Sulphur and lead isotopes of gold and base metal mineralisation of the Yerrida and Bryah Basins – mineralisation characteristics and implications for exploration.

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INTRODUCTION

The Bryah Basin is well endowed and has been mined for a number of commodities including copper and gold. Less mineralisation has been located in the Yerrida Basin. However, across both basins most deposits are small in size, with the DeGrussa Cu-Au VHMS only substantial deposit of its kind discovered in the district. Despite a renewed interest in the area, and an abundance of exploration, another deposit of significant size is yet to be located.

The Yerrida, Bryah and Padbury Basins form the eastern part of the Capricorn Orogen and are relatively understudied in comparison with the western parts. The Yerrida/Bryah Group sedimentary rocks, along with mineralisation at the DeGrussa and Horseshoe Lights deposits, were formed in an extensional basin setting during the Glenburgh Orogeny (2005-1970Ma). Recent geochronology by Hawke et al. (2015) assisted in constraining stratigraphic and mineralising events of the Paleoproterozoic Yerrida, and Bryah Groups with the regional orogenic events.
Formation indicates that basin sediments were deposited on a shallow evaporitic margin as evidenced fromstromatolites, algal mats and evaporite textures in the Bubble Well Member (El Tabakh et al., 1999, Pirajno et al., 2004). Deepening of the Yerrida Basin resulted in deposition of the Johnson Cairn Formation, including initial volcanism in an equivalent modern day tectonic setting to that of the Red Sea or Guaymas Basin in the Gulf of Carpentaria (Fisher and Becker, 1991). Mafic rocks occurring within the Windplain subgroup are alkalic and are most similar to rocks found in continental rift settings. The overlying Mooloogool subgroup comprises siliciclastic sedimentary rocks of the Thaduna and Doolganna Formations, the mafic Killara Formation, and the black shaley-rich Maralou Formation. Sedimentary rocks of the Thaduna and Doolganna Formations are intruded by volcanic rocks of the Killara Formation, which comprise low Ti subalkaline intrusive and extrusive rocks as well as high-Fe, high-Mg tholeiitic to calc-alkaline basalts and basaltic andesites emplaced as subaerial and subaqueous lava flows, intrusive sheets, sills and dykes (Pirajno et al., 2000). Rocks of the Mooloogool subgroup are not identified east of the Gascoyne River along the northern Bryah Basin margin and are not deposited in the DeGrussa area although are regionally extensive.

Rocks of the Thaduna Formation host fault-controlled epigenetic copper deposits including the Thaduna Copper Deposit. The copper lode follows the northwest trending Thaduna Fault with the majority of the lode consisting of sheared and brecciated sedimentary rock containing abundant hydrothermal graphite as a matrix to quartz and carbonate minerals. Mineralisation is dominated by copper oxide ore (namely malachite, azurite, chrysocolla, cuprite and chalcocite) with chalcopyrite, bornite and chalcocite forming primary mineralisation at depth under both the Thaduna and Green Dragon pits (Reid, 2013).

The Bryah Group

The Bryah Basin represents a 10km thick sequence of intrusive and extrusive volcanic rocks, volcanoclastic rocks and sedimentary rocks deposited between 2027 and 2011Ma (Pirajno et al., 2000, Hawke, 2015) which host significant amounts of gold and copper mineralisation. It consists of the Karalundi, Narracoota, Ravelstone and Horseshoe Formations. With the exception of the volcanic Narracoota Formation, all other formations consist of siliciclastic shales, siltstones and sandstone sequences, with prominent iron formations hosting manganese deposits within the Horseshoe Formation. The Narracoota Formation comprises peridotitic and high-Mg basalt, mafic volcanioclastic, pillow basalts, mafic intrusive rocks and mafic-ultramafic schists, interfingeriing with the Karalundi and Ravelstone Formations. Stratigraphy is often cross cut by late mafic dykes and sills of unknown age. The majority of the Bryah Group is affected by low to medium grade greenschist facies regional metamorphism as well as a retrogressive hydrothermal greenschist facies metamorphism (Pirajno et al., 2000).

The Bryah Group is in faulted contact with the Yarralweelor Gneiss Complex, the Marymia Inlier, and the Palaeoproterozoic Yerrida Group. The Goodin Fault, a north easterly trending, high-angle reverse fault, marks the divide between the Bryah Group and the Yerrida Group (Pirajno et al., 2000, Dentith et al., 2014). However, work by Jeffery (2013) indicates the contact as unconformable and in keeping with original geological interpretations of Gee (1987) in which the Mooloogool subgroup of the Yerrida Basin is a lateral equivalent of the Bryah Group.

