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Fe-isotope fractionation in magmatic-hydrothermal mineral deposits: a case study from the Renison Sn-W deposit, Tasmania

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ABSTRACT

We present 50 new iron isotopic analyses of source granite and mineral separates from the Renison tin deposit in north western Tasmania. The aim of the study is to characterise the composition of minerals within a tin deposit associated with a reduced, S-type magma. We have analysed bulk samples of granite, and separates of pyrrhotite, pyrite, arsenopyrite, magnetite, chalcopyrite and siderite by multi-collector inductively coupled mass spectrometry. The isotopic compositions of mineral separates are consistent with theoretical predictions of equilibrium fractionation based on Mössbauer spectroscopy and other parametric calculations. Mineral-mineral pairs yield temperatures of formation that are in agreement with prior detailed fluid inclusion studies, but are spatially inconsistent with declining fluid temperatures with distance from the causative intrusion, limiting the use of Fe isotopes as a potential geothermometer, at least in this case. Comparison of our data with published data from other deposits clearly demonstrates that pyrite, magnetite and chalcopyrite from the hottest ore fluids (>300-400°C) at Renison are isotopically heavier than minerals sampled from a deposit formed at similar temperatures, but associated with a more oxidised and less differentiated intrusion.

Keywords: iron isotopes, iron isotope fractionation, Multi Collector ICPMS, magmatic-hydrothermal minerals

1. INTRODUCTION

The use of Fe-isotope variation in tracking redox processes in Earth systems has resulted in a steadily increasing body of literature in the last decade. Thanks to the development of sensitive analytical equipment, it is now possible to characterise the isotopic composition of igneous rocks and minerals, formed from processes that have fractionated iron isotopes at high temperatures. The iron isotope literature now reports the composition of an increasingly diverse array of igneous systems. These include; mantle xenoliths (eg Williams et al., 2002), ocean basalts (eg Teng et al., 2008; Teng et al., 2013), mafic volcanics (eg Schuessler et al., 2008), dolerites (Sossi et al., 2012) and granites (eg Poitrasson and Freydier, 2005, Telus et al., 2012)

Researchers investigating the fractionation of magmas (eg Schuessler et al., 2008; Teng et al., 2008; Sossi et al., 2012) have found that the most evolved differentiates often have heavy iron isotope enriched compositions. These studies demonstrate measurable Fe-
isotopic fractionation at magmatic temperatures. Although fractional crystallisation is now
clearly demonstrated as one mechanism that drives felsic differentiates towards heavy iron
isotopic compositions, it has also been proposed by Poitrasson and Freydier, (2005) and
Heimann et al., (2008) that fluid exsolution from cooling siliceous plutons (>70% SiO₂) may
also lead to heavy isotopic enrichment; discharged Cl-bearing fluids preferentially stripped
these granites of isotopically light Fe²⁺ driving the residual magmas to heavy iron isotope
composition. A third mechanism of fractionating Fe isotopes, thermal diffusion, is
demonstrated in the experiment of Huang et al (2009), who melted the geostandard AGV-1
(a homogenous andesite powder) under hydrous conditions, with a steady temperature
gradient between 350 and 950°C. The run products showed that significant Fe-isotope
fractionation of 2.8‰ had occurred, with the hotter region being isotopically lighter than the
cold end.

The “light fluid” hypothesis is supported for some systems by the results from combined Fe
and Zn isotopic studies (Telus et al., 2012) which demonstrate a correlation between high
⁶⁶Zn and high ⁵⁶Fe in pegmatites and some granitic rocks. The Zn²⁺ ion, being divalent
shows similar geochemical behaviour to Fe²⁺, but is unaffected by redox processes being
monovalent. Zn is highly mobile in chloride-bearing hydrothermal fluids, and studies (eg
Gagnevin et al., 2012 and references therein) infer that kinetic Raleigh fractionation is one
explanation for isotopic evolution of Zn from light to heavy (ie positive δ⁶⁶Zn) isotopic
compositions in cooling fluids. Telus et al (2012) analysed pegmatites from the Black Hills in
Dakota, where the reaction between exsolved fluids and reacted country rock were well
documented. The authors used thermodynamic modelling to show that fractional
crystallisation alone cannot account for the large dispersion of Zn/Fe ratios observed in the
samples and concluded that fluid exsolution does control iron isotope fractionation to some
extent in magmatic processes.

