits has only recently been studied in detail (Cline et al., 2005; Maohong et al., 2011) in relation to other gold mineral systems such as classic orogenic gold and epithermal gold deposits. In addition, the complex and variable tectonic and environmental settings in which these deposits are hosted has hindered previous attempts to fingerprint the source of mineralising fluids. Examples of these deposits range from the mesothermal, ‘orogenic-gold’ type deposits, such as the supergiant Obuasi gold deposit in the Ashanti gold belt, Ghana (Fougerouse et al., 2016) to the ‘Carlin style’ deposits of the Youjiang basin, southwest China (Hou et al., 2016). Regardless of the specific genetic process, the source of gold and sulfur in most of these deposits is also heavily

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debated, with deep crustal/upper mantle rocks, magmas (Goldfarb and Groves, 2015 and references therein) and/or supracrustal basinal rocks (Large et al., 2011) being called on as the ultimate source. In this paper, we use a combination of sulfur isotopic and sulfide trace element geochemistry data to argue for the local sourcing of sulfur and gold in a black shale hosted gold deposit.

The use of sulfur isotopes as a method of evaluating the sources of sulfur in mineral systems has a long and distinguished history (Thode et al., 1962; Seal, 2006 and references therein). Advances in the theoretical understanding of the mass independent fractionation (MIF-S) of the minor sulfur isotopes, 33S and 36S, (Farquhar et al., 2000; Farquhar and Wing, 2003) have recently found application in mineral system science, particularly around Archaean ore bodies (Bekker et al., 2009; Fiorentini et al., 2012a; Penniston-Dorland et al., 2012; Sharman et al., 2014). However, most of these studies have used only bulk sulfur isotope measurement techniques, such as dissolution-fluorination, whereas the more complex paragenesis of sediment-hosted gold deposits call for more precise in situ measurements of the sulfur isotope compositions in multiple generations of pyrite. This is where recent advances in Secondary Ion Mass Spectrometry (SIMS) for the in situ determination of multiple sulfur isotopes in pyrite have been demonstrated (Kozdon et al., 2010; Kita et al., 2011; Farquhar et al., 2013).

In its application to gold systems, MIF-S has begun to be used in Palaeoproterozoic systems as a tracer of tectonic scale processes (Selvaraja et al., 2017a). Additionally, new work in relation to craton scale mineral forming events, e.g. the Yilgarn orogenic gold event at 2.65 Ga, has shown that MIF-S can be used to trace the source of sulfur in Archaean terranes (Selvaraja et al., 2017b). In this study, we move down another scale to use the presence of MIF-S signatures at the min- eral scale to highlight possible geological processes. This has been attempted previously for orogenic gold deposits yielding mixed results, with some work suggesting that MIF-S is preserved in orogenic gold associated pyrite (Agangi et al., 2016) but others dissenting from this finding (Xue et al., 2013; Steadman et al., 2015). We apply these techniques to the special case of shale hosted gold deposits which are widely argued to form through different processes to orogenic gold deposits (Su et al., 2009; Maohong et al., 2011) to elucidate the source of sulfur and gold in shale hosted gold deposits.

Recent work on black shale hosted gold deposits, particularly those in the Yangtze Craton, Sukhoi Log and the Carlin trend in Nevada, have also highlighted that in situ trace element analysis of pyrite associated with the gold yields key insights into the genetic processes leading to the formation of sediment-hosted gold systems (Large et al., 2007, 2011; Hou et al., 2016). This has been argued on the basis of the abundance and ratios of several metallic and semi-metallic trace elements which are known to substitute into the crystal structure of pyrite from the ore-forming fluid. These metals, including Ni, Cu, As, Sb, Tl, Se, Zn, Pb, Ag and others, are known to have significantly different abundances and mass ratios in various crustal environments, specifically being very elevated in black shales (Large et al., 2011). In the Archaean, where despite black shales being relatively common, shale hosted gold deposits are few and far between. The Paulsens deposit however, is one such example where we can test some of the genetic theories developed in the study of Phanerozoic shale hosted gold deposits.

Paulsens is a ~1 million ounce gold deposit (Bland et al., 2014) located at the southern edge of the Pilbara Craton, which is a major mineral province for iron ore but hosts very few known gold deposits. The deposit is hosted in a sequence of mafic volcanic and sedimentary rocks belonging to the Hardey Formation in the Wyloo Dome, which preserves a complete stratigraphic succession from the Palaeoarchean to the Proterozoic (Fig. 1; Thorne and Trendall, 2001). Mining began in this deposit in the 1930s, and to this date it has produced an estimated 742,000 oz of gold extracted from 3.7 million tonnes of ore at an average grade of 7.6 g/t (Bland et al., 2014). The deposit consists of several lenses of massive and disseminated sulfides, mainly pyrite, hosted primarily in thick laminated and moderately deformed quartz veins that formed synchronously with the mineralisation. These quartz veins are localised within and along the margins of a folded, coarse-grained gabbro dyke, which crosscuts the black shales of the Archaean Hardey Formation, referred to locally as the ‘Melrose Argillite’. There has been no previous work on this deposit due to its relatively small size and location in an understudied part of the Pilbara Craton. In the Archaean, the preservation of the mass independent sulfur fractionation signature in sedimentary units is well documented (Johnston, 2011). As Paulsens is a black shale hosted gold deposit in the Archaean, where MIF-S signatures may be preserved in the sedimentary pyrite, we attempt to correlate the MIF-S in the gold associated sulfides to the sedimentary host units. This may lead us to an incontrovertible answer on the source of sulfur and gold in black shale hosted gold deposits.

In this paper, we synthesise information regarding the structural setting of the deposit from internal unreported deposits and present new data on the textures, paragenesis, sulfur isotopic compositions and trace element geochemistry of the various stages of pyrite observed within the deposit and obtained via sampling of underground drives and drill core. We suggest that the various pyrite stages document the isotopic and geochemical evolution of the mineralising fluid. Through the application of MIF-S as an indelible marker we trace the source of the fluids and conclude that mineralisation at Paulsens is largely related to local sourcing of sulfur and gold from the diageneric sulfide phases of the black shales of the Hardey Formation that host the deposit.

1.1. Regional geology

The Wyloo Dome, which hosts the Paulsens gold deposit and several other small gold prospects and old workings, preserves a complete stratigraphic succession from the Archaean Metawandy Granite basement in the core, through the Mt. Bruce Supergroup, to the Palaeoproterozoic Ashburton Formation in the upper Wyloo Group (Fig. 3; Johnson et al., 2013). It is located at the southern end of the Hamersley Basin, which overlies the Archaean Pilbara Craton, one of the oldest blocks of continental crust in the world (Van Kranendonk, 2014).

The Paulsens deposit occurs in a folded succession of sedimentary and volcanic rocks that make up the Hardey Formation, which formed during active rifting on the margin of the Pilbara Craton throughout the depositional history of the Fortescue Group (~400 Ma; Tyler and Thorne, 1990). The Hardey Formation, which has been dated at 2750 ± 5 Ma from U-Pb dating of zircons in accretionary lapillli tuff interbedded with siltstone, is roughly 3000 m thick (Thorne and Trendall, 2001). However, this thickness varies significantly across the lateral dimensions of the formation, which stretches across the entire Pilbara Craton (Fig. 1; Hall, 2005; Johnson et al., 2013).

In the vicinity of the deposit, several local units have been outlined for the purposes of near-mine exploration (Fig. 4). These local members are the Melrose Member, which is a black shale with interbedded siltstones and minor sandstones, the Madang Member, which is a quartzose coarse grained conglomerate, the Tin Hut Volcanic Member, which is a conformable basaltic flow with intercalated doleritic and gabbroic sills, and the Beagy Member, which is a coarse sandstone. These units are all crosscut by a late gabbro, which rheologically bounds the mineralisation. This gabbro, referred to as the Paulsens Gabbro, has recently been inferred to have intruded the Hardey Formation at 2700 Ma, based on age dating using U-Pb in baddeleyite (Fielding et al. in review). The gabbro is itself crosscut by the mineralising quartz-pyrite veins and by several episodes of dolerite dyke emplacement, which correspond to major tectonic events in the 2.5 billion year history of the region (Fig. 4).

Most of the Wyloo Dome, as with the rest of the Hamersley Basin, preserves a low grade greenschist facies background alteration (Brown et al., 2004). Closer to the deposit calcite and chloride alteration is observed in hand specimens and in thin sections. The intensity of this
Fig. 1. Location of the Paulsens deposit. Adapted from Thorne and Trendall (2001) highlighting the location of the Wyloo Dome and the Paulsens Au deposit in the southern margin of the Hamersley Basin of Western Australia.

Fig. 2. The global sedimentary sulfur isotope record from 3.9 Ga to the present. The data have been compiled from the published literature and published in a publicly available database, the GSSID (http://www.cet.edu.au/research-projects/special-projects/gssid-global-sedimentary-sulfur-isotope-database). The data highlight that the narrowing of the range of primary sedimentary $\Delta^{33}S$ values occurs at 2.33 Ga, which is when the GOE is thought to have occurred (Luo et al., 2016a,b). The Hardey Formation is deposited during a period of very small variability in the $\Delta^{33}S$ values.
Fig. 3. A simplified stratigraphic section through the Wyloo Dome adapted from Johnson et al. (2013) displaying the tectonic evolution of the dome through a period of active rifting in the Neoarchaean, the development of a passive margin through the Palaeoproterozoic and two major orogenic events that define the tectonic fabric of the region.

Fig. 4. Local geological map of the near mine surroundings, which elaborates the locally defined stratigraphy of the Hardey Formation in the north western end of the Wyloo Dome. The mineralisation occurs at the boundary between the Paulsen Gabbrro intrusive suite and the Melrose Argillite Member of the Hardey Formation. The X-Y section is shown in Fig. 5.
chlorite-calcite alteration increases closer to the deposit, where it is regularly accompanied by thin, generally bedding parallel unmineralised quartz veins.

1.2. Deposit geology and structure

The large (~150 m thick and ~1 km long) quartz vein (Fig. 5) that hosts the bulk of the mineralisation as massive sulfide along its margins is localised by the contact between the Melrose Argillite and the shallowly dipping Paulsens Gabbro, which is oriented at a low angle to bedding. The bedding of the sedimentary packages highlight that it is located on the NE limb of an open fold whose fold axis dips 20° NW. The earliest foliations recorded in the geological record are the S1 fabric, which dips moderately-steeply SSW; however, this fabric is only observed in the sedimentary package. Conversely, the dyke, the mineralisation and the sedimentary package are all locally foliated by at least two ductile fabrics, termed S2 and S3, which roughly share the same dip as the S1 fabric but have a better developed NE-SW strike orientation. All of these fabrics occur at low angles to the bedding. The S2 foliation clearly folds the quartz veins and associated sulfide lenses in the deposit suggesting that mineralisation predated S2, thus forming earlier in the deformation history of the deposit as shown by the fact that the S2 foliation is clearly aligned with the fold axis of the synform structure (Fig. 6).

The mineralisation is not bound to a single geological unit; however, the largest massive and disseminated sulfide packages are found at the contacts between the Paulsens Gabbro and Melrose Argillite. Ore zones are best developed in the quartz veins, mainly as gold inclusions in massive pyrite (85%) and in nano inclusions within the crystal structure of pyrite. However, very high gold grades are also found in disseminated pyrite and pyrite rich fine and laminated bedding parallel quartz veins in the black shales of the Melrose Argillite.

The main quartz vein lodes contain upper and lower Au-rich mineralised zones and a lower grade core of bacy white quartz (Fig. 5). The upper mineralised zone is brecciated (Fig. 7a) and sulfide rich whereas the lower mineralised zones are commonly laminated and contain graphite in veins and stylolites (Fig. 7b). This variable morphology is possibly due to the changing sedimentary facies between the
lower and upper parts of the Melrose Argillite, moving from more finely bedded black shales in the lower part to coarser grained siltstones and sandstones in the upper part. Some of the mineralisation is also found in thin veins that cut the gabbro parallel to the S2 foliation (Fig. 7c). The upper part of the quartz veins also usually contain large rafts of the Paulsens Gabbro (Fig. 7d), which has been internally veined and is strongly foliated, indicating that the veins formed well after the intrusion of the gabbro.

The alteration assemblage associated with the formation of the deposit is primarily an ankerite-chlorite-sericite alteration, with the sericite alteration replacing much of the original clays in the black shales. This sericitic alteration produces the laminate appearance of the shale,
which is in fact a contrast of slightly different grain sizes reflected by changes in clay-quartz ratios (Fig. 8a). Ankerite and sericite grow in close association with the pyrite that hosts the mineralisation (Fig. 8b, c).

1.3. The multiple sulfur isotope record

In sedimentary rocks older than 2.45–2.33 Ga, e.g. prior to the Great Oxygenation Event (GOE), the $\delta^{34}S$, $\Delta^{33}S$ and $\Delta^{36}S$ values of sulfides hosted in those rocks reflect the production of anomalous fractions of $^{33}S$ and $^{36}S$ by mass-independent fractionation, which is a kinetic-magnetic isotope effect (Farquhar and Wing, 2003). $\Delta^{33}S$ and $\Delta^{36}S$ are defined relative to the predicted $\delta^{33}S$ and $\delta^{36}S$ for a given value of $\delta^{34}S$ if only mass dependent fractionation was occurring. These relationships are summarised in the following equations (Ono et al., 2006; Johnston, 2011):

\[
\Delta^{33}S = \delta^{33}S_{\text{measured}} - \left( \frac{\delta^{34}S_{\text{measured}}}{1000} + 1 \right)^{0.515} - 1 \times 1000
\]

\[
\Delta^{36}S = \delta^{36}S_{\text{measured}} - \left( \frac{\delta^{34}S_{\text{measured}}}{1000} + 1 \right)^{1.9} - 1 \times 1000
\]

It is thought that this anomalous mass independent isotope fractionation effect is generated by photochemical reactions involving the interaction of high-wavelength ultraviolet radiation and sulfur species in the atmosphere (Farquhar et al., 2000). These reactions can only occur in significant quantities when oxygen levels in the atmosphere are below $10^{-5}$ times the present atmosphere levels (Kump, 2008; Pavlov and Kasting, 2002). The observed collapse in the range of values of $\Delta^{33}S$ preserved in the global sedimentary record (Fig. 2; 2.45–2.33 Ga) is thus suggested to signal the beginning of the GOE, where oxygen concentrations in the terrestrial atmosphere became too high to allow the photochemical reactions discussed above to occur.

The fact that the primary MIF-S signal is only preserved in sedimentary rocks and is derived from atmospheric reactions carries the implication that the presence of MIF-S in ore deposits must be due to processes which involve non-magmatic or mantle derived materials (Sharman et al., 2014). This is because the sulfur in the mantle during the Archaean is thought to have near-zero $\Delta^{33}S$ values (Johnston, 2011). The chemically conservative nature of the MIF-S signature, as it cannot be changed other than by extreme dilution with non-MIF bearing sulfur, means that it can act as a robust isotopic tracer of geological and ore-forming processes.

2. Methods

In this study, we studied 22 samples obtained from drillholes and underground drives in the Paulsens deposit and nearby areas. These drillhole samples, which intersect various parts of the upper and lower lodes of mineralisation surrounding the quartz vein, come from holes PDU3242, PDU2353 and PDU1973, which are parallel holes to the ones outlined in Fig. 5. Samples were also obtained from the distal (> 1.5 km) holes PDU3294 and PDU3277, which contained diagenetic pyrite grains (Fig. 9a, b). These samples, together with those collected...
in several underground drives, represent the full diversity of mineralisation styles in the Paulsens deposit.

Of these samples, seven were selected for detailed investigation, including polished thin section microscopy, reflected light studies, scanning electron microscope (SEM) imaging, electron probe micro-analysis (EPMA), multiple sulfur isotope analysis through dissolution-fluorination and secondary ion mass spectrometry (SIMS), laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS) analysis, and NanoSIMS analysis.

2.1. Trace element analysis

2.1.1. NanoSIMS

Ion mapping was carried out using the Cameca NanoSIMS 50 at the Centre for Microscopy, Characterisation and Analysis (CMCA) at The University of Western Australia (UWA). The samples were prepared as polished one inch resin mounts. A carbon coat was applied to the samples to provide conductivity. Measurements were performed with a Cs+ primary beam, with a spot size of approximately 100 nm, impact energy of 16 keV, and a beam current of approximately 2 pA. The instrument was operated in multicollector mode, allowing the simultaneous detection of five ion species from the same analysis region. Secondary ion images were obtained by rastering the primary ion beam across areas measuring 50 × 50 µm, at a resolution of 512 × 512 pixels (each pixel measuring approximately 98 nm), with dwell times of 45 ms per pixel. Prior to imaging, the sample surface was presputtered with the primary ion beam (using 500 pA beam current) to > 2 × 10¹⁷ ions/cm², in order to remove surface contamination and implant Cs+ ions to a steady-state of ion emission.

2.1.2. EPMA

Compositional analyses were acquired using a JEOL 8530F hyperprobe EPMA equipped with five tuneable wavelength dispersive spectrometers at the CMCA, UWA. The operating conditions were 40 degrees take-off angle, and a beam energy of 20 keV. The beam was fully focused to give a spot size of about 1 µm with a 50 nA beam current. Elements were acquired using analysing crystals LiF for Cu, Ni, P238629. Sample in Fig. 9B, D is P238629. Sample in Fig. 9B, D is P238630.