The DeGrussa Cu-Au VHMS deposit is hosted by an interfingering sequence of sedimentary and mafic volcanic rocks of time equivalent to the Karalundi Formation and Narracoota Formation of the Bryah Group. DeGrussa host sedimentary rocks lie para-conformably on top of the Johnson Cairn Formation. These rocks also host the Red Bore and Monty VHMS deposits. The similar, but smaller Horseshoe Lights Cu-Au massive sulphide deposit is associated with felsic volcanic rocks and located stratigraphically at the upper contact of the Narracoota Formation with the Ravelstone Formation. Ultramafic, sheared-hosted copper mineralisation of the Forrest-Wodger deposit is hosted within ultramafic rocks of the Narracoota Formation.

Deformation in a southwest to northeast direction (Pirajno et al., 2000), related to closure of the late Paleoproterozoic basins during the Capricorn Orogeny is likely to have caused faulting and folding across the region of which multiple mineralising events are associated. Widespread pyrite related epigenetic/orogenic gold mineralisation is most likely associated dominantly with D4 deformation during the Capricorn Orogeny. Deposits of this style are located at Fortnum, Cassidy, Peak Hill/Fiveays, Labouchere, Horseshoe Lights (overprinting primary copper sulphide mineralisation) and Plutonic (within the Archean Marymia Inlier).

METHODS

Samples for S isotopes on mineralisation were collected from the DeGrussa and C1 lenses (VHMS), Horseshoe Lights (VHMS), Fortnum, Cassidy/Horseshoe (Orogenic) and Thaduna (Epithermal). Samples were collected petrographically for purity before drilling. Approximately 30μg of sulphide was collected by carefully drilling out the sulphides from the rock using a micro drill with a 300-micron diamond bit. Samples were analysed using flash combustion isotope ratio mass spectrometry (varioPYRO cube coupled to Isoprime100 mass spectrometer) at the Central Science Laboratory, University of Tasmania (Hawke, 2017).

Pb isotopes were constrained using Re-Os geochronology from the DeGrussa deposit. Pb isotopes on galena and pyrite were analysed as described in Hawke et al. (2015). Two galena-rich samples from the DeGrussa Conductor 5 ore lenses as well as three pyrite samples from Conductor 1 and Conductor 4 ore lens were analysed by LA-ICPMS at the University of Tasmania. Pb isotopes analysed by previous workers on a Cumming and Richards (1975) growth curve, were reprocessed using a Stacey and Kramers (1975) growth curve.

SULPHUR ISOTOPES

Comparison of δ 34 S values for base metal and gold deposits across the Bryah and Yerrida groups are shown in Figure 2.

DeGrussa Cu-Au VHMS

The DeGrussa deposit, contains δ 34 S values for pyrite of +0.66 to +9.82‰, chalcopyrite between +0.25 and 6.31‰, pyrrhotite between +0.93 and +3.31‰ and sphalerite between +1.22 and +5.3‰.

The pyrite, pyrrhotite, chalcopyrite dominant mineralogy of the DeGrussa deposit suggests high temperatures for deposition (pyrite at >350°C, chalcopyrite at 270-350°C (Huston and Large, 1989)).
The lack of sulphate minerals in the ore, but the presence of peripheral jasper, suggests that DeGrussa either formed in a silled reduced oceanic sub-basin with an oxic top layer, or from low Ba, highly reduced, fluids that were emplaced into a suboxic-oxic water column. The latter scenario produces barite-poor Cu-Zn deposits in modern mid-ocean ridge basins. Hydrographic conditions of the deep basin water were Fe-rich and sulfate free, leading to the high content of Fe-rich minerals (pyrite, minnesotaite, stilpnomelane, Fe-Mg chlorite) and the lack of a sulfate-bearing exhalite. The range of δ34S values for the DeGrussa sulfides (+0.3 to +10.5‰) with a peak at 1.0 – 3.0‰ (reflected in chalcopyrite (δ34S = +0.3 to +6.3‰), pyrrhotite (+0.9 and +3.3‰) and sphalerite (+1.2 and +3.5‰)) suggests that the best interpretation is for a uniform δ34S of dominantly igneous-sourced sulphur, mixed with minor seawater reduced sulphate.

A barite vein, in the footwall of the DeGrussa stratigraphy has an average δ34S value of +38.1‰ (n = 2). This sits close to the pyrite δ34S curve provided by Kump (2012), but is almost twice as heavy as the average seawater sulphate curve provided by Farquhar et al. (2010) (Fig. 3). The Δ34S seawater-sulphate – ore sulphate between the barite vein and the DeGrussa sulphide median is +29.3‰. The only comparable value to the heavy δ34S values of the barite vein are those of pyrite at Horseshoe Lights. It may be that the barite vein has no association with δ34S seawater compositions, and that it reflects an unknown heavy δ34S source.

**Horseshoe Lights Cu-Au VHMS**

Two different sulphur populations were identified. The first population contains δ34S values of +7.3 to 12.4‰. The second contains two analyses which have abnormally heavy values of +44.7 to +45.8‰ associated with a silicic/chert rich ‘sandy’ ore (Gillies, 1988).