It has long been recognised that cooling and crystallising magmas may exsolve chloride-rich,
metal-bearing fluids that form economic ore deposits (eg Lindgren, 1906; Candela and
Holland 1984; Eugster 1985). However important questions still await resolution. In particular
how can we link key variables that govern the evolution of the magmas that generate these
ore fluids to characteristics of the ore minerals themselves? One such key variable is
oxidation state. In this study we demonstrate that there is a strong relationship between the
iron isotope systematics of cooling plutons and the iron isotope composition of associated
hydrothermal sulphide ores. Furthermore it appears that this Fe-isotopic signature is
particularly a function of the oxidation state of the magma.

Magmatic-hydrothermal fluids that are released form cooling and crystallising plutons may
carry high concentrations of economic metals such as Cu, Au, Mo, Sn and W (eg Heinrich
1990; Simon et al., 2004; Webster 2004; Cerny et al., 2005; Williams-Jones and Heinrich,
2005; Zajacz et al., 2007; Audetat et al., 2008; Frank et al., 2011;). Suites of economic
metals that occur together in magmatic-hydrothermal deposits have a well-known
association with magma oxidation state (Blevin and Chappell 1992; Blevin 2004; Cerny et
al., 2005; Vigneresse 2007). Tin and Sn-W deposits are often associated with weakly to
strongly peraluminous, reduced or ilmenite-series granites using the terminology of Ishihara
(1977), whilst Cu-Au±Mo±W are associated with oxidised, magnetite-series intermediate to
felsic intrusives often found in magmatic arc terranes (Cerny et al., 2005; Seedorf et al.,
2005; Sillitoe 2010 and references therein).
To date, published case studies of iron isotope systematics in magmatic-hydrothermal deposits (e.g., Graham et al., 2004; Li et al., 2010) do not have results for both magmatic suites and associated Fe-bearing ore minerals. In this paper, we present 50 iron isotopic compositions of bulk granite (*sensu stricto*) and mineral separates from different structural and stratigraphic positions in the Renison Sn-W deposit. The Renison deposit is a world-class example of a stratabound carbonate replacement Sn deposit associated with reduced S-type granitic intrusion, and therefore represents one end of the magma oxidation state spectrum. Our results are compared to theoretical predictions for equilibrium mineral-mineral fractionation. We also compare our results to published data from the Xinqiao Cu-Fe-S-Au skarn, associated with a quartz-monzonodiorite stock (Wang et al., 2011), to examine the effect of magma oxidation state on the isotopic composition of fluids that later deposited the magmatic-hydrothermal minerals. Our results contribute a large new empirical dataset to a rapidly expanding field of research, and further illustrate the complex interplay of processes that fractionate iron isotopes.

2. GEOLOGY

2.1. Regional Geology

The geological setting and detailed descriptions of the Renison Sn-W deposit have been described by many authors (e.g., Patterson et al., 1981; Kitto, 1994; Bajwah et al., 1995; Walshe et al., 1996; Walshe et al., 2011), covering decades of research, and is summarised below.

The deposit is located in the Dundas Region in western Tasmania (Patterson et al., 1981). The Dundas region comprises a linear basin of Late Proterozoic to Early Paleozoic sedimentary sequences, allochthonous ultramafic to mafic sequences, and the Cambrian Mt Read Volcanics (Patterson et al., 1981). The Trough is bounded to the northwest and southeast by blocks of Proterozoic metasediments (Fig. 1).