2.1.3. Laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS)

Laser ablation inductively coupled mass spectrometry (LA-ICP-MS) analyses were performed at UQAC-LabMaTer (Université du Québec à Chicoutimi, Canada). An excimer 193 nm laser system (RESOlution – Australian Scientific Instruments Pty. Ltd.) equipped with a dual-volumes cell (S-155 Laurin Technic, Australia) was coupled to a 7900 Agilent mass spectrometer. Helium flow in the ablation cell was 350 mL/min and mixed to the ICP-MS argon carrier gas (~ 1.0 mL/min), and 2 mL/min nitrogen was added to the line. A tiny flow of helium (1 mL/min) was injected in the collision cell of the ICP-MS to reduce the formation poly-atomic interferences without a permanent decrease in sensitivity. Isotopes studied to generate a fully quantitative dataset are: 34S, 51V, 55Cr, 59Co, 59Fe, 60Ni, 65Cu, 66Zn, 69Ga, 75As, 77Se, 85Rb, 86Sr, 90Zr, 95Mo, 107Ag, 111Cd, 116Sn, 121Sb, 125Te, 137Ba, 178Hf, 191Ta, 195Pt, 197Au, 202Hg, 207Th, 209pb, 208Bi, 235U. A combination of 3 reference materials (RM) was applied light studies, and Telluride. Count times were 80 s for all elements.

Chemical maps were acquired using the calibration set up described above for S, As, Fe, Cu, and Ni. Detection limit maps were acquired for these elements and applied as the minimum cut-off values for all maps. Map acquisition utilised an 80 nA beam current with a 2 × 2 µm pixel dimension and 200 ms dwell time per pixel. Data were processed using the Calcimage software package and output to Surfer® for further processing and enhancement.
Table 1 Summary of common textures and interpreted timing of main sulphide mineralisation styles at the Paulsens deposit.

<table>
<thead>
<tr>
<th>Sulphide Type</th>
<th>Texture Description</th>
<th>Matrix/Inclusions</th>
<th>Interpretation of timing</th>
<th>Evidence for timing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diagenetic Pyrite</td>
<td>Fine grained stratiform preserving euhedral shapes</td>
<td>Fine micas in small microinclusions and larger inclusions</td>
<td>Synsedimentary to diagenetic</td>
<td>Framboidal textures and inclusions of clays replacing clays and grains of detrital heavy mineral phases could have only occurred under sedimentary conditions.</td>
</tr>
<tr>
<td>Nodule Pyrite</td>
<td>Aggregate of euhedral and subhedral cubes to form a single thumb shaped nodule</td>
<td>Inclusions of chalcopyrite and other base metal sulphide phases</td>
<td>Late diagenetic?</td>
<td>Likely similar timing with nodule pyrite – aggregates of micas after clays, quartz and other inclusions of micas could have formed from the metamorphic breakdown of diagenetic pyrites during prograde metamorphism.</td>
</tr>
<tr>
<td>Pyrite 1</td>
<td>Large euhedral grains, randomly oriented, clean with Pyrite 2</td>
<td>Inclusions of base metal sulphides, particularly arsenopyrite, Fe-Ti oxides and free gold inclusions</td>
<td>Hydrothermal</td>
<td>Hydrothermal overgrowth of Pyrite 3 similar to Pyrite 1 as well, possibly as internal exsolution.</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>Variably sized globular to blebby grains overgrowing pyrite, filling cracks and as small to large inclusions in Pyrite 3</td>
<td>Inclusions of base metal sulphides, particularly arsenopyrite, Fe-Ti oxides and free gold inclusions</td>
<td>Late diagenetic?</td>
<td>Likely similar timing with Pyrite 1 – similar timing with nodule pyrite.</td>
</tr>
</tbody>
</table>

2.2. Sulfur isotopes

2.2.1. Fluorination

Samples for fluorination coupled with gas-source mass spectrometry were analysed at the Stable Isotope Laboratory of the Department of Earth and Planetary Sciences at McGill University, Montreal, Canada. Sulfur was chemically extracted from sulfide minerals to form silver sulfide by chromium reduction as described by Canfield et al. (1986). Silver sulfide was fluorinated at 225 °C in a Ni bomb under F2 atmosphere for nine hours to produce SF6. The samples were purified cryogenically and by gas chromatography and introduced by SF6 line into a Thermo Electron MAT 253 mass spectrometer fitted with a dual inlet to measure 32SF5, 33SF5, 34SF5, and 36SF5. All sulfur isotope ratios in this paper are expressed on the V-CDT scale, on which the δ34S, Δ32S, and Δ36S values of the Ag2S reference material, IAEA-S-1, are taken to be -0.3‰, 0.094‰, and -0.7‰, respectively (Wing and Farquhar, 2015). The precision and accuracy of the bulk fluorination system is evaluated by repeat analyses that return uncertainty (2σ) on δ34S, Δ32S, and Δ36S values as better than 0.25‰, 0.02‰ and 0.2‰, respectively.

2.2.2. SIMS

Methods utilised to obtain, reduce, standardise and process the SIMS data collected from the CAMECA IMS1280 large-geometry ion probe at the CHCA, UWA are detailed in LaFlamme et al. (2016), and specific analytical conditions are specified below. Quadruple sulfur isotopic (δ34S, δ33S, δ32S, and δ36S) analysis was performed with the ion microprobe operating in multicollection mode using a 10 kV Cs+ primary beam (~1–4 nA; Gaussian mode) and a normal incidence electron flood gun for charge compensation during all analyses. Following a 30 s pre-sputter, secondary sulfur ions from the target sample were extracted at ~10 kV and admitted to the mass spectrometer with a field magnification of 133 ×, with automated centering of the secondary beam in the field aperture (both x and y; aperture size 4000 μm) and entrance slit (x direction only; slit width 60 μm or 90 μm in some cases). The NMR magnetic field controller locked the axial mass at the beginning of each session, and the mass spectrometer operated at a mass resolution (M/ΔM) of about 2500 (exit slit width of 500 μm on the multicollector). δ32S, δ33S and δ34S were simultaneously detected by three Faraday Cups using amplifiers with 1011 Ω (L2) and 1010 Ω resistors (L1 and H1). Count rates on δ32S varied from 5 × 104 to 3 × 105 cps on pyrite. 36S was measured using a low-noise ion counting electron multiplier (EM). A primary beam current of 5 nA, raster size of 30 μm for pre-sputter and 20 μm for analysis and an acquisition time of 279 s in 45 integration cycles were necessary to achieve good precision on 36S. The count rates on 36S of typically 2–4 × 105 cps for pyrite cause a significant gain drift for the EM. Hence, the EM high voltage was optimised using a Pulse Height Amplitude (PHA) distribution curve at the start of each session, and the grain drift was measured more than three times during each analysis (at the beginning, middle and end). Measurements of unknowns were interspersed with matrix-matched reference material, Sierra for pyrite analyses to calibrate isotope ratios and monitor internal precision.

2.3. Textural microscopy

2.3.1. Backscatter electron imaging (BSE)

Samples and standard blocks were coated with 10 μm carbon for Secondary SEM imaging. BSE and secondary electron images were acquired using a Tescan Vega-3 SEM or a Verios XHR SEM at the Centre necessary to cover the elements ranges: GSE-1g (USGS), MASS-1 (USGS) and PO-727 (Memorial University) and 3 more RM were used for quality control: AI-3 (UQAC house RM), JBS (James Brenan house-RM) and G-Probe-6 (USGS). Limits of detection (LoD) as calculated by IOLITE typically range between 0.001 ppm and 1 ppm for elements of interest. All working values are presented in the Supplementary Data.
for Microscopy, Characterisation and Analysis (CMCA), The University of Western Australia (UWA). Images were acquired at 15 kV with a focused 0.4 nA beam.

3. Results

3.1. Pyrite and other sulfide textures

5 different kinds of pyrite were observed in the Paulsens deposit and nearby unmineralised black shales. These can be grouped primarily on grain size, texture and interpreted paragenesis (Tables 1 and 2). The individual types of pyrite are discussed in the order of their paragenetic...
sequence. The different generations of pyrite are essentially indistinguishable at the hand specimen or even thin section scale. They are only obvious under SEM microscopy. There are no clear relationships between the pyrite types and the styles of mineralisation as observed at the hand specimen scale; however, the earlier types of pyrite are mainly observed in the black shale samples.

3.1.1. Diagenetic pyrite

The diagenetic pyrite, collected from drillhole PDU3277 at a depth of 291 m, consists of fine grained layered and banded concentrations of pyrite, forming parallel to bedding in the black shales (Fig. 9a). This type of pyrite is only observed in relatively unaltered samples of the Melrose Argillite distal to the Paulsens ore deposit. The sample studied here is from over 2 km away from the mineralisation. The pyrite occurs as euhedral to slightly recrystallised aggregates, which are commonly between 100 and 200 µm across and contain abundant silicate inclusions at all scales. These stratiform recrystallised aggregates are texturally similar to those reported in black shales in other gold forming environments (Large et al., 2007; Hou et al., 2016).

3.1.2. Nodule pyrite

These thumb shaped massive pyrite-chalcopyrite nodules (Fig. 9b, d) are typically composed of pyrite grains that are massive and blebby with euhedral and subhedral cube-shaped aggregates and inclusions of blebby chalcopyrite. In the study of pyrite rich sedimentary rocks, others have suggested that the nodule textures similar to those observed here are consistent with formation of the nodules during sedimentation and continuing through to late diagenesis (Large et al., 2007; Hofmann et al., 2009; Steadman et al., 2015).

3.1.3. Pyrite 1

These coarser grained large euhedral to subhedral grains are mostly clean but have minimal fine microinclusions, except where they have been deformed and digested by Pyrite 2 (Fig. 10d). They are typically only well developed in the black shale samples. They form in a variety of sizes, ranging from 80 to 350 µm across but commonly preserve their euhedral shapes. They appear to closely resemble the pyrite nodules in texture but not in shape.

3.1.4. Pyrite 2

This generation of pyrite consistently forms very distinct porous and inclusion rich overgrowths around grains of Pyrite 1 (Fig. 10b, c). In other samples, especially in the centre of the quartz vein hosted mineralisation, Pyrite 2 forms porous and sooty cores to massive Pyrite 3 grains. Pyrite 2 is rarely ever thick, forming 20–40 µm thick overgrowths, and postdates Pyrite 1. It has been suggested that pyrite grains with similar textures observed in other deposits have formed from the metamorphic breakdown of earlier pyrite (Large et al., 2007), however in the reverse order.
3.1.5. Pyrite 3, 3A/B

The coarse grained Pyrite 3 generation forms in a variety of shapes and textures depending on the host rock where it forms. Some grains of this generation of pyrite also demonstrate complex internal zonation (Fig. 11b, c) with significant compositional differences. These internal zonations have been termed Pyrite 3A, for the earlier, less trace element rich (as shown by the darker colours in the backscattered electron images; Fig. 10b, c), and Pyrite 3B, for the later and more trace element rich zones. In other grains, there is a repeated banding of very fine grained alternations in Pyrite 3A-3B (Fig. 12a, b). This fine grained banding is observed at the scale of nanometers, with some fine bands occurring at 500 nm intervals, which has been observed in other mineralised occurrences such as at the Porgera deposit in Papua New Guinea (Peterson and Mavrogenes, 2014). At that deposit, it was suggested that fault valve operation of the faults, which were interpreted to be the pathways for the mineralising fluids, caused the sharp compositional differences in each growth band (Peterson and Mavrogenes, 2014).

3.1.6. Chalcopyrite

Chalcopyrite is the second most abundant sulfide at Paulsens (after pyrite), comprising up to 1–2% of the sulfides in some ore lenses. It forms blebby shapes of up to 3 mm across (Fig. 8b) where forming in quartz-ankerite veins, but is commonly seen as fine inclusions (∼10–50 µm) and veinlets (∼100 µm across) in Pyrite 3 and as overgrowths on Pyrite 3 (Fig. 11a, b, c). Chalcopyrite is considered to have formed synchronously with Pyrite 3A and 3B (Table 2). Free grains of native Au commonly occur as inclusions within the chalcopyrite and on the edge of chalcopyrite-pyrite contacts (Fig. 10e). Chalcopyrite was not analysed by any of the micro-analytical techniques.

3.2. Trace element analyses

3.2.1. NanoSIMS analyses

In attempting to understand the precise siting and elemental relationships between gold and the other trace elements in the different generations of pyrite, the NanoSIMS – a high resolution, small spot size secondary ion mass spectrometer – was employed. This instrument produces semi-quantitative calibrated maps of elements which can be compared down to nanometre resolution. Fig. 14 shows some of the variations observed and the correlation between Ni-As and Au. We employed EPMA data to quantify the relative levels of Ni and As in the enriched zones in Pyrite 3.

3.2.2. EPMA maps

Fig. 15 quantitatively demonstrates the presence of the high Ni and As zones observed in the NanoSIMS analyses. The brighter layers contain up to weight percent levels of As and Ni, whereas the darker layers are poorer in Ni and As (down to low ppm levels). This pattern is very similar to that observed in Carlin style deposits (Simon et al., 1999; Su...
shown in Fig. 15. The widespread presence of arsenian pyrite is similar to that observed in the Youjiang Basin (Maohong et al., 2011) and the Northern Carlin Trend (Cline et al., 2005). Common (arsenian pyrite de- occur in the deposit; however, arsenian pyrite is relatively common (arsenopyrite with minor intergrowths of pyrite). SE = Secondary electron image. In Fig. 14B, C and D we observe that Pyrite 1 is very poor in Ni and little Au; conversely, the porous growth band of Pyrite 2 around Pyrite 1 shows higher Au, Ni and As levels. In Pyrite 3, which is the main host for Au in the deposit, Au, Ni and Cu occur in the same locations (Fig. 14F, G, H). Finally, the zones of enrichment of Ni in Pyrite 3 also closely resemble the pyrite growth textures which were documented in Fig. 11. The relationship between Au and Ni-As in Pyrite 2 and Pyrite 3 is exists even at the nanometre scale.

3.2.3. LA-ICPMS spot analyses

LA-ICPMS analyses were performed to more clearly understand, quantitatively, the relationship between the distribution and enrichment of Au and other related trace elements, as documented by other workers in black shale hosted gold deposits (Reich et al., 2005; Large et al., 2007, 2011; Hou et al., 2016). Pyrite 1 and 2 contains a wide range of trace elements, the most abundant of which are the lithophile Al, K, Na, Rb, Sr, Ba and to a lesser extent Si, Mg, V, Cr, Zr and Sn. Most of these elements are hosted in the silicate micro-inclusions within Pyrite 1 and 2. Pyrite 1 also displays up to 2.05 ppm Au. Pyrite 3 A/B is variably enriched in Ni, As, Cu, Co and Se but has very low levels of Al, Zr, Cr, V, Si and Sb (due to the much smaller amount of silicate micro-inclusions within this generation of pyrite) and relatively lower levels of Pb (Figs. 16, 17 and 18). The trace element patterns of the diagenetic and nodule pyrites are similar to those of Pyrite 1, except that the pyrite nodule is enriched in Tl, Sb and Bi relative to Pyrite 1 and depleted in Al relative to Pyrite 1. Further, the early generations of pyrite (1, 2, Diagenetic and Nodule) demonstrate clear Bi, Sb and Tl enrichments with increasing Au content. However, this enrichment trend is attenuated significantly in the later generations of pyrite (Fig. 16). Generally, it is clear that the incompatible lithophile elements are most enriched in Py 1, 2 and Diagenetic relative to Py 3, 3A and 3B.

Pyrite 1, 2 and the diagenetic and nodular pyrite grains have low gold contents, with a mean Au concentration of 0.1 ppm and 0.4 ppm, respectively. These values, and those of the other trace elements (Bi, Sb, V, Te, Se, As, Zn, Pb, Cu, Co, Ni) are nevertheless comparable in range and total concentrations to those reported by Large et al. (2011) for the gold productive shales of the Northern Carlin Trend, Sukhooi Log and Bendigo-Ballarat deposits. A further observation is that the Se contents, and thus the S:Se ratios are (aside from a small sub population in the pyrite nodule) very consistent across all the samples. The 3B pyrite is the most enriched in gold, which aligns with the petrographic observations of visible gold inclusions and chalcopyrite in the 3B pyrite. Pyrite 3 and 3A however only has a few high gold peaks but a low average (Figs. 18, 19). All of the data, with additional exploratory plots can be found in the Supplementary data section.

The range of Au:As molar ratios sit very comfortably within the range observed in Carlin type deposits, Sukhooi Log and the Huijiabao trend (Fig. 17; Reich et al., 2005; Large et al., 2007; Hou et al., 2016). Furthermore, the observed enrichment trends of Au to chalcophile trace element ratios, marked in Fig. 18 in the dashed arrows, are opposite to those documented in Sukhooi Log (Large et al., 2007) but similar to those documented in the Huijiabao trend, Youjiang Basin (Hou et al., 2016). These trends reflect increasing gold concentrations (Fig. 18) from the earlier to later generations of pyrite but narrowing ranges of chalco- phile trace element ratios, in many cases turning into extremely high concentrations of Ni and Cu in chalcopyrite and gersdorffite micro-inclusions (Fig. 10; 15f). However, the enrichment trends for Pyrite 3A/3B seem to be slightly different relative to the earlier generations of pyrite across the chalcophile elements.