Sulfide textures included massive pyrite sometimes with chalcopyrite rims in a cherty matrix with consistently heavy δ34S values of +44.7 to +45.8‰; irregular and angular-subangular pyrites (δ34S +12.2 to +12.3‰) in quartz-muscovite-epidote-schist with chalcopyrite and chalcocite located in pressure shadows. Horseshoe Lights end member values of +45.0‰ provide evidence of a 34S-enriched source of seawater sulphate or a closed system mode of sulphur fractionation, capable of isolating extremely 34S enriched H2S. On the basis of high temperatures needed to form the chalcopyrite-pyrite-gold assemblage, surface weathering processes can be discounted for Horseshoe Lights.

**Thaduna Copper Deposit**

Sulphide textures include massive chalcopyrite, carbonate ± quartz vein hosted chalcopyrite, blyb boreite associated with pervasive carbonate alteration with chalcopyrite, and pyrite stringers. Chalcocite is in association with blybore and chalcopyrite, with all three considered primary (Reid, 2013). δ34S values for 16 samples are constrained between +18.6 and +26.7‰. Pyrite is rare but where present it contains heavier δ34S values (above +23.5‰; n = 2; mean = +24.3‰) than the main ore bearing chalcopyrite (δ34S values between +18.6 and +23.5‰; n = 7; mean = 20.7‰).

Mobilisation of saline fluids derived from the Bubble Well Member along the faults by hydrothermal circulation may have transported the Cu. The host rocks for Thaduna mineralisation are pre- to syn- DeGrussa host rock deposition and mineralisation (2.1 - 2.0 Ga), and the estimated age of Thaduna mineralisation is 1475 ±50 Ma (Hawke et al., 2015). At this time, the δ34S of ocean sea water was approximately +20 to +25‰ (Farquhar et al., 2010).

The large range (+18.6 and +26.7‰) and characteristic very heavy δ34S values of the Thaduna pyrite-chalcopyrite-chalcocite-borneite mineralisation are very likely to have required a large component of a sea water source for sulphur.

**Fortnum and Cassidy (Orogenic Gold)**

Eight samples were analysed from Fortnum (Yarlarweelor and Starlight) and three from Cassidy/Horseshoe. Both deposits have similar geological formation described as ‘orogenic’ by Groves (1996) and are hosted by ultramafic-mafic rocks of the Narracoota Formation. Pyrite at Fortnum and Cassidy is euhedral, varying from millimetres to centimetres both in quartz-carbonate veins and in the surrounding wall rock.

The Fortnum deposits (Yarlarweelor and Starlight) and Cassidy have δ34S values between +0.1 and +8.4‰ (n=12; mean = +3.6‰). Fortnum is at the lighter end with δ34S values between +0.1 and +7.6‰ with an overlap of Cassidy values of +2.3 to +8.4‰. Light δ34S values are found in association with quartz-carbonate veins (0 to +3.3‰), while smaller disseminated pyrites have heavier values (+4.1 to 8.4‰). The Fortnum and Cassidy deposits are highly deformed and much younger than the VHMS mineralisation (920±50Ma and 1910±50 Ma respectively). The Fortnum and Cassidy δ34S values are comparable to igneous values and could represent leaching of the host narracoota Formation rocks (estimated at 0 to +1% similar to estimated values of the DeGrussa host rock sequence)
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or Archean basement sulphur. As with DeGrussa, the heavy tail may indicate mixing with $\delta^{34}S$ values of host rocks which have preserved the seawater sulphate at the time of their deposition (c. 2.0 Ga, and $\delta^{34}S$ of seawater of +10 to +18 %).

**PB ISOTOPES**

Re-examination of the Pb isotopic evolution models for this area and the Capricorn Orogen suggests that the model of Stacey and Kramers (1975) is more appropriate than Cumming and Richards (1975). The latter led to a 150 million year offset in ages. The former model led to revised model ages for mineralisation (Hawke et al., 2015) which coincide with major regional orogenic events. Pb isotope values were constrained by comparing the Pb isotope (pyrite and galena) and Re-Os (molybdenite) geochronology of DeGrussa mineralisation. Re-Os geochronology of molybdenite resulted in ages of 2027 ± 7 Ma and 2011 ± 7 Ma for mineralisation, similar and within error to Pb-Pb model ages for galena of 2060 ± 50 Ma and 2075 ± 50 Ma (Hawke et al., 2015).