The oldest sedimentary sequence in the mine area is the Upper Neoproterozoic Success Creek Group (Fig. 1). The Success Creek Group comprises shallow water to subaerial siliceous clastic sediments, shales and dolostones (Patterson et al., 1981). The Crimson Creek Formation overlies and is in faulted contact with the Success Creek Group (Patterson et al., 1981). The Crimson Creek formation comprises a shelf sequence of siltstones, shales and volcanioclastics with minor dolostones (Patterson et al., 1981; Kitto, 1994). The contact between the Success Creek Group and Crimson Creek Formation is marked by the Red Rock Member (Fig. 2), a variably hematitic unit comprising siltstones and volcanioclastics, conglomerates and greywackes, cherty ironstones and thin dolostones (Patterson et al., 1981; Kitto, 1994). Strata comprising the upper Success Creek Group and lower Crimson Creek Formation are termed the Mine Sequence by mine geologists.

Polyphase folding in Middle Devonian resulted in north-west trending open folding (Patterson et al., 1981; Kitto, 1994) Syn- to post kinematic I and S-type granites intruded at around 390 Ma, during the later stages of the Taberabberan orogeny (Black et al., 2005).

2.1. Deposit Geology

The Renison deposit is controlled by the NW striking, normal Federal Bassett Fault (‘FBF’), located on the north east limb of a south east plunging anticline (Fig. 1,2). Intrusion of the
Renison granite caused brittle fracturing and normal fault reactivation in the intruded Late Neoproterozoic Success Creek and Crimson Creek Formations. This allowed magmatic fluids accumulated in a probable cupola structure on the upper surface of the cooling Meredith Granite pluton, to be tapped and ascend along the FBF and invade the sedimentary strata depositing base metal and tin ores, as a result of replacement of carbonate units. Stratabound, massive pyrrhotite-cassiterite with minor pyrite and base metals (eg, galena sphalerite chalcopyrite) replaced 3 dolomite horizons within the Success Creek Group and Crimson Creek Formation (Fig. 2). Although the bulk of the mineralisation is replacement style, fault controlled veins are also economically exploited. Faulted blocks of the Mine Sequence are mined within the FBF and are referred to as 'Stratafault' Ore.

2.2. The Renison Granite

The Renison granite is a fractionated, shallow (2-4 km) S-type intrusion, ranging in composition from adamellite to alkali-feldspar granite (Sawka et al., 1990; Bajwah et al., 1995; Black et al., 2005). Interpretation of gravity data by Richardson and Leaman (1989, referenced in Kitto, 1994) shows that the Renison Granite forms part of the larger Meredith Pluton which includes the Heemskirk intrusion to the west and Granite Tor to the east (Kitto, 1994; Fig. 1).

The Renison granite is a grey, medium to coarse grained biotite granite (Fig. 4). Bajwah et al. (1995) describes four texturally distinct types; K-feldspar porphyry, fine-grained porphyritic granite, fine grained non-porphyritic granite and medium to coarse grained equigranular granite. Unaltered granite comprises quartz, K-feldspar, plagioclase and biotite, with ilmenite, monazite, apatite, zircon, fluorite, topaz, tourmaline and rare allanite as accessory phases. Phenocrysts in the porphyritic varieties are either quartz or K-feldspar up to 1 cm across. Plagioclase phenocrysts are recorded in the quartz-feldspar porphyry. These types are interpreted, on the basis of geochemistry and petrography (Bajwah et al., 1995; Walshe et al., 2011) to be related by fractional crystallisation.

The Renison granite has been variably albitised, sericitised and tourmalinised via boron-fluorine metasomatism from hydrothermal fluids (Patterson et al., 1981; Kitto, 1994; Bajwah et al., 1995).