3.3. Pyrite S isotope compositions

The results obtained by fluorination analyses are presented in Table 3, whereas summary statistics of the S isotope compositions measured by SIMS are presented in Table 4 and are plotted in Fig. 4. Most of the data from this study fall outside the range of Δ33S formed after the Great Oxygenation Event (GOE; Johnston et al., 2011). Thus the mineralised pyrite analysed in our study display the MIF-S signature, which is tied to Archaean atmospheric processes. Further, the data highlights that there is only a small amount of variation in the Δ33S and δ34S values obtained from the various generations of pyrite in the deposit indicating that they are mostly similar in S-isotope space. Generation 3 A/B Pyrite grains (i.e. the ones that have the highest gold contents and contain inclusions of native Au) display the exact same Δ33S signature as the early Pyrite 1 and Pyrite 2 samples and are within

Fig. 14. NanoSIMS semi-quantitative data of the abundance of various trace elements in the different grains of pyrite. SE = Secondary electron image. In Fig. 14B, C and D we observe that Pyrite 1 is very poor in Ni and little Au; conversely, the porous growth band of Pyrite 2 around Pyrite 1 shows higher Au, Ni and As levels. In Pyrite 3, which is the main host for Au in the deposit, Au, Ni and Cu occur in the same locations (Fig. 14F, G, H). Finally, the zones of enrichment of Ni in Pyrite 3 also closely resemble the pyrite growth textures which were documented in Fig. 11. The relationship between Au and Ni-As in Pyrite 2 and Pyrite 3 is exists even at the nanometre scale.

et al., 2008; Barker et al., 2009). However, there is no collinear abundance relationship between Cu and Ni-As. Fig. 15e also shows the presence of a small grain of arsenopyrite with minor intergrowths of gersdorffite at the edge of a pyrite grain. This is a relatively uncommon occurrence in the deposit; however, arsenian pyrite is relatively common (arsenopyrite defined to have up to 5 wt% As in pyrite), as shown in Fig. 15. The widespread presence of arsenian pyrite is similar to that observed in the Youjiang Basin (Maohong et al., 2011) and the Northern Carlin Trend (Cline et al., 2005).
error of the diagenetic and nodule pyrite samples.

It has been suggested that the $\Delta^{34}S$ and $\Delta^{36}S$ anomalies observed in the Archaean primary atmospheric record could be derived from processes that do not involve photochemical reactions but instead call upon abiotic processes during diagenesis such as Thermochemical Sulfate Reduction (TSR) to create the observed anomalies (Ohmoto et al., 2006). The data from Fig. 21, which shows the distribution of the $\Delta^{36}S$ values from the various generations of pyrite studied, highlight that the $\Delta^{36}S$ values in this study fall completely outside the MIF-S range formed from TSR experimental simulations ($0\% < \Delta^{36}S < 1\%$; Oduro et al., 2011). Thus, it is clear that the sulfur in this study is derived from a source that preserves Archaean photochemical reaction
products, such as an Archaean black shale formation like the Hardey Formation.

Further, in environments where the magnitude of $\Delta^{33}S$ is relatively low (e.g. $-1\% < \Delta^{33}S < +1\%$), it has been postulated that the relationship between the $\Delta^{33}S$ and $\Delta^{36}S$ may be used to tell apart mass-dependent (MDF-S) and MIF-S processes (Johnston, 2011; Selvaraja et al., 2017b). This is because MDF-S, which is primarily driven by biological processes, can create small $\Delta^{33}S$ and $\Delta^{36}S$ signatures (Johnston, 2011). However, the MDF-S derived $\Delta^{33}S$ and $\Delta^{36}S$ anomalies would sit along a fractionation array of $-7$ to $-9$ (Fig. 21), as compared to the Archaean MIF-S array of $-0.9$ to $-1.5$ (Fig. 21; Johnston, 2011; Roerdink et al., 2016). Further, generation of large biologically derived MIF-S signatures requires significant fractionation of $\delta^{34}S$ to very positive or negative values (Jamieson et al., 2006). The maximum biologically derived MIF-S signature is dependent on the $\delta^{34}S$ variation, and as our samples show a very narrow range of $\delta^{34}S$, the MIF-S anomalies in our data must have been generated by photochemical processes. Our data plot between the two arrays, which may indicate mixing between MDF-S and MIF-S reservoirs (Roerdink et al., 2016). However, it is more likely that this variation of $\Delta^{36}S$ is an artefact of the high uncertainty of our $\Delta^{36}S$ analyses ($\sim 1\%$). The subset of our data obtained with the highly precise fluorination technique however correlates very well with the $-0.9$ array, thus confirming its Archaean surficial origin.

4. Discussion

4.1. Mineralisation paragenesis

The data presented in this study allow us to use the Paulsens deposit as a proxy for understanding the nature and genesis of black shale hosted gold deposits. Due to its age and location in the 2.7 Ga Hardey Formation of the Pilbara Craton, we were able to combine established techniques in the study of black shale hosted gold deposits such as pyrite textural analysis and chemistry with the use of in situ multiple sulfur isotope analysis. This is because the MIF-S signature preserved in Archaean sedimentary pyrites is an indelible isotopic tracer, which cannot be removed by any process other than dilution by sulfur without any MIF-S signature. Thus, it is inferred that the observed similar MIF-S signatures between the diagenetic and mineralised generations of pyrite (+0.4% vs +0.35% respectively) at Paulsens fingerprint the origin of the mineralising fluids to the Archaean Hardey Formation.
The analyses reported in this study highlight four distinct features about this deposit. (1) The mineralised quartz veins have been folded by the most obvious deformation event in the deposit, i.e. the dominant S2 foliation fabric. (2) The mineralisation is hosted primarily as free gold in inclusions within pyrite. (3) The deposit underwent repeated periods of pyrite growth during the main mineralising event. (4) The pyrites that host the gold contain significant amounts of Ni, As and other base metals. The paragenetic sequence of pyrite growth involves Pyrite 1 being overgrown by Pyrite 2, which is in turn overgrown by Pyrite 3 and chalcopyrite (Fig. 10). The mineral overprinting, overgrowth and post formation folding evidence presented in this study suggests that the gold hosting pyrites formed early in the structural and tectonic evolution of the package.

As demonstrated through the pyrite trace element chemical data (3B) and textural observations (3A, 3B) the later stages of pyrite contains most of the gold found in the deposit, both in the form of native grains of electrum, as seen texturally in Fig. 10c, but also as dissolved Au in pyrite, as observed from the NanoSIMS and LA-ICPMS data (Figs. 13 and 15). This evidence ties the genesis of Au in the deposit to the growth of pyrite, which is closely coupled with quartz veining and the precipitation of ankerite and small amounts of chlorite. Pyrite growth and hence gold mineralisation in this environment however contains certain distinct features that have also been observed at other black shale hosted gold deposits (Table 5; Large et al., 2007; Hou et al., 2016).

Additionally, it is important to observe that all of the deposits form at the edge of craton margins in either active rifts or passive margins and that they are all stratabound ore blocks. This relationship is similar to the one suggested by Mole et al. (2013) which postulated, using the mineral systems framework (McCuaig et al., 2010), that the edges of cratons are sites of massive heat and fluid transfer thus making them highly prospective areas for komatiite nickel mineralisation. They also exhibit very similar alteration types, though the lack of carbonate rocks in the stratigraphy at Paulsens makes the decarbonization related alteration forms observed at other black shale hosted gold deposits impossible. As such, we argue that Paulsens, though not a Carlin type deposit sensu stricto, has strong similarities with Carlin style and other sediment-hosted gold deposits.

4.3. Complex pyrite textures

The textures observed in the diagenetic pyrites, pyrite nodules as well as in Pyrite 1 and 2 generations can be explained by reference to previous work on the processes that drive the formation of euhedral and porous pyrite in sedimentary environments through diagenesis and early low grade metamorphism (e.g. Large et al., 2007, 2011).
Fig. 18. Chalcophile metal:Au ratios for the different generations of pyrite observed in the Paulsens deposit. Particularly high Cu and Ni:Au ratios are likely to reflect micro-inclusions of gersdorffite and chalcopyrite. Enrichment trends in some of the chalcophile elements seem to exist with higher gold contents but depletion trends exist with later stages of mineralisation, however these relationships are weak. All abundances are reported in parts per million (ppm).
However, the textures documented for Pyrite 3A/B require some further explanation. We propose that the enrichment of Ni-As-Au in Pyrite 2 relatively to Pyrite 1 (Fig. 14C) could be seen as evidence of the sourcing and transport of base and precious metals from the pyrite breakdown process, as suggested by Large et al. (2011). The resultant metal rich fluid could have then precipitated Pyrite 3A/3B at structural traps. This however does not explain the lack of collinear abundance between Cu and Ni-As, which is likely due to the fact that precipitation of Pyrite 3 occurred in the chalcopyrite stability field, whereby all the Cu preferentially partitioned into the chalcopyrite phase instead of remaining in the pyrite phase.

It is thus likely that the pyrite textures in Pyrite 3A/B reflect the replacement textures of Ni-As rich rims and edges observed in Fig. 15a, b and d. These textures are likely to be coupled dissolution-reprecipitation (CDR) textures (Putnis, 2002; Putnis and Putnis, 2007; Ruiz-Agudo et al., 2014), such as the ones in gold rich arsenian pyrites previously observed at the Sunrise Dam and Obuasi gold deposits (Sung et al., 2009; Fougerouse et al., 2016). In these cases it was argued there that these reactions were responsible for upgrading the gold contents in newly reprecipitated pyrite zones. Sung et al., (2009) also argue that the CDR reactions were caused by later, separate episodes of fluid flow. In Paulsens however, taking into account the observations of coexisting

### Table 3

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>δ²⁴S (‰)</th>
<th>Δ³³S (‰)</th>
<th>Δ³⁶S (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P238571</td>
<td>0.533</td>
<td>0.327</td>
<td>−0.77</td>
</tr>
<tr>
<td>P238572</td>
<td>0.313</td>
<td>0.353</td>
<td>−0.83</td>
</tr>
<tr>
<td>P238573</td>
<td>−0.030</td>
<td>0.403</td>
<td>−0.72</td>
</tr>
<tr>
<td>P242338</td>
<td>−0.503</td>
<td>0.232</td>
<td>−0.65</td>
</tr>
<tr>
<td>P242337</td>
<td>0.869</td>
<td>0.225</td>
<td>−0.66</td>
</tr>
<tr>
<td>P242336</td>
<td>0.433</td>
<td>0.215</td>
<td>−0.54</td>
</tr>
<tr>
<td>P238627</td>
<td>0.464</td>
<td>0.293</td>
<td>−0.03</td>
</tr>
<tr>
<td>P238626</td>
<td>−0.084</td>
<td>0.290</td>
<td>−0.64</td>
</tr>
<tr>
<td>P238625</td>
<td>−0.572</td>
<td>0.448</td>
<td>−1.01</td>
</tr>
<tr>
<td>P238624</td>
<td>−0.075</td>
<td>0.466</td>
<td>−0.87</td>
</tr>
<tr>
<td>P251398</td>
<td>0.241</td>
<td>0.364</td>
<td>−0.36</td>
</tr>
<tr>
<td>P251399</td>
<td>0.484</td>
<td>0.324</td>
<td>−0.75</td>
</tr>
<tr>
<td>P251397</td>
<td>0.896</td>
<td>0.258</td>
<td>−0.55</td>
</tr>
<tr>
<td>P251400</td>
<td>0.765</td>
<td>0.240</td>
<td>−0.75</td>
</tr>
<tr>
<td>P251401</td>
<td>0.103</td>
<td>0.373</td>
<td>−0.71</td>
</tr>
<tr>
<td>P242340</td>
<td>0.631</td>
<td>0.222</td>
<td>−0.64</td>
</tr>
</tbody>
</table>

However, the textures documented for Pyrite 3A/B require some further explanation. We propose that the enrichment of Ni-As-Au in Pyrite 2 relatively to Pyrite 1 (Fig. 14C) could be seen as evidence of the sourcing and transport of base and precious metals from the pyrite breakdown process, as suggested by Large et al. (2011). The resultant metal rich fluid could have then precipitated Pyrite 3A/3B at structural traps. This however does not explain the lack of collinear abundance between Cu and Ni-As, which is likely due to the fact that precipitation of Pyrite 3 occurred in the chalcopyrite stability field, whereby all the Cu preferentially partitioned into the chalcopyrite phase instead of remaining in the pyrite phase.

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### Table 4

<table>
<thead>
<tr>
<th>Pyrite Generation</th>
<th>Mean δ²⁴S (‰)</th>
<th>Range δ²⁴S (‰)</th>
<th>Mean Δ³³S (‰)</th>
<th>Range Δ³³S (‰)</th>
<th>Mean Δ³⁶S (‰)</th>
<th>Range Δ³⁶S (‰)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diagenetic</td>
<td>0.69</td>
<td>−0.72 to 1.64</td>
<td>0.40</td>
<td>0.32 to 0.48</td>
<td>−1.58</td>
<td>−2.69 to −0.86</td>
<td>62</td>
</tr>
<tr>
<td>Nodule</td>
<td>−0.95</td>
<td>−4.32 to 0.02</td>
<td>0.31</td>
<td>0.21 to 0.43</td>
<td>−2.45</td>
<td>−3.28 to −1.91</td>
<td>23</td>
</tr>
<tr>
<td>1</td>
<td>1.08</td>
<td>0.17 to 2.51</td>
<td>0.23</td>
<td>−0.01 to 0.30</td>
<td>−1.69</td>
<td>−2.93 to −0.20</td>
<td>52</td>
</tr>
<tr>
<td>2</td>
<td>−0.32</td>
<td>−3.39 to 1.46</td>
<td>0.25</td>
<td>0.19 to 0.42</td>
<td>−3.45</td>
<td>−3.44 to −0.05</td>
<td>73</td>
</tr>
<tr>
<td>3A</td>
<td>0.24</td>
<td>−3.98 to 1.18</td>
<td>0.22</td>
<td>0.06 to 0.29</td>
<td>−3.10</td>
<td>−3.52 to −0.53</td>
<td>42</td>
</tr>
<tr>
<td>3B</td>
<td>0.15</td>
<td>0.04 to 0.22</td>
<td>0.26</td>
<td>0.20 to 0.32</td>
<td>−2.18</td>
<td>−3.39 to −1.60</td>
<td>4</td>
</tr>
</tbody>
</table>

However, the textures documented for Pyrite 3A/B require some further explanation. We propose that the enrichment of Ni-As-Au in Pyrite 2 relatively to Pyrite 1 (Fig. 14C) could be seen as evidence of the sourcing and transport of base and precious metals from the pyrite breakdown process, as suggested by Large et al. (2011). The resultant metal rich fluid could have then precipitated Pyrite 3A/3B at structural traps. This however does not explain the lack of collinear abundance between Cu and Ni-As, which is likely due to the fact that precipitation of Pyrite 3 occurred in the chalcopyrite stability field, whereby all the Cu preferentially partitioned into the chalcopyrite phase instead of remaining in the pyrite phase. It is thus likely that the pyrite textures in Pyrite 3A/B reflect the replacement textures of Ni-As rich rims and edges observed in Fig. 15a, b and d. These textures are likely to be coupled dissolution-reprecipitation (CDR) textures (Putnis, 2002; Putnis and Putnis, 2007; Ruiz-Agudo et al., 2014), such as the ones in gold rich arsenian pyrites previously observed at the Sunrise Dam and Obuasi gold deposits (Sung et al., 2009; Fougerouse et al., 2016). In these cases it was argued there that these reactions were responsible for upgrading the gold contents in newly reprecipitated pyrite zones. Sung et al., (2009) also argue that the CDR reactions were caused by later, separate episodes of fluid flow. In Paulsens however, taking into account the observations of coexisting
nano-scale banding of Ni-As observed in Pyrite 3 (Figs. 12, 14 and 15c, e and f) and CDR textures in Pyrite 3A/B, we argue that both of these textures are generated by the introduction, repeatedly and at short intervals, of fluids in extreme disequilibrium with the mineral surface (c.f. Peterson and Mavrogenes, 2014; Ruiz-Agudo et al., 2014).

The only mechanism that is capable of creating these extreme fluid disequilibria, while still maintaining the same fluid source (as will be suggested later based on the sulfur isotopic data) is fault-valve dynamics during fluid release (Sibson, 1990, 1992; Peterson and Mavrogenes, 2014). As the fluid pressure builds up in the feeder fault to the vein, the fault fails and releases the fluid episodically. However, the difference in fluid pressure varies dramatically between each episode of fluid release due to the changing stress fields. This variation in fluid pressure can affect the solubility of various metals, including Ni-As, as suggested by Peterson and Mavrogenes (2014) to explain the dramatic differences in the Ni-As compositions of the fine growth bands. It is proposed that in some cases the variations in the fluid chemistry between each episodic failure can be so great as to drive dissolution and reprecipitation of pyrite, which end up being enriched in various trace elements (Fig. 15).

### 4.4. Source of sulfur and gold

It is widely accepted that the transport of gold in any hydrothermal environment is dependent on the presence of complexing cations, the most important of which is the bisulfide cation (HS)−2, which has been called on as the complexing cation for Carlin style gold deposits in the Twin Creeks deposit (Simon et al., 1999) and other kinds of gold deposits by Goldfarb and Groves (2015). We have observed that the gold in the Paulsens deposit is hosted as free inclusions within the pyrite grains and as sub-micron inclusions in the crystal structure of Pyrite 3A/B. Following from this, if the source of the fluid from which Pyrite 3A/B was precipitated from can be determined, it is most likely to be also the source of the gold.