![Figure 4. Pb isotopes for DeGrussa pyrite and galena with higher $^{238}\text{U}/^{204}\text{Pb}$ (µ) in the source of the mineralizing fluids.](image)

The Pb isotopic compositions of the DeGrussa mineralization plot above the average growth curve of Stacey and Kramers (1975) implying higher $^{238}\text{U}/^{204}\text{Pb}$ (µ) in the source of the mineralizing fluids. High µ values such as these are typically interpreted to represent Pb source from upper crustal sedimentary rocks (Zartman and Doe, 1981) rather than the average crust in the models discussed above.

![Figure 5. Comparison of Pb isotopic data for regional mineralisation across the Bryah and Yerrida Groups. Data is plotted with respect to the Stacey and Kramers (1975) growth curves.](image)

Comparison with East Capricorn Regional Pb isotopes

Magellan Pb deposit and lead in carbonates from the ‘Sweetwaters Well Member’ in the Earaheedy basin have Pb isotopic compositions which plot on a high µ (10.8) growth curve of Stacey and Kramers (1975) indicating a crustal component in the source of the mineralising fluids. Gold deposits of Nathans, Peak Hill and Labouchere (Dyer, 1991; Thornett, 1995) also conform to the high µ (10.8) growth curve indicating high µ is a characteristic of the district (Fig. 5).

The Fortnum gold and Thaduna Cu deposits are coincident with the Stacey and Kramers (1975) growth curve with µ values of ~ 9.75 to 10.0 respectively. Lead occurrences in the Frem Formation (Earaheedy Basin) also conform to a Stacey and Kramers (1975) µ ~10 growth curve as does the Horseshoe Lights (Windh, 1992) VHMS deposit (µ ~10).

The Plutonic gold deposit formed from different pulses of mineralisation, largely conform to the $\mu = 9.75$ growth curve for part of the mineralisation that is relatively radiogenic (Palaeoproterozoic model ages), but display high µ ≥ 10.8 for the part of the mineralisation with the least radiogenic Pb isotopes (Archean model ages).

**Comparison with Western Australia Pb isotopes**

The oldest VHMS deposit in Western Australia are those of the Panorama district in the Pilbara (model ages of 3262-3084Ma using Cumming and Richards (1975) growth curve) (Vearncombe et al., 1995, Brauhart, 1999). The Panorama district has Pb isotope ratios comparable to Stacey and Kramers (1975) high µ values (~10.8) similar to the Bryah. Similarly, the Golden Grove VHMS deposit (Browning et al., 1987) in the Murchison/Yoouamni Terrane of the Yilgarn, has Pb isotopes which plot on a high µ (~14) Stacey and Kramers (1975) growth curve. Kalgoorlie Super pit (Steadman et al., 2015) values largely conform to the high ~10.8 growth curve, with a spread of values to ~9.75. Mineralisation of the Patterson Orogen forms a Pb isotope array at 1000Ma with µ values between 9.75 and 10.8 (Stacey and Kramers, 1975) (Fig. 5).

The similar Pb isotopes across Western Australia are likely to represent the same Archean source of sulphur, and the comparison with deposits of the Bryah group suggest that a similar Archean Pb source was active during formation of the DeGrussa deposit. The exception for Western Australian VHMS deposits is Teutonic Bore (Vaasjoki, 1985) in the Eastern Goldfields Province. Teutonic Bore displays Pb isotopes which are lower than the average Pb growth curve (µ ~9.75 Stacey and Kramers (1975)). Lower Pb ratios in the Horseshoe Lights etc deposits indicates that a second source of lead, probably sedimentary, has affected the Pb results, possibly in much the same way as the S isotopes.

**CONCLUSIONS**

Sulphur isotope data does not clearly distinguish the DeGrussa deposit from the orogenic gold deposits, and regional sulphur isotopes are best used to determine source of sulphur and mineralising processes, rather than the type of deposit the mineralisation is from. The heavier $\delta^{34}S$ values at DeGrussa, also similar to those seen at Horseshoe Lights, infer interaction of hydrothermal sulphur with sea water sulphur at the sea floor interface, and may indicate the unique depositional environment of the VHMS deposits in the district.

High µ values such as those found across the Bryah and Yerrida Groups are typically interpreted to represent Pb sourced from upper crustal sedimentary rocks and is typical of lead and ore deposits across the Capricorn Orogen as well as the Yilgarn and Pilbara Cratons. Hence it is likely that Pb was derived from leaching of Archean basement and sedimentary host rocks in the Bryah Basin.
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Used as an exploration indicator, there is no unequivocal value at which a DeGrussa-style VHMS can be distinguished from the orogenic gold deposits of Fortnum and Cassidy. It is unclear whether obtaining δ34S for regional sulphides of unknown affiliation would enhance prospectivity ranking in the basin on its own. However, combined with other geological evidence, such as rock type, Pb isotope composition, and association with tectonic event they may provide a better indication. Further work, however, should be done around the Fortnum gold deposits and the relationship of gold bearing cherts to possible VHMS mineralisation as resetting of pyrite Pb isotope ages may be possible in this region.

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