2.3. Mineralogy and paragenesis

Researchers (eg Patterson et al., 1981; Kitto, 1994) have documented several different paragenetic stages. We use the interpretation and terminology of Kitto (1994), which places alteration and paragenesis in a temporal context of structural evolution and declining fluid temperatures, and can be summarised as follows:

1) Oxide – Silicate stage

Rare assemblages of carbonate and magnetite may represent the earliest magmatic fluid (Kitto, 1994; Fig. 5), followed by quartz-arsenopyrite ± cassiterite ± wolframite ± pyrrhotite-pyrite-chalcopyrite-ilmenite-rutile (Fig. 6C)
This stage is interpreted by Kitto (1994) to be coincident with the onset of normal-dextral movement along the FBF system. Fluid inclusion studies showed minimum formation temperatures of 340-420°C, and salinity varied between 8-12 equivalent wt% NaCl.

2) **Main Sulphide stage**

This stage is the dominant carbonate replacement stage and is characterised by pyrrhotite- cassiterite ± arsenopyrite ± pyrite ± quartz-fluorite (Fig 6B,C). Base metal phases such as chalcopyrite-sphalerite-galena-bismuth-argenite-chlorite may also be present, typically interstitial to pyrrhotite-arsenopyrite. Chalcopyrite is more common within the FBF where Cu grades of up to 0.3% occur. These stratabound bodies are interpreted to have been deposited in dilational zones along structures in the FBF caused by dextral wrench reactivation. This stage is recognised in thin section by brittle deformation of arsenopyrite, with fractures infilled by chalcopyrite and pyrrhotite (Fig. 6F). Fluid inclusion studies results in minimum formation temperatures of 170-300°C. and salinity varied between 0-14 equivalent wt% NaCl.

3) **Late Base Metal Stage**

Crustiform rhodocrosite-lined veins are characteristic of this stage. Vein mineralogy comprises sphalerite- galena- quartz- pyrrhotite- pyrite-chalcopyrite-fluorite-calcite-chlorite. The interpretation of this stage being associated with brittle reactivation is based on textural features such as syntactical crack-seal veins and microfolding (Kitto, 1994 and references therein). Fluid inclusion studies record lower temperatures (150° -210°C) and bimodal salinities (2 or 10wt%NaCl), suggesting mixing of magmatic-hydrothermal fluids with meteoric groundwaters (Patterson et al., 1981; Kitto, 1994; Walshe et al., 1996).

4) **Carbonate Stage**

Dolomite, fluorite, clear quartz, chalcopyrite and calcite comprise a carbonate-dominant mineral assemblage infilling brecciated sediments or vugs and fault cavities. A hydrothermal magnesian siderite halo surrounds the stratabound ore surfaces (Patterson 1981; Kitto, 1994), and is interpreted to form via dissolution of the host dolomites by magmatic fluid. The limit of the reaction front is usually very sharply defined as an abrupt transition to largely unaltered sedimentary rock (Fig. 6A,D).

Sulfur isotope, oxygen and hydrogen isotope studies have been carried out by previous workers (eg Patterson et al 1981; Kitto 1994 and references therein). The δ³⁴S, δ¹⁸O and δD values of minerals from the Oxide-Silicate and Main Stages are 6‰, +10‰ and ~-90‰, respectively, interpreted to represent magmatic sulfur and water sources. However, Walshe et al., (1996) present an alternative model of reduced, sedimentary sulfur–bearing meteoric waters homogenizing at depth with magmatic fluids, prior to ascent through fault conduits.

3. **ANALYTICAL METHOD**

3.1. Sample Selection
Sample locations and descriptions are described in Table 1, and illustrated in Figures 1-3.

Samples of stratafault ore, which contain both arsenopyrite-pyrrhotite-chalcopyrite-pyrite assemblages and massive pyrrhotite, were sampled from the Central Federal and Rendeep's mine areas. Siderite alteration of host dolomite units was sampled from core drilled in the North King mine area. Dolomite-hosted replacement ore was sampled from several historic mines along the Black Face Fault, adjacent to the Blow Fault. Samples thus encompass a strike length of approximately 1.2km, and vertical extent of about 1km from surface.

The Late Base Metal and Carbonate stages were not analysed as part of this study, to eliminate variability owing to multiple vein crack-seal events and lower temperature fluid mixing.

Samples of fresh, unaltered Renison granite were collected from drill core, and tourmalinised granites were sampled from outcrop at Pine Hill.