Considering that pyrite is a sulfide phase, the sulfur source of the pyrite must then be the source of the Au as well. Our use of multiple sulfur isotope analyses to evaluate the source of sulfur then acts as a direct proxy for the source of gold in the Paulsens deposit, and potentially, if the situation can be extrapolated, many other Carlin style and black shale hosted gold deposits. This brings us to evaluating what the data displayed in Figs. 20 and 21 imply, which is the presence of MIF-S in the pyrites of the Paulsens deposit. As can be seen in Fig. 20, almost all the pyrite generations in the deposit plot outside the post 2.33 Ga mass dependent fractionation dominated zone of Δ33S values (Johnston et al., 2011; Luo et al., 2016a, b).

This means that the sulfur is clearly sourced from pre 2.33 Ga sedimentary units which contained sulfur derived from atmospheric photochemical reactions (Farquhar et al., 2000; Farquhar and Wing, 2003, 2005). Specifically, the sulfur isotope record of Pyrite 3A/B indicates that the Δ33S of the sulfur in that gold rich generation of pyrite is derived from a sulfur source which can be readily explained by a mix of the Δ33S signatures of the near deposit and distal diagenetic pyrites studied in Ohmoto et al. (2006), both of which are contained within the 2.7 Ga Hardey Formation. An additional constraint is the finding from Farquhar et al. (2013), which constrains the presence of positive Δ34S to sedimentary pyrite forming in carbonaceous shales in the Archaean due to the reaction pathways and settling mechanism of elemental sulfur in the Archaean atmosphere and oceans. We can thus conclude that the most likely scenario for the source of sulfur for the mineralised pyrite in the Paulsens deposit is the diagenetic pyrite of the Hardey Formation.

The Δ33S values coupled with Δ34S values in the Paulsens deposit pyrite may then allow us to explain some of the large observed Δ34S variation in the mineralised pyrite (−10% < Δ34S < 20%) from the Carlin Trend and the Youjiang Basin (Cline et al., 2005; Hou et al., 2016). This wide range of Δ34S values has previously been used as evidence for a range of possible fluid sources in different sediment-hosted gold deposits (Cline et al., 2005). Although our observations occur in Archaean stratigraphy, which has a far more limited range of Δ34S values due to the limited amount of biological and thermochemical driven fractionation which in turn is due to the reduced nature of the oceans prior to the GOE, the evidence of a basin scale derivation of sulfur rich fluid helps to explain the heterogeneous distribution of Δ34S values in non-Archaean sediment-hosted gold deposits (Cline et al., 2005; Chang et al., 2008; Hou et al., 2016). This is because the mineralised pyrite contains Δ34S values that are on average slightly lower than those of the immediately adjacent diagenetic pyrite (Fig. 20),

![Fig. 21. Δ34S vs Δ33S data for the pyrite generations at the Paulsens deposit. The high precision bulk fluorination analyses show the MIF-S trend perfectly, however the in-situ analyses show a wide range of Δ33S values, which do not correlate well with any of the major trends observed in the atmospheric or biological multiple sulfur isotope fractionation literature (Johnston, 2011; Roerdink et al., 2016). This is possibly due to the effects of differential metamorphic re-equilibration of the S3 isotopes, or the effect of the $S_{\text{aq}}^{-}$ anion as discussed in Selvaraja et al. (2017b).](image-url)
Table 5

Data extracted from Cline et al. (2005), Ohmoto et al. (2006), Large et al. (2007), Barker et al. (2009), Maohong et al. (2011) and Hou et al. (2016). Org C = Organic carbon.

<table>
<thead>
<tr>
<th>Basin</th>
<th>Sukhoi Log</th>
<th>Paulsens</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Age</strong></td>
<td>&lt; 140 Ma</td>
<td>Mid Tertiary (≈ 140 Ma)</td>
</tr>
<tr>
<td><strong>Key Host Lithologies</strong></td>
<td>Carbonaceous shales, siltstones and minor sandstones</td>
<td>Carbonaceous shales, siltstones and minor sandstones</td>
</tr>
<tr>
<td><strong>Intrusive Relationships</strong></td>
<td>No significant intrusive or extrusive rocks</td>
<td>Basaltic extension and rifting</td>
</tr>
<tr>
<td><strong>Tectonic Framework</strong></td>
<td>Edge of craton margin – fluvial intrusives and small lamprophyres</td>
<td>Calc-alkaline magmatism</td>
</tr>
<tr>
<td><strong>Deposit Size</strong></td>
<td>Likely &gt; 3 Moz</td>
<td>All ranges and &gt; 5 Moz</td>
</tr>
<tr>
<td><strong>Depth of Formation</strong></td>
<td>1.5 – 5 km</td>
<td>0.5 – 5 km</td>
</tr>
<tr>
<td><strong>Gangue Mineralogy</strong></td>
<td>Quartz, carbonate, clays, Orpiment, Realgar, Cinnabar, Stibnite + Carbon, Org C</td>
<td>Quartz, carbonate, clays, Orpiment, Realgar, Cinnabar, Stibnite + Carbon, Org C</td>
</tr>
<tr>
<td><strong>Grade</strong></td>
<td>6.0 gpt Au</td>
<td>1.0 gpt Au</td>
</tr>
</tbody>
</table>

5. Conclusions

The results from this work on sulfide textures, growth paragenesis, trace element geochemistry and sulfur isotopic compositions on the Paulsens deposit suggest that the sourcing of sulfur and gold in sediment-hosted gold systems may be purely endogenous, in that all the sulfur and gold required to form the deposit may be sourced from the local stratigraphy. The inference then is that 1) gold and other base metals may be mobile over significant distances in basin derived sulfur rich fluids, and 2) these fluids precipitate gold deposits at structural

despite reflecting the accurate isotopic average of the linear mix of near and distal sedimentary sulfur sources within the stratigraphic package. This implies that in the formation of this style of deposit, the ore forming fluid is derived from the entire stratigraphic package. This helps to explain the greater variability of δ34S in modern sediment-hosted gold systems, as the various sedimentary sulfur sources in a more modern basin would display a much greater range of δ34S than in an Archaean basin due to the presence of biological fractionation and evaporite formation.

4.5. Source of gold and metals

If the source of sulfur is locally derived sedimentary sulfur, then it can be reasonably surmised that the gold is also sourced locally, as suggested by Large et al. (2011) for Carlin style gold deposits. However, to test if this is indeed likely, our pyrite trace element data of Au contents in sedimentary diagenetic pyrites and pyrite nodules provide a good constraint on the system, suggesting that up to 0.29 ppm Au (with a mean of 0.12 ppm) occurs in the diagenetic pyrite, and up to 1.57 ppm Au (with a mean of 0.42 ppm) is present in the pyritic nodules. These data are in close agreement with the findings of Large et al. (2011) on the prospective source rocks for the Sukhoi Log, Northern Carlin Trend and Bendigo sediment-hosted Au deposits. At a pyrite abundance of about 0.5% in the unmineralised host rocks, 1.5 * 10^-9 g of Au would be available per g of host rock, thus requiring ~10–100 km^2 of host rocks to be fluxed depending on the extraction efficiency of the fluid to produce the Paulsens deposits. The Hardey Formation, being on average 200 km across easily contains this volume rock. This calculation is in line with estimates of rock volume required in other sediment-hosted gold deposits (Large et al., 2011).

Finally, the widespread presence of Ni, As, Co, Se and Cu (as chalcopyrite) in the Pyrite 3A/B generation can be explained readily by the fact that a circulating basinal fluid in the stratigraphy of the Hardey Formation would not only leach the Au and As from the diagenetic pyrites (Large et al., 2011), but also a whole range of chalcophile and chalcopyrite trace elements from the sedimentary, mafic and ultramafic components of the volcanic pile, which both underlies the Hardey Formation in the greenstone belts of the Pilbara Cratonic basement and forms the dominant portion of the Hardey Formation itself (Figs. 1 and 3). This is also supported by the consistently high S:S ratio (~50,000–100,000) between the diagenetic and 3B generations of pyrite. Se is mobilised in the same way as S in geological fluids and has markedly different ratios in mantle derived (~3000) vs crustal sulfur reservoirs (~30,000) thus supporting a crustal origin for the Se and the S (Queffurur and Barnes, 2014). The very high concentrations of Au in diagenetic pyrites in carbonaceous shales may be derived from several different possibilities, one of which is bacterial sequestration of Au in pyrite (Large et al., 2011). An alternative mechanism that could enrich shales in Au in the Archaean may be drawn from Frimmel and Hennigh (2015) who suggest that an elevated Au flux off the Archaean land surface, as a consequence of the low pH of surface waters, could increase the amount of Au that can be adsorbed onto clay surfaces by an order of magnitude. This possibility is echoed by Large et al. (2015) who further add that the erosive flux was also very rich in Au due to the relatively Au enriched mafic rocks eroded at this time.
traps. In the case of the Paulsens deposit, this depositional site is most likely the rheological boundary created by the intrusion of the Paulsens gabbro into the Melrose Argillite of the Hardey Formation.

Based on the observation textures and integrated LA-ICPMS and NanoSIMS analyses of pyrite, the data show that gold occurs in the diagenetic pyrites and in the early Pyrite 1 and 2 generations, which formed during late diagenesis and early metamorphic breakdown reactions. The gold rich Pyrite 3A/B formed later due to hydrothermal episodic fluid flow occurs during dynamic deformation. This process would be consistent with the complex trace element banding and textures observed in the Pyrite 3A/B generation.

The paragenetic sequence of multiple episodes of pyrite formation in this deposit, and by extension in sediment-hosted gold systems, along with a gold mineralising episode associated with one particular stage of pyrite growth suggest that the processes outlined by Large et al. (2007) and Large et al. (2011) are likely to be accurate. However, with the use of multiple sulfur isotope analyses, we can now incontrovertibly pin point the source of sulfur, and hence the source of Au, in sediment-hosted gold deposits to the local stratigraphic package. This knowledge could be used in conjunction with other routinely acquired datasets to aid in strengthening prediction exploration strategies for the localisation of mineralised camps.

Acknowledgements

The authors would like to acknowledge the support of the Northern Star Limited for providing samples for this study. We would also like to thank Boswell Wing for his assistance in performing the fluorination analyses. This work was financially supported by the Minerals Research Institute of Western Australia (MRWA), the Science and Industry Endowment Fund (SIEF) and the Australian Research Council (ARC), through the Centre of Excellence of Core to Crust Fluid Systems and the Future Fellowship awarded to MLF. This work is part of the PhD thesis of VS, who acknowledges support from the University of Western Australia through a SIRF scholarship. This is contribution no. 1000 for the ARC Core to Crust Fluid Systems Centre of Excellence. The Stable Isotope Laboratory in the Earth and Planetary Science department at McGill is supported by the FQRNT through the GEOTOP research center. We thank Jeffrey Steadman and an anonymous reviewer for their reviews which greatly improved this manuscript. We also thank Franco Pirajno for his editorial handling.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.oregeorev.2017.07.021.

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CHAPTER FIVE

P-T-X CONDITIONS AND PRECIPITATION MECHANISM
OF GOLD MINERALIZATION AT THE PAULSENS GOLD
DEPOSIT

This chapter is presented as peer reviewed thesis chapter which is currently under revision for submission to the journal *Mineralium Deposita*. All the figures are presented in the text, in the appropriate order that they are to be read. Sample locations from this study are included in Appendix 1 and three further spreadsheets are included in the electronic appendices attached to this thesis. Chapter 5 – SM1 presents the full modelling results for the thermodynamic model presented in this thesis. Chapter 5 – SM2 presents the entirety of the sulfur isotope data acquired on the secondary ion mass spectrometer and the calculations performed as part of the sulfur isotope geothermometry process. Chapter 5- SM3 presents the total microthermometry and RAMAN analysis dataset acquired as part of this study.
Authors

Vikraman Selvaraja\textsuperscript{1,2}, Katy A. Evans\textsuperscript{3}, Steffen G. Hagemann\textsuperscript{1}, Laure Martin\textsuperscript{4}, Paul Duuring\textsuperscript{1,5}, Terence P. Mernagh\textsuperscript{6}, Heejin Jeon\textsuperscript{4}, Marco L. Fiorentini\textsuperscript{1,2}

\textsuperscript{1}Centre for Exploration Targeting, School of Earth Sciences, University of Western Australia, 35 Stirling Highway, Crawley, 6009 WA, Australia

\textsuperscript{2}ARC Centre of Excellence of Core to Crust Fluid Systems, University of Western Australia, 35 Stirling Highway, Crawley, 6009 WA, Australia

\textsuperscript{3}Department of Applied Geology, Curtin University, Kent Street, Bentley, 6102 WA, Australia

\textsuperscript{4}Centre for Microscopy, Characterisation and Analysis, University of Western Australia, 35 Stirling Highway, Crawley, 6009 WA, Australia

\textsuperscript{5}Geological Survey of Western Australia, Department of Mines and Petroleum, Mineral House, 100 Plain Street, East Perth, 6004 WA, Australia

\textsuperscript{6}Research School of Earth Sciences, Australian National University, Canberra, 0200 ACT, Australia

Title

Conditions for the genesis of a low temperature sediment–hosted gold deposit

Abstract

The Paulsens gold deposit is an enigmatic million ounce gold deposit in the Pilbara Craton, Western Australia. It is an Archean deposit that displays key characteristics typical of orogenic gold type mineralisation; however, it also shows features that are akin to Phanerozoic sediment-hosted and Carlin–style systems. This study questions whether such possibly hybrid mineral
systems may be more common than previously recognised by using Paulsens as a natural laboratory to understand the $P$-$T$-$X$ conditions of ore formation. Fluid inclusion microthermometry and quartz paragenesis revealed two generations of fluid inclusion growth. The initial primary assemblage is in equilibrium with gold-bearing pyrite forming at $\sim$150°C. A later secondary series of fluid inclusions forms between 270-350°C. Applying a stratigraphic pressure constraint on the primary assemblage, a temperature of formation of $\sim$230°C was obtained. This temperature is in agreement with the sulfur isotope geothermometry performed using co-precipitated pyrite-chalcopyrite pairs. The chemical composition of the primary assemblage is $\sim$10 wt. % NaCl equivalent and has a small carbonic phase, which is evenly split between CO$_2$ and CH$_4$. Our findings suggest that the mineralising fluids at Paulsens were different from the known median of orogenic systems, being closer to the Phanerozoic deposits hosted in the Carlin and Guizhou Trends. Using mass independent sulfur isotope anomalies as indelible tracers (constant $\Delta^{33}$S), the $\sim$+1‰ $\delta^{34}$S shift in the sulfur isotopic composition of the gold bearing pyrite is the basis to construct a thermodynamic model that shows gold solubility to be controlled by the redox conditions of the source rocks, the carbonaceous shales of the Hardey Formation. Outcomes from this multi-disciplinary integrated approach have resolved some of the uncertainties in our knowledge of the $P$-$T$-$X$ conditions and thermodynamic processes governing the formation of gold-bearing pyrite assemblages. Results indicate that Paulsens may be an Archean analogue of Phanerozoic low temperature sediment–hosted gold systems.

1 Introduction

The processes and conditions that govern gold solubility and transport in Archaean sediment–hosted gold deposits, remain uncertain as these deposits are relatively rare and understudied with some notable exceptions, e.g. the New Holland deposit in the Agnew belt, Western Australia (Ackroyd et al., 2001) or the Obuasi deposit in the Ashanti belt (Fougerouse et al.,
Key knowledge gaps include the nature of the source rocks that generate the fluids that transport and deposit gold in sedimentary rocks, the temperature of formation of these deposits and the composition of the ore forming fluid. In addition, there is a lot of debate on the relationship between what is known as Archaean–Palaeoproterozoic sediment-hosted gold mineralisation and its younger equivalents, as reflected for example in the deposits of the Northern Carlin Trend in Nevada, the Youjiang Basin and the Guizhou Trend in China (Cline et al., 2005; Su et al., 2009; Hou et al., 2016) and Sukhoi Log (Large et al., 2007).

Previous findings by Su et al. (2009) suggested that sediment-hosted deposits may be formed by low salinity fluids that contain high CO₂ contents. They suggested that these fluids may be the “basin-hosted and relatively cool end member... of orogenic gold deposits formed from deep metamorphic fluids”. However, although temperature of deposition is similar to cooler end-member orogenic gold deposits (180 – 240°C), the tectonic setting and chemical composition of those fluids can be dramatically different (Cline and Hofstra, 2000). Further, organo-metallic ligands may be involved in gold transport and precipitation in the sediment-hosted deposits (Emsbo et al., 2005; Large et al., 2011). Finally, the physico-chemical conditions which are necessary to create efficient dissolution and transport mechanisms for gold in sediment-hosted deposits remains a matter of significant uncertainty, mainly due to the nature and grain size of the quartz breccias and the very small fluid inclusion sizes (<5 µm), which have hampered the collection of robust and reliable fluid inclusion data.

The mineral system framework may aid in addressing some of the existing knowledge gaps related to sediment-hosted gold systems (Wyborn et al., 1994; Hagemann and Cassidy, 2000; McCuaig et al., 2010; Hagemann et al., 2016; Wyman et al., 2016). One of the key elements in applying the mineral system framework to the understanding of the genesis of mineral deposits is to clearly delineate pathway processes and source processes from the observed mineralisation. Therefore, in order to evaluate the contrasting models and suggestions around
the formation of sediment-hosted gold deposits we have chosen to study the Paulsens Archaean meta-sediment-hosted gold deposit. This enigmatic deposit is one of the few sediment-hosted gold deposit examples that formed in the Archaean during a period of tectonic quiescence, in a passive margin (Fielding et al., in press). Selvaraja et al. (in review) demonstrated that the source of sulfur and gold in the deposit is the local sedimentary package.

In the present investigation, we combine the observed variability in the multiple sulfur isotopic signature in single gold bearing pyrite grains with fluid inclusion compositions to demonstrate that systematic variation in the redox conditions of local source rocks, such as is observed in a laterally discontinuous sedimentary basin, can have a major influence on both gold solubility and the associated evolution of the sulfur isotope signature of the mineralising fluids. A combination of microthermometry and sulfur isotope geothermometry data is used to constrain the \( P-T \) conditions of the formation of the deposit. Our findings confirm the arguments of Selvaraja et al. (in review) that the Paulsens deposit is analogous to Phanerozoic sediment-hosted gold deposits, and show that the variability in redox conditions of the source rocks of the mineralising fluids can address some of the presently unanswered questions around sediment-hosted gold deposits.

1.1 Paulsens sediment-hosted gold deposit

Paulsens is a ~1 million ounce gold deposit (Bland et al. 2014) located at the southern edge of the Pilbara Craton, which is a major mineral province for iron ore but hosts very few known gold deposits. The Paulsens deposit is hosted in a sequence of mafic volcanic and sedimentary rocks of the Hardey Formation in the Wyloo Dome, which preserves a complete stratigraphic succession from the Palaeoarchaean to the Proterozoic (Fig. 1; Selvaraja et al., in review and references therein). Mining began in this deposit in the 1930s with an estimated 742,000 ounces of gold extracted from 3.7 million tonnes of ore at an average grade of 6.3 g/t (Bland et al.
The deposit consists of several lenses of massive and disseminated sulfides, mainly pyrite, hosted primarily in thick laminated and moderately deformed quartz veins that formed synchronously with the mineralisation. These quartz veins are localised within and along the margins of a folded, coarse-grained gabbro dyke, which crosscuts the black shales of the Archaean Hardey Formation, referred to locally as the ‘Melrose Argillite’.

Figure 1: Location of the Paulsens Au deposit and the Wyloo Dome in the southern margin of the Hamersley Basin of Western Australia. The figure also shows the sampling location for the multiple sulfur isotope study of Ohmoto et al. (2006). Adapted from Thorne and Trendall (2001).

The Wyloo Dome includes lower greenschist facies metamorphic rocks (Rasmussen et al., 2005). Generally, the metamorphic grade in the deposit is relatively low and a simple hydrothermal alteration assemblage associated with gold mineralisation is preserved, comprising quartz-pyrite-ankerite±chlorite with later quartz-calcite veins cross-cutting the
hypogene alteration assemblage (Selvaraja et al., *in review*). Dating of the gabbro dyke, referred to as Paulsens Gabbro, provides a maximum age constraint on the deposit of c. 2700 Ma (Figs. 2 and 3; Fielding et al., *in press*). Direct dating of the mineralisation by U-Pb analysis of monazite grains that are intergrown with gold bearing pyrite grains that have abundant inclusions of gold suggest that the main mineralising event occurred at c. 2400 Ma (Fielding et al., *in press*). A later episode of fluid flow in the structures that host the deposit may have remobilised some of the gold at c. 1700 Ma (Fielding et al., *in press*).

Figure 2: Local interpreted geological map of the near mine surroundings, which elaborates the locally defined stratigraphy of the Hardey Formation in the north western end of the Wyloo Dome. The mineralisation occurs at the boundary between the Paulsens Gabbro intrusive suite and the Melrose Argillite Member of the Hardey Formation. Most of the faults are dominantly dextral strike-slip with a thrust component. A general dip of 50°N is seen in this part of the
Wyloo Dome. The X–Y section is shown in Figure 3. Adapted from Selvaraja et al. (*in review*). Fm. = Formation.

Figure 3: Cross section of the mineralised section shown in Figure 4, which shows that 1) the Paulsens gabbro is folded around the same fold axis that defines the regional fold in the Hardey Formation, and 2) the mineralisation is mainly focused in the black shale dominant lower section of the Melrose Argillite. The highest grade mineralisation (>6 g/t Au) is located on the margins of the quartz vein that cross cuts the Paulsens gabbro. The Upper Melrose Member is
more sand rich than the Lower Melrose Member which is a silty shale. Adapted from Selvaraja et al. (*in review*).

The main quartz vein lodes contain upper and lower gold mineralised zones and a core of bucky white quartz. The brecciated and laminated zones on the margins of the vein (Fig. 3) contain multiple generations of pyrite which can be distinguished on the basis of textural and microchemical analyses (Selvaraja et al., *in review*). Pyrite 1 and 2 are thought to be diagenetic and do not host much gold in the deposit. The bulk of the gold in the deposit is hosted as visible inclusions in Pyrite 3 (85%), whereas a smaller share occurs as lattice dissolved gold in Pyrite 3B (15%; Selvaraja et al., *in review*). Chalcopyrite is in equilibrium with gold, in microinclusions within the pyrite grains (Tab. 1). Several generations of pyrite can be distinguished by a combination of textural observations and trace element chemistry. For the purposes of this work, the main gold bearing pyrite stages, defined as Pyrite 3A/B are studied. These generations of pyrite are intergrown with chalcopyrite with chalcopyrite forming in small inclusions and infilling cracks in the pyrite. Gold inclusions are commonly found in the margins of chalcopyrite inclusions within Pyrite 3A/B. For a thorough treatment of the paragenesis, hydrothermal alteration, mineralogy and sulfide chemistry of the Paulsens mineralisation, readers are referred to Selvaraja et al. (*in review*).

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<th>Minerals</th>
<th>Early</th>
<th>Time</th>
<th>Late</th>
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<td>Diagenetic pyrite</td>
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<td>Nodule pyrite</td>
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<td>Pyrite 1</td>
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<td>Pyrite 2</td>
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<td>Pyrite 3 - A/B</td>
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<tr>
<td>Au</td>
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<td>Chalcopyrite</td>
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<td>Muscovite</td>
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<td>Calcite</td>
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<td>Chlorite</td>
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<td>Quartz</td>
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<td>Ankerite</td>
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Table 1: Paragenetic sequence of ore minerals and related hydrothermal alteration minerals in the Paulsens deposit. Adapted from Selvaraja et al. (in review).

2 Methods

2.1 Fluid Inclusions methods

2.1.1 Optical microscopy and SEM-CL-EDS

Seventeen samples of mineralised veins and host rocks were cut from 7 different hand specimens which were obtained from two drillholes and four development stopes in the Paulsens deposit (Supplementary Material). These samples are a subset of those that were initially acquired for pyrite and gold characterisation and the study of sulfur and gold sources, (cf. Selvaraja et al., in review). Derived 100 µm doubly polished thick sections were studied petrographically. Seven of these thick sections were coated with 10 µm carbon for cathodoluminescence (CL) imaging on the TESCAN Vega-3 scanning electron microscope (SEM) at the Centre for Microscopy, Characterisation and Analysis (CMCA), The University of Western Australia (UWA). Images were acquired at 15 kV with a focused 0.4 nA beam at a working distance of 10 mm.

2.1.2 RAMAN Spectroscopy

A Renishaw inVia Reflex Spectrometer System equipped with a standard confocal microscope was used for Raman spectral analysis at the Research School of Earth Sciences, Australian National University (ANU). A Renishaw diode-pumped solid state laser provided 532 nm laser excitation with 5 mW power at the sample. A 2400 grooves/mm grating was used giving a spectral resolution of 0.5 cm$^{-1}$. Single Raman spectra were obtained using a 1 second integration time with 30 accumulations within a scanning range of ~1,000 to ~4,000 cm$^{-1}$. Specific attention was focused in the regions for CO$_2$ (the Fermi diad at ~1285 and 1388 cm$^{-1}$), CH$_4$ (~2917 cm$^{-1}$), N$_2$ (~2331 cm$^{-1}$) and H$_2$S (~2611 cm$^{-1}$). The attached microscope was
equipped with a 50x Leica microscope objective, which focused the beam to a spot size of 1.6 µm. Wavenumber calibration was carried out using an internal silicon standard and was performed as an automated procedure using the Wire version 4.2 software.

2.2 Secondary Ion Mass Spectrometry Isotope Analysis

Methods utilised to obtain, reduce, standardise and process the secondary ion mass spectrometry (SIMS) data collected from the CAMECA IMS1280 large-geometry ion probe at the CMCA, UWA are detailed in LaFlamme et al. (2016), and specific analytical conditions are specified below. Quadruple sulfur isotope ($^{32}$S, $^{33}$S, $^{34}$S, and $^{36}$S) analysis was performed with the ion microprobe operating in multicollection mode using a 10 keV Cs$^+$ primary beam (~3 nA; Gaussian mode) and a normal incidence electron flood gun for charge compensation during all analyses. Following a 30 s pre-sputter, secondary sulfur ions from the target sample were extracted at -10 kV and admitted to the mass spectrometer with a field magnification of 133×, with automated centering of the secondary beam in the field aperture (both x and y; aperture size 4000 µm) and entrance slit (x direction only; slit width 60 µm or 90 µm in some cases). The NMR magnetic field controller locked the axial mass at the beginning of each session, and the mass spectrometer operated at a mass resolution (M/ΔM) of about 2500 (exit slit width of 500 µm on the multicollector). $^{32}$S, $^{33}$S and $^{34}$S were simultaneously detected by three Faraday Cups using amplifiers with $10^{11}$ Ω (L’2) and $10^{10}$ Ω resistors (L1 and H1). Count rates on $^{32}$S varied from $5 \times 10^8$ to $3 \times 10^9$ cps on pyrite. $^{36}$S was measured using a low-noise ion counting electron multiplier (EM). A primary beam current of 5 nA, raster size of 30 µm for pre-sputter and 20 µm for analysis and an acquisition time of 279 s in 45 integration cycles were necessary to achieve good precision on $^{36}$S. The count rates on $^{36}$S of typically $2-4 \times 10^5$ cps for pyrite cause a significant gain drift for the EM. Hence, the EM high voltage was optimised using a Pulse Height Amplitude (PHA) distribution curve at the start of each session, and the grain drift was measured more than three times during each analysis (at the beginning,
Measurements of unknowns were interspersed with matrix-matched reference material, Sierra for pyrite analyses to calibrate isotope ratios and monitor internal precision.

3 Fluid Inclusion Analysis

3.1 Quartz vein mineralogy

Two generations of quartz are observed in the quartz-ankerite-pyrite veins which form the core of the ore zones. These are identified as $Q_{(g)}$, where $g$ is ‘grey’ and $Q_{(m)}$, where $m$ is ‘milky’.

The syn-pyrite $Q_{(g)}$ quartz is easily identifiable due to its light grey colour in hand specimen and clarity with relatively few inclusions in thin section. It shows evidence of intracrystalline plastic strain (e.g., undulose extinction) in some areas, but is usually undeformed. It is commonly intergrown with ankerite which is usually located at the margin of the pyrite grains (Fig. 4). The later $Q_{(m)}$ quartz is located in the main core of the veins and consists of coarse-grained (1 – 2 cm) crystals which display a milky colour in hand specimen and are very rich in fluid inclusions (Fig. 4). The sulfide petrography, mineralogy and paragenesis, together with the other aspects of the hydrothermal alteration mineralogy is summarised in Selvaraja et al., (in review); a paragenetic sequence from that study is reproduced in Table 1.
Figure 4: Sample P251401B, showing some of the key minerals and fluid inclusion features observed in the Paulsens deposit. An – Ankerite, $Q_{(g)}$ – Grey Quartz, $Q_{(m)}$ – Milky Quartz, Py – Pyrite, Cpy – Chalcopyrite

3.2 Cathodoluminescence

All domains of quartz luminesce slightly (Fig. 5). Variation in luminescence intensity can be noted in two features: (1) $Q_{(m)}$ – internal grain complexity highlighted by highly variable luminescence intensity, and (2) $Q_{(g)}$ – with relatively low luminescent response and minimal internal variation on the margins of pyrite grains (Fig. 5).
Figure 5: Cathodoluminescence image highlights multiple generations of quartz. $Q_{(g)}$ forms adjacent to pyrite 3A. Due to instrumental drift, noisy signal is seen on the left of the image, generating bright zones which are not reflective of real variation in luminescence.

3.3 Fluid inclusion petrography

Inclusions were investigated based on textural criteria using the fluid inclusion assemblage (FIA) concept, whereby single FIA represent groups of temporally coeval inclusions occurring in clusters, trails, or along grain boundaries. Two distinct fluid inclusion types were observed in quartz (at room temperature), and these are designated as Types 1 and 2.

Fluid inclusion assemblages containing Type 1 inclusions consist of two-phase ($L_{aq} + V_{aq}$) H$_2$O-NaCl-(KCl ± MgCl) ± CO$_2$ ± CH$_4$ inclusions hosted in $Q_{(g)}$ (Fig. 4). These inclusions show relatively isometric shapes (dominantly oval, circular and rectangular), lack evidence of...
decrepitation or necking down, and range in size from ~1 to ~5 µm in length and width. These inclusions are located in groups or internal trails which range in number from 6 to 30+ on the margins of the pyrite and chalcopyrite grains in the Q(g). Evidence for Type 1 inclusions trapped along primary growth zones is difficult to establish as quartz growth zones are rare in these veins, with the exception of the clearly later relative timing of the Q(m) vis a vis the Q(g). A CO2-CH4 phase is detected using Raman spectra (Fig. 6); however, as the concentration of the carbonaceous phases is very low (<2 mol %), they do not form a gas phase, hence it is not possible to measure the volume fraction of those phases.

Fluid inclusion assemblages composed of Type 2 inclusions are relatively rare in Q(g) adjacent to sulfides but they are dominant in the later Q(m) which is not adjacent to sulfides. They are interpreted to be secondary as they are not observed in textural equilibrium with the gold bearing sulfides. In the few instances where they do cut the host mineral boundaries, clear evidence of quartz deformation is observed (undulose extinction and variable cathodoluminescence responses). Only a few assemblages were studied due to their clear secondary nature. They consist of three-phase (L CO2 + L aq + V aq) H2O-CO2-NaCl-CH4 inclusions at room temperature. The inclusions nucleated a CO2 vapour bubble on cooling and have approximate V CO2/LCO2 ratios of 0.1. These inclusions typically have highly variable shapes that range from irregular to isometric and are typically much larger than the Type 1 inclusions, ranging from ~3 to ~10 µm in size.
Figure 6: Sample P242340C displays a FIA trapped in an internal trail within Q\(_{(g)}\) close to the margins of pyrite grains. This FIA consists of Type 1 inclusions. A second FIA is trapped in a trail that cross-cuts the grain boundary and the internal fluid inclusion trail. This FIA, in red, consists of Type 2 inclusions. Note that the green mark results from a marker pen. All images are taken in plane polarised light with the exception of the top right image, which was taken under cross-polarised light.
3.4 Fluid inclusion microthermometry and Raman spectroscopy

The results for microthermometry are reported in Table 2 and summarised in Figures 7 and 8 where data are grouped according to FIAs. A total of 183 inclusions in 24 FIAs are used to characterise the two types of fluid inclusions observed.

Table 2: Summary table of the fluid inclusion microthermometry observations

<table>
<thead>
<tr>
<th>FI features</th>
<th>FIA that trapped Type 1</th>
<th>FIA that trapped Type 2</th>
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<tbody>
<tr>
<td>Number of FIAs analysed</td>
<td>20</td>
<td>4</td>
</tr>
<tr>
<td>Number of single FIs analysed</td>
<td>168</td>
<td>15</td>
</tr>
<tr>
<td>Salinity (wt % NaCl equivalent)</td>
<td>10 ± 3</td>
<td>18 ± 1</td>
</tr>
<tr>
<td>Min–max Salinity (wt % NaCl equivalent)</td>
<td>4.2 – 16.1</td>
<td>16.5 – 18.7</td>
</tr>
<tr>
<td>Th_{TOT (L–V)} min–max (°C)</td>
<td>123 – 347</td>
<td>271 – 345</td>
</tr>
</tbody>
</table>
Figure 7: $\text{T}_{\text{TOT (L-V)}}$ and salinity for each FIA. FIA no. 10 and no. 20 are outliers, and have been affected by post entrapment modification (Diamond et al., 2010; Neyedley et al., 2017).
The data are reported as a box and whisker plot with the boxes bounding the 1Q–3Q interquartile range. The actual data points are reported in a faded grey colour in the background of the boxes.

Figure 8: \( T_{h,TOT(L-V)} \) (°C) v salinity, for individual FIA. The Type 1 inclusions have very consistent total homogenisation temperatures but variable salinities across the entire Type, but the variation within individual FIAs is very limited (<5 wt%).

The average \( T_{h,TOT(L-V)} \) for the 18 unmodified Type 1 FIAs (No. 1–9, 11–19) is 147 °C with a range of 123 to 182 °C. The average salinity for these FIAs is 10.3 wt. % NaCl equivalent with a range of 4.2 – 16.1 wt. % NaCl equivalent. The average first melt of -39 °C implies a
significant KCl and minor MgCl component to the salinity (Davis et al., 1990). Estimated bulk densities range from 0.99 to 1.05 g/cc for these FIAs which were all homogenised by vapour bubble disappearance ($L_{aq} + V_{aq} -> L$). Individual FIAs show limited ranges but all the FIAs together show a large spread in salinities. The ratio of CO$_2$ to CH$_4$ in the inclusions where an accurate measurement could be taken from Raman spectroscopy was 1:1 ($n = 9$), although characterised by large variability. Two outlier FIAs (No.10 and No. 20) have a much higher total homogenisation temperatures (~251 °C and ~345°C) resulting from post entrapment modification, as evidenced by 1) their anomalously low L/V ratio ($\leq 9$) compared to other FIAs in similar quartz grains and 2) by the indication of high strain by virtue of highly variable undulose extinction in the quartz grains hosting these two FIAs (Diamond et al., 2010; Neyedley et al., 2017). Leakage of the aqueous contents of some inclusions is also supported by the presence of small empty inclusions coexisting with inclusions showing typical L/V ratios.

The four FIAs that contain Type 2 inclusions ($n = 15$) show a tight average range of clathrate melting temperatures that corresponds to a range of salinities between 16.5 and 18.7 wt % NaCl equivalent, using the equation of state of Kerrick and Jacobs, (1981). The melting temperatures of the carbonic phase ($T_{mCO_2}$) ranged from -64.4 to -57.8 °C suggesting the presence of other dissolved gases besides CO$_2$. Raman analyses indicated that the ratio of CO$_2$/CH$_4$ in these inclusions is 65/35 suggesting that a significant share of the carbonic phase is derived from CH$_4$ (methodology for this calculation is derived from Wopenka and Pasteris, 1987; Fu et al., 2014). Using these ratios to constrain the microthermometric calculations, 2–5 mol % of the inclusions are CO$_2$ equivalent and 1–3 mol % are CH$_4$ equivalent (Supplementary Material). The partial homogenisation of the carbonic phase ($T_{hCO_2}$; $L_{aq} + L_{CO_2} + V_{CO_2} + V_{aq} -> L_{aq} + L_{CO_2}$ + $V_{aq}$) occurred by vapour bubble disappearance between -1.6 and 9 °C corresponding to bulk densities between 1.024 – 1.104 (Kerrick and Jacobs, 1981). The total homogenisation
temperature into liquid \( T_{\text{HOT}}(L) \); \( \text{Laq} + \text{LCO}_2 + \text{VCO}_2 \rightarrow \text{L} \) ranges between 271 and 345 °C. All
the thermometry data, processed by MacFlincor (Brown and Hagemann, 1995), and Raman
gas ratio data are included in the Supplementary Materials.

4 Multiple sulfur isotopes

4.1 \( \delta^{34}S \) evolution through time

We present here multiple sulfur isotope data that has been reinterpreted spatially from Selvaraja
et al., (in review) and new multiple sulfur isotope data collected in this study. In both datasets,
we collected multiple isotopes of sulfur \( (^{32}\text{S}, ^{33}\text{S}, ^{34}\text{S} \text{ and } ^{36}\text{S}) \), which allows us to quantify both
the mass dependent fractionation parameter, \( \delta^{34}\text{S} \) and the mass independent fractionation
parameter, \( \Delta^{33}\text{S} \) and \( \Delta^{36}\text{S} \) (Wing and Farquhar, 2015). The combination of these sulfur isotope
parameters opens the possibility of separating the relative isotopic variations driven by the
initial composition of the Archean surficial source of sulfur (Selvaraja et al., in review) from
process driven changes during the operation of the mineral system. As can be observed in
Figure 9, a shift of about +1‰ in \( \delta^{34}\text{S} \) is observed from the cores to the rims of the pyrite grains.
This is despite there being no micro-chemical heterogeneity in the grains. Thus the observed
evolution of the \( \delta^{34}\text{S} \) mass dependent fractionation signature must have been the result of
changes in the fluid isotopic budget as the \( \delta^{34}\text{S}_{\text{H}_2\text{S}} = \delta^{34}\text{S}_{\text{Py}} \) in the temperature conditions
observed in this system (Ohmoto, 1972). The \( \Delta^{33}\text{S} \) of all the analyses in this image is \( \sim +0.35‰ \),
establishing that the source of the fluid is not changing during the course of precipitation. A
thermodynamic model has been constructed below to understand the drivers of this isotopic
shift and the constraints this places on the processes leading to pyrite and gold precipitation in
the deposit.
Figure 9: A high contrast backscatter image with an overlay of the interpreted $\delta^{34}\text{S}$ shifts in the gold bearing pyrite, such as shown in this image, precipitated in the Paulsens deposit. Grey tones are pyrite, whereas white tones are of a coating film unrelated to the sample. The data presented in this image is a spatial reinterpretation of data that was first published in Selvaraja et al. (in review).

4.2 Sulfur isotope geothermometry

Constraining the temperature of formation of sulfides (and by extension the mineral deposit in question) by using the relative $\delta^{34}\text{S}$ between pairs of coexisting sulfides or sulfide-sulfate mineral assemblages is a complex process. Inconsistencies between the observed values and the experimentally predicted values are often found. This is because in mineralogically
complex ores, it is difficult to sample mineral pairs that are definitely in isotopic equilibrium even where textural and paragenetic relationships seem to indicate co-precipitation (Jamieson et al., 2006; Hodkiewicz et al., 2008). In ancient ore deposits, such as the Archaean, various complex overprinting, replacement, coupled dissolution-reprecipitation (CDR) and metamorphic reactions can make it impossible to differentiate textural equilibrium or disequilibrium.

An additional limitation on previous work has been a reliance on dissolution techniques to study the sulfur isotope compositions of co-existing mineral pairs. Such work usually involves crushing and manual separation of grains of different sulfides from each other, dissolving them separately and then analysing them. This technique resulted in multiple different generations of sulfides in ore deposits being analysed together, which led to incorrect results. However, when the sulfide pairs are clearly demarcated, and only one generation of sulfide growth exists, the geothermometry data generated by these isotope equilibrium pairs can be robust (McDermott et al., 2015). Further, the initial experimental constraints on sulfur isotope equilibrium fractionation factors generated by Kajiwara and Krouse (1971) have been validated by modern observations of natural samples in thermally constrained submarine hot-springs (McDermott et al., 2015).

It is in this context that we used \textit{in-situ} multiple sulfur isotope analysis as an improved method of geothermometry of co-existing sulfide pairs, in our case, pyrite-chalcopyrite pairs. Jamieson et al., (2006) pioneered this technique, which involves a combination of results generated by measurement of the chemically conservative Archaean atmospheric $\Delta^{33}$S isotopic signature with the $\delta^{34}$S values to produce a more robust way to establish that co-existing sulfide pairs were in isotopic equilibrium. $\Delta^{33}$S is a product of specific photo-chemical processes in the Archaean atmosphere and is considered to be constant in any given sulfur reservoir (Johnston, 2011 and references therein). Thus, minerals that are in isotopic equilibrium and which
precipitated from the same fluid will have identical $\Delta^{33}S$ values, within error. Measurement of $\Delta^{33}S$ provides an independent means of evaluating the suitability of mineral pairs for sulfur isotope geothermometry. In the Paulsens deposit, the presence of a consistent $+\Delta^{33}S$ signature of $\sim+0.35\%$ in both the pyrite and chalcopyrite, gave us a further line of evidence to support the textural and paragenetic relationship of co-precipitation of pyrite and chalcopyrite. Thus, we assume that the variations in $\delta^{34}S$ between the mineral pairs were not due to changes in the source of the fluid, but rather due to equilibrium isotopic partitioning into different phases.

We analysed co-existing chalcopyrite-pyrite pairs (Fig. 10) in the Paulsens deposit for their sulfur isotope composition and the results are shown in Figure 10. The originality of our approach is that S isotope analyses were performed in-situ using by SIMS, which has a beam size of $<10 \, \mu m$ in our analytical conditions. Thus, the analyses performed could minimise the potential isotopic disequilibria as the distance between spots was minimised. The $\delta^{34}S$ of sulfide pairs that were determined to be in equilibrium on the basis of textural observations as well as their $\Delta^{33}S$ and $\delta^{34}S$ signatures (Fig. 11) were then processed through the equation that governs isotopic fractionation between pyrite and chalcopyrite (Kajiwara and Krouse, 1971; McDermott et al., 2015)

$$T \, (^\circ C) = \sqrt{\frac{4.5 \times 10^5}{\delta^{34}S_{py} - \delta^{34}S_{cpy}}} - 272.15$$

The results of this calculation are plotted in Figure 12. The full set of isotopic data is provided in the Supplementary Material sections. The chalcopyrite grains studied had a range of $\delta^{34}S$ values of between $-7.2 \pm 0.5\%$ to $+1.1 \pm 0.3\%$. The pyrite grains studied had a range of $\delta^{34}S$ values of between $-8.2 \pm 0.4\%$ to $+1.5 \pm 0.2\%$. The $\Delta^{33}S$ values of the samples showed a range between $+0.50$ to $+0.21 \pm 0.17\%$ in pyrite and $+0.50$ to $+0.19 \pm 0.29\%$ in the chalcopyrite grains. However, after taking into account the textural and $\Delta^{33}S$ constraints on isotopic
equilibrium, the range of δ^{34}S of the pairs considered to be in isotopic equilibrium is significantly narrower at between -0.6 to +1.5‰ in pyrite and -5.1 to +0.1‰ in chalcopyrite. The range of temperatures these pairs generate are between 11 ± 12°C and 605 ± 280°C. A wide distribution of values is observed with a peak close to the median value and a secondary peak at a temperature slightly higher than the mean value. Uncertainty in each value ranges from 10–40%, and the 1σ for the entire dataset is 48 °C (Fig. 12). The uncertainty in each value is derived from the compounded uncertainties in the δ^{34}S measurements of each respective pyrite-chalcopyrite pair. There is also no systematic variation in pair generated temperatures between the different pyrite textures in Pyrite 3A/B (Fig. 12).
Figure 10: A pyrite-chalcopyrite association showing chalcopyrite in white, possibly in textural equilibrium with pyrite, which is in grey tones depending on the As and Ni content of the growth zone, as Ni-As has a higher atomic mass than Fe-S. The lighter colours reflect Pyrite 3B and the darker colours reflect Pyrite 3A. These two generations of pyrite form under the same conditions as the Type 1 fluid inclusions based on quartz-pyrite textural relationships (Fig. 4).
Figure 11: Plot of the various pairs of pyrite and chalcopyrite studied. The grey outlined box is constrained by, 1) the $\delta^{34}S$ difference of py - cpy being a positive value less than 6.5‰ and 2) the difference in $\Delta^{33}S$ between py and cpy being smaller than the compounded analytical errors for the pairs of $\Delta^{33}S$ measurements. This is because $\delta^{34}S$ differences greater than 6.5‰ would result in negative temperature estimates on the known fractionation curve. The ability to differentiate $\Delta^{33}S$ values in an isotopic pair is limited by the analytical uncertainty.
4.3 Sulfur isotope geothermometry discussion

It is clear that despite the availability of an internal isotopic evaluation of equilibrium, i.e. the presence of the Archaean $\Delta^{33}$S signature, as demonstrated in Selvaraja et al. (in review), and the usage of that parameter to remove pairs that were not in isotopic equilibrium from the calculations, a wide range of temperatures were obtained from the same generation of sulfides in the same sample. This finding could perhaps be interpreted as evidence that none of the chalcopyrite was in equilibrium with the pyrite; as such, all the analysis would be of sulfides in isotopic disequilibrium. In our view, this possibility is unlikely because of two reasons, the source of the fluid which precipitated the pyrite and chalcopyrite is the same, due to its similar
magnitude of the $\Delta^{33}\text{S}$ in addition, the overall paragenetic sequence of the sulfides in the deposit is well constrained, with pyrite and chalcopyrite co-precipitating (Selvaraja et al., *in review*).

Although chalcopyrite is known to be highly mobile at temperatures above 300°C (Cox et al., 1987) and temperatures at the Paulsens deposit did reach ~340°C during the formation of Type 2 FIA$s$, no chalcopyrite is observed to have been redistributed into the late veins of quartz-calcite or $Q_{(m)}$ seen in the Paulsens deposit. As such, we can assume that the paragenetic sequence was unmodified. The observed mean and median temperature estimates of the overall dataset are very similar to the pressure corrected temperature of trapping estimates (230°C; $T_{\text{h. tot}}$; discussed in Section 6 below) of the Type 1 fluid inclusions hosted by quartz that co-precipitated with Pyrite 3A (dark colour), 3B (light colour) and chalcopyrite in this sample. Thus, at a more macro scale, i.e., the overall grain, isotopic equilibrium was probably reached.

However, this still does not explain why in previous attempts to use pyrite-chalcopyrite equilibria for sulfide geothermometry, much more precise estimates of temperatures were obtained (Jamieson et al., 2006; Shelton and Rye 1982). We argue that this difference is due to the fact that we have used *in situ* methods for our sulfur isotope analysis. We postulate that these data indicate that isotopic distribution in minerals grown in hydrothermal systems may be highly heterogeneous at the micron scale. This hypothesis is supported by the fact that trace element (e.g. Ni, As, Co etc.) distributions in hydrothermally grown mineral phases are highly heterogeneous due to the nature of adsorptive reaction pathways in these systems (Farquhar et al., 2002).

Alternatively, mineral re-equilibration due to hydrothermal processes are more likely to happen at the rim of the grains and at grain junctions where fluids may be more mobile. Thus, by analysing at 10µm from the grain junctions, we may be sampling alteration, metamorphic replacement or diffusion processes which have occurred after the initial growth of the grain.
The general point still stands however, that the use of *in situ* techniques, compared with solution chemistry techniques, can outline grain scale heterogeneities which are homogenised by solution chemistry. These micro-scale heterogeneities may be driven by the kinetic mass dependent fractionation that occurs in reaction pathways which do not reach equilibrium or are terminated without the reaction proceeding to completion (Young et al., 2002), which are documented at the micron scale. As fluid infiltrates the rock, it may form a series of closed systems where each individual subsystem is at equilibrium but the fluid is reacting and fractionating its sulfur as it proceeds so each different subsystem could have a slightly different isotopic composition, yet the overall sulfur isotope composition of the fluid and sulfides may still have been near equilibrium through an averaging process. Thus, when the entire population of an *in situ* data set is considered at the grain to thin section scale however, it then becomes possible, by the usage of statistical techniques to compare them to data obtained by dissolution techniques (Farquhar et al., 2013).

5 Thermodynamic Model

5.1 Model Design

Following on from the observation that in some grains of gold bearing Pyrite 3A/B, the $\delta^{34}$S signature varies systematically from the core to the rim of the grains, i.e. through the mineral precipitation process, while preserving the same $\Delta^{33}$S Archean surficial signature, we have developed a thermodynamic model to understand the causes of this variability. The ore-forming system was simulated using the HCh software and the associated Unitherm database (Bastrakov and Shvarov, 2007). The modelled system is $\text{SiO}_2$-$\text{Al}_2\text{O}_3$-$\text{FeO}$-$\text{Fe}_2\text{O}_3$-$\text{MgO}$-$\text{CaO}$-$\text{Na}_2\text{O}$-$\text{K}_2\text{O}$-$\text{Cl}$-$\text{Au}$-$\text{Cu}$-$\text{Zn}$-$\text{Pb}$-$\text{S}$-$\text{C}$-$\text{As}$-$\text{H}_2\text{O}$. Nickel was omitted because the principal Ni-bearing phase in the rocks of interest, gersdorffite, was not present in the Unitherm database.
However, Ni-systematics are not a focus of this investigation and Ni concentrations are low, so this omission does not have significant implications for the results.

Conceptually, the system was visualized in two distinct parts (Fig. 13). Ore fluids were generated by equilibration of a salt-bearing aqueous fluid with sediments at 300°C and 2 kbar (Box 1; Fig. 13). This fluid was then assumed to be transported upwards rapidly in a vein network, without re-equilibration with the surrounding wall rock, to infiltrate host sedimentary rocks of the same composition higher up in the rock column at 230°C. Fluid-rock interaction at a rheological boundary in the host rock, controlled by fault-valve depressurisation processes, at the intersection of the Paulsens Gabbro with the Melrose Argillite, was then simulated by equilibration of the fluid with the composition of the Melrose argillite. Au precipitation in the deposit occurs at this rheological boundary (Selvaraja et al., *in review*).

In detail, the ore forming fluid was generated in shale with the bulk composition in Table 3 below. The composition of this modelled shale, named VIKav1, is that of an average of black shale compositions for the Hardey Formation (Ohmoto et al., 2006), with three modifications:

- The Fe$^{3+}/\sum$Fe of the shale, which is not reported in Ohmoto (2006), was varied to investigate the effect of changes in source rock redox on sulfur speciation and sulfur isotope composition;
- the source rock was set to contain an excess of gold;
- organic carbon was set to 0.03 wt% in the bulk composition.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>57.07</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>20.24</td>
</tr>
<tr>
<td>Fe$_2$O$_3$ tot</td>
<td>6.03</td>
</tr>
<tr>
<td>MnO</td>
<td>0.06</td>
</tr>
<tr>
<td>MgO</td>
<td>2.86</td>
</tr>
<tr>
<td>CaO</td>
<td>1.40</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>1.77</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>3.45</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.99</td>
</tr>
<tr>
<td>Substance</td>
<td>Value</td>
</tr>
<tr>
<td>-----------</td>
<td>-------</td>
</tr>
<tr>
<td>P2O5</td>
<td>0.11</td>
</tr>
<tr>
<td>LOI</td>
<td>5.49</td>
</tr>
<tr>
<td>Total</td>
<td>99.47</td>
</tr>
<tr>
<td>Co (ppm)</td>
<td>37.00</td>
</tr>
<tr>
<td>Cu (ppm)</td>
<td>65.50</td>
</tr>
<tr>
<td>Zn (ppm)</td>
<td>100.75</td>
</tr>
<tr>
<td>Pb (ppm)</td>
<td>17.88</td>
</tr>
</tbody>
</table>

Table 3: Modelled bulk composition of VIKav1

The primary consequence of the low assumed organic carbon value is that organic carbon can be exhausted by devolatilisation reactions. Without organic carbon, redox conditions are not effectively buffered so variation in the ferric to ferrous ratio of the shale results in variation in the oxidation state of the rock during fluid production. Without this modification the ferric:ferrous ratio of the shale is effectively fixed by the presence of the organic carbon, which buffers fluid compositions such that sulfate concentration in the fluid is negligible. The physical implications of this assumption are discussed below. The host sedimentary rock also has the composition of VIKav1, with the addition of 0.6 wt% graphite. The ferric:total iron ratio of the host rock was set to 0.1.

The first step of the simulation involves equilibration of water, with 10 wt% NaCl, with the source rock at 300°C at a fluid:rock ratio of 0.1. The equilibrated fluid is then transferred into a box or cell containing the host rock at 230°C (Box 2–10; Fig. 13), equilibrated, and passed sequentially into another nine boxes or cells containing the host rock at 230°C. These salinities and temperatures were chosen from fluid inclusion microthermometry derived estimates obtained from this study (see above). This simulation was performed for Fe3+/∑Fe in the source rock from 0 to 0.19. This range was chosen because the full range of sulfur speciation in the host is seen across these values. The sulfur isotope composition of pyrite in the host rock was calculated assuming that pyrite precipitated from the infiltrating fluid, and that the sulfur isotope composition of the infiltrating fluid was fixed by equilibration with pyrite in the source...
rock with a $\delta^{34}S$ value of 0 ‰. Fractionation factors for the relevant temperatures were taken from Seal (2006).

Figure 13: Two box model of sulfur, Au transport and transfer from a source rock with variable redox conditions. Redox is controlled by the Fe$^{3+}/\Sigma$Fe ratio of the source rocks, and then maintained during transport within a fluid-buffered fault system similar to that observed underlying the Paulsens deposit to a major rheological boundary which is the intersection between the Paulsens Gabbro and the Melrose Argillite. The concentration of gold dissolved into the fluid is controlled by the redox conditions of the source rocks. The red arrows reflect fluid flow direction.

5.2 Model Results
The mineralogy of the host rock is consistent with that observed in the samples (Fig. 14). The predicted silicate mineral assemblage is quartz-muscovite-feldspar-chlorite-carbonate for simulations. Predicted accessory phases are graphite, pyrite, sphalerite, galena, chalcopyrite, arsenopyrite and gold (present only in the first few cells of the host rock).

Figure 14: The evolution of mineral stability in the fluid that created the deposit through different redox conditions of the source rock of the fluids. The proportion of gold in the host rock is fundamentally controlled by the Fe$^{3+}/\Sigma$Fe ratio that buffers the redox conditions of the host rock. It is clear that the more oxidised the source rock, the lower the gold solubility in the fluid, with the result that less gold is transported overall.

Pyrrhotite was predicted to co-exist with pyrite and the other sulfides up to a Fe$^{3+}/\Sigma$Fe iron ratio of 0.09, arsenopyrite was predicted at Fe$^{3+}/\Sigma$Fe iron ratio up to 0.12, and anhydrite was predicted at Fe$^{3+}/\Sigma$Fe iron ratios of 0.16 and higher. The transition from pyrite-pyrrhotite to pyrite-anhydrite assemblages was associated with a shift in the speciation of sulfur in the ore-
forming fluid, with \( \text{H}_2\text{S} \) and \( \text{HS}^- \) providing the dominant sulfur species at ferric:total iron ratios up to 0.13, and sulfate-species dominating at ferric:total iron ratios greater than 0.15 (Fig. 15). The shift from sulfide- to sulfate-dominated ore fluid drives a change in the sulfur isotope values with \( \delta^{34}\text{S}_{\text{fluid}} \) predicted at -1.4 ‰ for the sulfide dominated fluids and 18.5‰ for the sulfate dominated fluids (Fig. 15). The presence of graphite in the host rock buffers \( f_{\text{O}_2} \) in the infiltrating fluid, so that sulfur speciation in the ore fluid within the host rock is sulfide dominated for all simulations. However, the heavy isotope signature inherited from the source rock is retained for fluids produced in the more oxidized source rocks, and these fluids produce pyrite, with heavy sulfur isotope values with \( \delta^{34}\text{S} \) up to 18‰.

Figure 15: Modelled control on sulfur speciation in the mineralising fluid. The ferric iron proportion of the source rock is again the main control on the sulfur speciation and small
changes in the ferric iron ratio can generate significant shifts in the fluid oxidation state and thus control the speciation of sulfur.

5.3 Model Discussion

These thermodynamic results demonstrate that relatively small shifts in the redox budget of the source rock can produce large shifts in the sulfur isotope value of ore fluids and precipitated pyrite. This can occur if these shifts in redox budget are such that the redox state of the fluid crosses significant speciation thresholds such as the sulfide:sulfate threshold. These redox shifts can also exert a significant impact on the gold solubility in the fluid, such that the amount of gold in the fluid can decrease by almost half an order of magnitude with only a 17% increase in the Fe$^{3+}/\sum$Fe ratio. In Figure 16, we demonstrate that the model reproduces the observed shift in $\delta^{34}$S values that occurs during gold precipitation as the $\delta^{34}$S value of the pyrite that hosts the gold in the Paulsens deposit (Figure 9; Pyrite 3A/B; Selvaraja et al., in review) increases by 1‰ on average. Thus, as the amount of gold in solution declines, due to increasing ferric iron proportion in the source rocks, the $\delta^{34}$S value of the fluid increases. The signature pyrite in the Paulsens deposit in Figure 9 thus documents the waning gold concentrations in the fluids as the deposition process continues in response to the increasing oxidation state of the source rocks, which may be driven by metamorphic mineral reactions occurring in the source rocks. Alternatively, an oxidized magma and associated oxidised magmatic hydrothermal fluids may drive these reactions, however this possibility is precluded as an oxidised magmatic fluid would carry a $\Delta^{33}$S signature of 0 ‰, thus it would change the $\Delta^{33}$S signature of the gold bearing pyrite, which we do not observe to be the case.

This is the first time that source rock redox controls on the gold solubility of mineralising fluids have been identified for fluids derived from a sedimentary source, as opposed to previous work which focused only on magmatic sourced fluids (Cameron and Hattori, 1987). One of the key
barriers to this work in the past has been the inability of researchers to determine the difference between variations in $\delta^{34}S$ in pyrite that have been due to changes in the composition and location of the source of the fluid, as opposed to changes that have been driven by the physico-chemical conditions governing the fluid. This is because attempts to use a uni-dimensional data approach (i.e., $\delta^{34}S$) to explore a system that bears two degrees or more of freedom (source difference and thermodynamic changes) is inherently limited. Conversely, in our dataset we have for the first time the ability to uniquely fingerprint the source of the mineralising fluid by using the consistent Archaean surface derived $\Delta^{33}S$ signature of the pyrite. With this indelible tracer, it is possible to interpret the $\delta^{34}S$ signature of the pyrite in a dynamic context, evaluating the effects of changes in the physico-chemical conditions of the fluid. Our model may thus explain the shifts in $\delta^{34}S$ in gold bearing pyrite at several other gold deposits e.g. Porgera and the Waroonga deposit (Peterson and Mavrogenes, 2014; LaFlamme et al., in prep).

As it is commonly observed, consistent and small shifts in Fe$^{3+}/\Sigma$Fe ratios (i.e., redox conditions) often occur in sedimentary rocks, following minor variation in the oxidative surfaces. These variations can generally be caused by areas of high concentration of biological matter or during the evolution of the paleosurface and weathering profiles. As such, the conclusions of Selvaraja et al. (in review) on the local sedimentary origins of the sulfur and the gold in the Paulsens deposit are consistent with the results of our modelling exercise. These also support the contention that gold is soluble in basinal brine fluids, with moderate salinities and at relative low temperatures. This provides a reasonable line of support to the thesis advanced by Tomkins (2010) as to the source of the fluid, ligands and metals in some orogenic gold deposits, although Paulsens itself may not be a ‘classic’ orogenic gold deposit in its expression.
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Figure 16: Combining the effects of control on the oxidation state of the fluid and sulfur speciation by the proportion of ferric iron in the source rock, it can be demonstrated that the Au concentration in the fluid, which is controlled by the sulfur speciation, is dependent on the ferric iron proportion in the source rock. This speciation change can also have a significant impact on the \( \delta^{34}S \) values of the fluid, which are documented to a smaller extent in the signature of the pyrite grains from the Paulsens deposit.

**6 Discussion**

The combination of microthermometry, Raman spectroscopy and sulfur isotope geothermometry allows us to create a paleohydrothermal model of fluid flow in the deposit as shown in Figure 17. The pressure constraints were obtained by considering the stratigraphic depth of the Hardey Formation during mineral deposition at \( \sim 2400 \) Ma (Fielding et al., *in review*), which is suggested by Johnson et al., (2013) to be under 4 – 6.5 km (\( \sim 140 \) MPa) of stratigraphic overburden at that time. Thus the composition of the mineralising fluid is around 10 wt. % NaCl equivalent, \( \sim 1-2 \) mol % CO\(_2\)+CH\(_4\) and has a trapping temperature of 230 ±
30°C, which coincides well with the isotope geothermometry based estimate of 239 ± 48°C. The peak metamorphic conditions in the Wyloo Dome, which were clearly achieved after mineralisation (Selvaraja et al., *in review*) is lower greenschist facies (Rasmussen et al., 2005) which, applying a standard P-T boundary for greenschist facies (Vernon and Clarke, 2008) overlaps well with the P-T window for the Type 2 FIAs (Fig. 17). The latter, due to the presence of CO₂/CH₄ ratios of 65:35 based on Raman spectroscopy and thermometrically generated NaCl contents, can only have formed at a pressure of ~280 MPa (Kerrick and Jacobs, 1981). This temperature is significantly cooler than the average orogenic gold deposit (~350 °C; Groves et al., 1998; Hagemann and Cassidy, 2000; Goldfarb and Groves, 2015), although orogenic gold deposits *sensu lato* have been found to form at temperatures as low as 180 °C (Hagemann et al., 1994).

Finally, the CH₄:CO₂ ratio in the Type 1 FIAs is 1:1, which is very unusual compared to most orogenic gold deposits where a 1:10 ratio is more commonly observed (Goldfarb and Groves, 2015). The high CH₄:CO₂ ratio can also be read as a line of evidence supporting the argument put forward by Selvaraja et al. (*in review*) that the fluids and metals that formed the Paulsens deposit are derived from the local carbonaceous shales, which would naturally be rich in CH₄ but poor in CO₂ owing to their usual high proportion of biological matter. Experiments performed by Connolly and Cesare (1993) demonstrate that water in equilibrium with carbonaceous shales forces a 1:1 CO₂ to CH₄ ratio and changes from that ratio require significant inputs of carbonate of loss of hydrogen, further supporting our contention.
Figure 17: $P$-$T$-$t$ diagram summarizing the evolution of the Paulsens gold system based on fluid inclusion microthermometry and depth estimates from Johnson et al., (2013). Solve for two fluid compositions which bracket the range that the Type 1 FIAs are obtained from Hagemann and Brown, (1996) and Bowers and Helgeson (1983) and show that the mineralising fluid was a one phase stable fluid at those $P$-$T$ conditions. The yellow line traces the proposed $P$-$T$-$t$ path of the mineral deposit from formation to the present. The initial dashed segment of the path suggests significant uncertainty in that segment.

Table 4: Comparison of key characteristics of low temperature orogenic gold deposits, Carlin type deposits and Paulsens (data sourced from Gebre-Mariam et al., 1993; Groves et al., 1998; Hagemann and Luders, 2003; Cline et al., 2005; Su et al., 2009)
<table>
<thead>
<tr>
<th>Attributes</th>
<th>Low – T Orogenic gold (e.g. Racetrack &amp; Wiluna)</th>
<th>Carlin type (NCT, Guizhou Trend)</th>
<th>Paulsens</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>180 – 240</td>
<td>150 – 250</td>
<td>230</td>
</tr>
<tr>
<td>Salinity (NaCl equiv. wt%)</td>
<td>3 – 10</td>
<td>2 – 10</td>
<td>10</td>
</tr>
<tr>
<td>Fluid composition</td>
<td>&gt; 5 mol % CO₂, trace CH₄, N₂</td>
<td>Low CO₂, CH₄</td>
<td>1 – 2 mol % CO₂, CH₄</td>
</tr>
<tr>
<td>Depth of emplacement (km)</td>
<td>2 – 3</td>
<td>2 – 4.5</td>
<td>5</td>
</tr>
<tr>
<td>Metamorphic grade at formation</td>
<td>Lower greenschist</td>
<td>Sub-greenschist</td>
<td>Sub-greenschist</td>
</tr>
<tr>
<td>Peak metamorphic grade</td>
<td>Lower greenschist</td>
<td>Sub-greenschist</td>
<td>Lower greenschist</td>
</tr>
<tr>
<td>Tectonic setting</td>
<td>Compressional margin</td>
<td>Passive margin</td>
<td>Passive margin</td>
</tr>
<tr>
<td>Lithostratigraphy</td>
<td>Granites, greenstones, rare sedimentary rocks</td>
<td>Carbonate sedimentary rocks, silicic sedimentary rocks, shales</td>
<td>Carbonaceous shales overlying mafic magmatic rocks and granitic basement</td>
</tr>
<tr>
<td>Key alteration phases</td>
<td>Chlorite-epidote-quartz-calcite</td>
<td>Decalcification, orpiment+realgar, intense silicification</td>
<td>Quartz-ankerite-minor chlorite</td>
</tr>
</tbody>
</table>
The \( P-T-X \) (\( X = \) composition) conditions of the mineralising fluid in this deposit show strong similarities to those observed for gold mineralisation in the Nevada Carlin Trend (NCT), the Youjiang Basin in China and the Macraes deposit in New Zealand (Cline et al., 2005; Pitcairn et al., 2006; Su et al., 2009; Hou et al., 2016). The temperature of formation of 230 °C is compatible with the 150 – 250 °C range observed in the NCT and Youjiang Basin and the depth of formation is also similar (~5 km). Finally, the prediction of the thermodynamic model that Au was transported as \( \text{Au(HS)}^- \) complex in a H\(_2\)S buffered fluid under the prescribed \( P-T-X \) conditions matches the observations made in the Carlin Trend and Youjiang Basin. This further supports conclusions made in Selvaraja et al. (in review) that the Paulsens deposit is an Archean analogue of Phanerozoic sediment-hosted gold deposits.

The observation of the secondary inclusion generation, Type 2 FIAIs, forming after the Type 1 FIAIs is consistent with prediction of two phases of fluid flow by Fielding et al., (in review), with their later hydrothermal event occurring during the Capricorn Orogeny at ~1750 Ma (Johnson et al., 2013). Thus a cohesive model that explains the thermal evolution of the Wyloo Dome, and by extension, the Paulsens deposit involves initial lower temperature mineralisation (precipitating the gold, pyrite, alteration phases, \( Q(g) \) and Type 1 FIAIs) at the end of the Archaean (2400 Ma) followed by a period of quiescence and a reactivation of the fault system during the higher temperature and higher metamorphic grade Capicorn Orogeny at ~1750 Ma, where the \( Q(m) \) overgrew the \( Q(g) \). The latter contains the secondary Type 2 FIAIs. This second event is also where the peak lower greenschist facies of the Wyloo Dome were achieved (Rasmussen et al., 2005). It is possible that there are in fact two \( P-T \) loops, and that the second event is a total overprint of the first, instead of a continuation, however geological evidence for this theory is limited. The fact that the Paulsens deposit formed in what is considered to be a passive margin (Johnson et al., 2013) on its prograde metamorphic path, several hundred
million years before peak metamorphism supports the idea that Paulsens is unlikely to be similar to a classic orogenic gold deposit (Groves, 1993; 1998).

Thus, it is our contention, that although Paulsens may lack some key elements of Carlin style deposits, e.g. the lack of the mercury rich alteration phases and widespread decalcification, it is also sufficiently dissimilar to classic orogenic gold deposits to warrant some consideration as a unique deposit. It is perhaps best placed as an Archaean hybrid between the classic orogenic gold deposit, albeit at relatively low temperatures, and the Phanerozoic Carlin style deposits, which form on passive margins, commonly driven by distant thermal gradients.

7 Conclusions

The Paulsens gold deposit is an Archaean analogue of Phanerozoic sedimentary rock hosted gold deposits. Our observations demonstrate that low temperature (~230 °C) and moderate salinity (10 wt. % NaCl equivalent) fluids are associated with an economic gold deposit in sedimentary host rocks in the Archaean. Integration of thermometric observations with the results of the modelling exercise makes it clear that the source rock redox conditions can have a significant impact on the gold solubility and likely total gold mobilising capacity in this style of gold mineralisation. A possible class of deposits which are a hybrid between Carlin style and classic orogenic gold deposits may exist and we argue that it is possible that Paulsens sits in this continuum. Future work on sediment-hosted gold deposits should attempt to establish the baseline P-T-X conditions using careful fluid inclusion studies, with the addition of further work on cation, anion and metal contents of the inclusions and tie this to the thermodynamic conditions of the basin where the deposit is hosted.

8 Acknowledgements

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CHAPTER SIX

CONCLUSIONS

Introduction

Differentiating between sources and pathways from processes in the genesis of mineral systems is crucial in the effective application of the mineral systems framework to the study of ore forming processes. In the Archaean and Paleoproterozoic, this is even more problematic than in the Phanerozoic due to a complex pattern of overprinting relationships and multiple tectonic events, many of which are completely unrelated to the mineral forming event. The use of stable and radiogenic isotopes to resolve this problem has seen significant development and expansion as analytical techniques, both using wet chemistry and \textit{in situ} methods, have improved. Further, some of these techniques can be applied at the mineral scale in mineral deposits to identify fuzzy differences between mantle and crustally derived reservoirs (e.g. Pb-Pb, Re-Os systematics) but they cannot be tied to any individual crustal reservoir due to their secular evolution. Additionally, there are still significant limitations to most stable isotope systems as their values and relative fractionation patterns are affected by both source- and process-driven variation.

It is in this context that we have further developed both the theoretical basis and the empirical reality of the application of the time limited mass-independent fractionation of sulfur to the task of delineating sources and processes in Archaean and Paleoproterozoic mineral systems. The usage of MIF-S, the photochemically derived fractionation pattern of the minor isotopes of sulfur, $^{33}$S and $^{36}$S, opens an avenue to incontrovertibly separate the variation in isotopic composition driven by source reservoir properties from the ones generated by thermodynamic processes in fluid pathways that form mineral systems. Work presented in this thesis has
successfully demonstrated the application of the MIF-S to the study of mineral system genesis and evolution at multiple scales, creating inferences about processes ranging from the large-scale transfer of mass and fluid in the Earth in subduction zones (Chapter 2; Selvaraja et al., 2017) to those that are occurring within a single sedimentary unit (Chapters 4 and 5). Importantly, this thesis has also addressed the fundamental problem of establishing a MIF-S baseline concentration across different Archaean gold systems, and to constrain the previously unknown variability in the nature of the anomalies associated with different deposits (Chapter 3). Finally, as part of this work, I have compiled a database of the sedimentary sulfur isotope analyses published in the literature up to January 2017, so as to establish a baseline of atmospheric variation through time. This is basis from which we attempt to connect surficially derived Archaean sulfur sources with those observed in mineral deposits in the Archaean and Paleoproterozoic.

**Chapter Summaries and Original Scientific Implications**

**Chapter 2: ‘Anomalous sulfur isotopes trace volatile pathways in magmatic arcs’**

Applying multiple sulfur isotope analysis to gold mineralisation in a Paleoproterozoic continental arc and contemporaneous granitic batholiths in the vicinity of the deposit allowed us to draw some scientifically significant inferences about the processes governing fluid and mass transfer underneath continental arcs. There remains considerable uncertainty about the source of sulfur and metals in continental arcs as the observed concentrations and volumes of sulfur and metals in arc related magmatism and mineralisation is significantly higher than the mantle wedge can theoretically provide. The key problem to resolving this area of uncertainty is the shortage of chemically conservative tracers that are not easily redistributed by geological processes, thus preserving the initial isotopic of chemical ratios from their source reservoir.
The mass independent fractionation of sulfur in the Archaean that generated the $\Delta^{33}S$ and $\Delta^{36}S$ anomalies is thus a highly useful tracer in this environment as it is chemically conservative and is reflective of a single coherent isotopic reservoir, i.e. that of Archaean surficial rocks. However, in modern arcs the likelihood of cratonised Archaean supracrustal rocks being subducted is low. As such, we studied the Glenburgh arc, a Paleoproterozoic continental arc where the subduction of the Yilgarn Archaean craton underneath it has been established. The results of our study of sulfides associated with the mineralising process in the Glenburgh orogenic gold deposit and contemporaneous granites show a consistent $+\Delta^{33}S$ anomaly. Further, the $\delta^{34}S$ of both the mineralised and unmineralised granitic samples show a spread of $\sim8\%$. Combining these two datasets the following implications were drawn:

1) Sulfur from devolatilised Yilgarn Craton carbonaceous sediments that were subducted underneath the Glenburgh craton contributed significantly to the overall sulfur budget of the entire arc. Modelling presented in this work suggests that the minimum sedimentary sulfur contribution is $\sim15\%$ of the total volume of sulfur in the arc;

2) The second contributor to the sulfur budget of the arc rocks is Paleoproterozoic seawater, most likely sequestered as sulfate phases in the altered crust subducted as part of the downgoing slab;

3) A contribution from the mantle wedge cannot be ruled out however as MIF-S compositions of the mantle wedge relative to unaltered mafic crust cannot be differentiated;

4) The fact that large granitic batholiths had their sulfur isotopic budgets significantly and homogeneously changed suggests that the contribution of Archaean sulfur occurred while the melts were being generated in the upper mantle and lower crust.

These findings have significant implications for theories surrounding the relative contribution of oceanic crust vs sedimentary crust to the volatile and metal budget of the sub-arc mantle and
open the door for new metamorphic phase modelling and geochemical study of exhumed sub-arc mantle sections to clarify the exact relativities in their contributions in different arc environments. Further, these findings may have exploration implications on the mineral fertility of different continental arc segments, as a larger sediment load being subducted underneath a specific arc section may contribute to a larger volatile and metal flux into the sub-arc mantle, thus generating more/larger mineral deposits in the continental arc.

Chapter 3: ‘Atmospheric sulfur in the Orogenic Gold Deposits of the Archaean Yilgarn Craton’

The range of models which exist to explain the genetic process of Archaean orogenic gold deposits generally call for an exogenous source of sulfur, whether it is magmatic sulfur exsolved from magmatic intrusions or sulfur source from deep mantle fluids or sulfur sourced from metamorphic dewatering of supracrustal rocks. The different sources of sulfur called upon in these models, which must account for craton wide mineralising events such as those observed in the Yilgarn and Superior cratons, have significant implications for the transport pathways of fluids and processes leading to orogenic gold mineralisation. This is where the use of the chemically conservative $\Delta^{33}$S and $\Delta^{36}$S tracers is very insightful. As these anomalies, their magnitudes and importantly their relative rations (c.f. $\Delta^{33}$S/$\Delta^{36}$S ~ -0.9 to -1.5) are specific to individual Archaean surficial reservoirs of sulfur, the application of multiple sulfur isotope analysis to craton wide gold mineralising events can provide a new avenue of tackling the question of the source and pathway of sulfur in Archaean orogenic gold deposits.

The research we presented in this paper is based on the study of gold associated sulfide phases from 24 orogenic gold deposits which formed contemporaneously in the Archaean Yilgarn Craton at ~2660 Ma. The deposits spread throughout the various greenstone belts of the Yilgarn Craton are hosted in a variety of host rocks and range 4 orders of magnitude in size.
Remarkably, the results show that 23/24 orogenic gold deposits studied display an Archaean surficial sulfur derived $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ anomaly, with the additional constraint that most of the anomalies detected were $+\Delta^{33}\text{S}$ and $-\Delta^{36}\text{S}$. However, the magnitude of the anomalies were smaller than the database record of $\Delta^{33}\text{S}$ anomalies of the sedimentary rocks which were deposited in the Yilgarn Craton and globally in the 100 Ma prior to the mineralising event. This suggests that the sulfur in these deposits were unlikely to have been derived purely from sedimentary rocks and the more likely model is that it is derived from a mixture of sulfur sourced from supracrustal magmatic and sedimentary rocks. A secondary finding was that the larger deposits contained positive $\Delta^{33}\text{S}/\Delta^{36}\text{S}$ ratios and trend slopes which had not been observed in any previous studies of MIF-S. We invoke the role of the newly discovered high temperature $\text{S}_3$ ligand of Au, which has been suggested to create anomalous fractionation patterns to explain these $\Delta^{33}\text{S}/\Delta^{36}\text{S}$ ratios.

The implications of our work presented in this paper are twofold. Firstly, they validate the metamorphic devolatilisation model for the formation of Archaean orogenic gold deposits in the Yilgarn Craton and the argument that much of the gold in orogenic gold deposits may be sourced from carbonaceous sedimentary rocks, owing to their preservation of the $+\Delta^{33}\text{S}$ anomaly in the Archaean. Further, the new findings around the $\Delta^{33}\text{S}/\Delta^{36}\text{S}$ ratios may provide a pathway to understanding how deposits of dramatically different sizes could form during the same mineralising event, along the same structures. The stability of the $\text{S}_3$ anion at different temperatures and its metal scavenging efficiency may thus be crucial to the understanding of supergiant orogenic gold deposits. These findings have significant implications for the exploration of orogenic gold deposits, as it suggests that exploration efforts should be targeted at prospects where both the $\Delta^{33}\text{S}$ signature appears and positive/anti-correlated $\Delta^{33}\text{S}/\Delta^{36}\text{S}$ ratios are found.
Chapter 4: ‘Evidence of local sourcing of sulfur and gold in an Archaean sediment hosted gold deposit’

Sediment hosted gold deposits are relatively rare in the Precambrian record, however they are a significant component of modern economic gold production resources, both in the Carlin Trend in Nevada and in the Guizhou Trend and Youjiang Basin of China. The genetic model of this style of gold mineralisation has several variants, all of which call for some degree of crustal sulfur and gold input; however, the degree to which this is necessary is under some contention. The range in δ$^{34}$S values of gold hosting sulfides in these deposits is highly variable and has been interpreted by different workers as reflective of a variety of sulfur sources. In Phanerozoic deposits however, chemically conservative tracers can once again be applied to delineate some of the questions surrounding the source of sulfur and gold. We chose to study the Archaean Paulsens sediment hosted gold deposit, where the presence of Δ$^{33}$S anomalies allows us to connect the sulfur and gold sourced from the host sedimentary rocks to the gold deposit.

A combination of in situ sulfur isotope analysis of carefully constrained pyrite generations which host the bulk of the gold in the deposit and micro-chemical analyses of the same generations of pyrite proved that gold is hosted both in solution and as inclusions by a hydrothermally grown generation of pyrite which contains an abundance of a range of chalcophile trace elements (e.g. Ni, As, Cu, Zn, Pb etc.). This generation of pyrite also carries a positive Δ$^{33}$S signature of ~0.35‰, which is associated with the Archaean carbonaceous shales. Further analysis of diagenetic pyrite in the host Archaean shales of the deposit, distally from the mineralisation, shows that the diagenetic pyrites contain the same range of trace elements and up to ppm levels of gold with the same positive Δ$^{33}$S signature as observed in the hydrothermal pyrite generation which hosts the gold in the Paulsens deposit. However, some of the trace elements and sulfur could also be derived from intercalated extrusive magmatic.
rocks. These findings provide conclusive evidence that a moderately sized sediment hosted gold deposit can be formed from sulfur, gold and fluids generated from the local sedimentary host rocks.

The implications of these exciting findings are significant, as they provide a pathway to understanding the large variability in $\delta^{34}S$ values in Phanerozoic sediment hosted gold deposits. Applying the model we present for the formation of the Paulsens deposit to more modern environments, we can interpret the genesis of Carlin Trend and Guizhou/Youjiang Basin sediment hosted gold deposits under a new light. Accordingly, these systems would be deriving their sulfur and gold from a range of intercalated sedimentary and extrusive magmatic rocks, which would have widely different $\delta^{34}S$ values reflecting the range of biological and atmospheric processes occurring in the Phanerozoic atmosphere. The exploration implications of our findings in this study are also significant as they suggest that Archaean sedimentary units are highly prospective for sediment hosted gold deposits as contrasted with the current focus on Archaean greenstone belts for classic orogenic gold deposits.

Chapter 5: ‘P-T-X conditions and precipitation mechanism of gold mineralization at the Paulsens gold deposit’

In this paper, which is also focused on the Paulsens deposit, we unravelled the P-T conditions of the deposition of the gold and sulfides and constrained the chemical composition of the fluids that generated the deposit. Owing to the relative rarity of sediment hosted gold deposits and to the fact that the fluid inclusions in quartz associated with the mineralisation in these deposits are generally understudied, the inferred P-T-X conditions are poorly constrained. Having established in previous work that the Paulsens deposit is geochemically and texturally analogous to Phanerozoic sediment hosted gold deposits, in this work we demonstrate that the
P-T conditions of formation and chemical compositions of the fluid are quite different to those of Archaean orogenic gold deposits.

Through the combination of fluid inclusion microthermometry and RAMAN spectroscopy, we suggest that the gold was most likely precipitated from a ~10 wt. % NaCl equivalent salinity fluid, with low CO$_2$ and CH$_4$ contents but an equal CO$_2$:CH$_4$ molar ratio. Further, combining in situ sulfur isotope analysis in the $\Delta^{33}$S bearing pyrite and observation of $\delta^{34}$S fractionation during the deposition of the gold bearing pyrites were then fed into a fluid evolution model, which suggests that the redox conditions of the source rocks of the fluids, which were compositionally equivalent to the host rocks of the fluid, are the fundamental control on gold solubility in the fluid.

These findings support the thesis that Paulsens is has some differences to most Archaean orogenic gold deposits and as such its genetic model, as developed in our work, could be the basis of exploration for new types of gold mineral systems in reduced Archaean sedimentary rocks that form from basinal methanogenic fluids. They also further highlight the power of multiple sulfur isotope analysis to answer questions around thermodynamic processes occurring in a single mineral system.

**Scientific Contributions and Significance**

From the work I have presented in this thesis, it is clear that multiple sulfur isotope analysis, both on its own and in conjunction with other types of geochemical datasets, can be used to unravel significant areas of uncertainty in the study of mineral systems. The use of the MIF-S as a tracer for sulfur as it is sourced and then transported through the mineral system process is also not only limited to the Archaean. I have also demonstrated the utility of MIF-S as a tracer of processes and sources at multiple scales, ranging from the tectonic mass transfer in subduction zones, through craton wide mineralising events and down to the movement of fluid
and metals in a single basin. MIF-S is also critically useful in understanding mineral
equilibrium in deposits where the signature is preserved, as we have demonstrated in the
Paulsens deposit. Finally, I have proven that gold deposits in multiple environments and at
multiple scales can derive their sulfur from supracrustal sedimentary rocks, and that MIF-S is
an effective way of determining this contribution. The conclusions presented in my research
should hopefully convince readers that multiple sulfur isotope analysis should be integrated
into the workflow of mineral systems research in all Archaean and Proterozoic mineral
deposits. This tracer is of great use in understanding the interplay between source and process
in the formation of mineral deposits within a mineral system framework.

Recommendations for Future Work

A range of future work can be drawn out of my thesis, which split into several segments:

1) Further experimental work on the sulfur exsolution of melting of sedimentary rocks at
subduction zone P-T conditions and the transfer of metals and sulfur out of these melts
into the mantle wedge are now necessary to demonstrate if the model we propose for
the addition of sulfur into the mantle wedge under subduction zones is in fact possible.
Additional metamorphic petrology modelling of phase transitions in sedimentary rocks
undergoing transition through subduction geotherms may also aid in this cause;

2) Further multiple sulfur isotope studies of Paleoproterozoic mineral deposits which sit
on top of or are reworked Archaean crust to see if the processes which lead to the
transfer of sulfur and metals from the Archaean to the Proterozoic are broader than pure
subduction mass transfer driven processes, and if these processes are widespread
through the geological record;

3) An expansion of the orogenic gold MIF-S record through time to include the deposits
which formed in the Superior Craton, the Amazon Craton and the West African Craton
to investigate if the metamorphic devolatilisation of supracrustal rock model presented here with data from the Yilgarn Craton can be exported consistently to other Archaean systems. This would have the added effect of confirming if my thesis that orogenic gold deposits may be recorders of secular evolution of the earth’s crust;

4) Further experimental investigation of the effect of the S$^{3-}$ anion sulfur isotope fractionation patterns, specifically of $^{36}$S is highly pertinent; a clearer idea of these effects may help us understand aspects of the global sulfur isotope record which remain cryptic;

5) A continuous expansion of the sedimentary sulfur isotope record through time, as it is clear from the database I have compiled that the Yilgarn and the sedimentary units it represents across the Neoarchaean are relatively understudied compared with many Archaean cratons around the world. This would have the added effect of more clearly constraining the crustal reservoir signature in MIF-S space of the Yilgarn Craton, which was then recycled into orogenic gold deposits and other mineral systems that may cluster along its margins.

I also suggest that a review paper be written about MIF-S in mineral systems within the next 5 years, as there has been a dramatic growth in the generation of multiple sulfur isotope data from Archaean and Proterozoic mineral systems during the course of my PhD and it would be necessary that a substantial reinterpretation of previous models of sulfur recycling in mineral systems be undertaken to synthesise the range of new findings.
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Gold mineralised sulfides in shales and quartz veins

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**Wyloo Dome**

- Hardey Formation, Wyloo Dome

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### Appendix 1

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