Mineral separates were obtained by crushing samples in an agate mortar and pestle, then passing a hand magnet over crushed samples to separate magnetite. Pyrrhotite, pyrite, arsenopyrite, chalcopyrite and siderite were separated by hand-picking under a binocular microscope. Composition of siderite was verified by X-ray diffraction. Mineral separates were cleaned with ethanol prior to dissolution.

### 3.2. Preparation for Fe-isotope analysis

Fresh, unaltered, unmineralised granite samples were crushed and milled in their entirety, to produce a whole rock powder. These were dissolved in a mixture of concentrated HNO₃-HCl-HF overnight at 80°C. Sulfide mineral separates were dissolved in HNO₃-HCl only. Samples were then dried, following further additions of concentrated HNO₃ to drive off the HF. The samples were converted to chloride in 6M HCL, dried again, and finally taken up in 6M HCL and centrifuged to remove insoluble cassiterite or silicate mineral inclusions prior to ion-exchange chromatography.

Iron in the samples was purified using Bio-Rad AG 1X4 200-400 mesh anion exchange resin, and HCL, following the method of Poitrasson and Freydier, (2005).

### 3.3. Mass spectrometry

Iron isotope measurements were performed at the University of Adelaide on a Thermo Finnigan Neptune Multi-Collector ICP-MS. Measurements were performed in medium resolution mode, with H-geometry skimmer cones. Some samples were measured with X cones on high resolution mode, owing to degradation of the entrance slit precluding satisfactory peak resolution in medium resolution mode.

Sample introduction was via a glass spray chamber and Scott double pass assembly, together with a low flow, self-aspirating PFA nebulizer (between 50-70 ul/min). Samples were analysed in a 0.05M HCL solution. Iron was set to a concentration of 3.5 ppm to give a sensitivity of ~1V on ⁵⁷Fe. Ni spiking was set to a concentration of ~8 ppm, to give a signal of ~1V on ⁶¹Ni.

Sample take-up time to achieve a stable signal was set at 45s. A measurement consisted of 35 cycles of 8s integration time in static mode. A baseline measurement was done before each sample measurement. Each sample was run a minimum of 3 times.
Delta values were corrected for mass bias using the Ni-spiking method described by Poitrasson and Freydier, 2005. Data quality control was assured through the running of a hematite internal standard every 10th analysis, in addition to running replicates of geostandard GSP2. Our long term average for GSP2 is 0.176 ±0.13‰ (2σ) for δ$^{56}$Fe and 0.29±0.17‰ (2σ) for δ$^{57}$Fe, which compare well with the published composition of 0.159 ±0.013‰ for δ$^{56}$Fe, and 0.23 ±0.021‰ for δ$^{57}$Fe (Craddock and Dauphas, 2011).

All data are reported using delta notation, in units of per mil (‰)

$$\delta^{56}\text{Fe} = \left( \frac{^{56}\text{Fe} / ^{54}\text{Fe}_{\text{sample}}}{^{56}\text{Fe} / ^{54}\text{Fe}_{\text{IRMM14}}} - 1 \right) \times 10^3$$

4. RESULTS

The isotope data for different minerals and whole rock granite samples are presented in Table 1 and Figure 7, and discussed below.

4.1. Isotopic composition of whole rocks

The δ$^{57}$Fe of fresh Renison granite (n=4) vary between +0.27±0.09‰ (2σ) and +0.43± 0.01‰ (2σ) as shown in Table 1 and Fig. 7. They are similar in composition to isotopically heavy felsic (>65-70 wt%SiO$_2$) igneous rocks reported by Poitrasson and Freydier (2005), which ranged between 0.137±0.027‰ (2SE) and 0.584±0.034‰ (2SE). In comparison, δ$^{57}$Fe of mafic igneous geostandards range from 0.074 ± 0.077‰ to 0.247 ±0.022‰ (Craddock and Dauphas, 2011), and a wide ranging study of oceanic basalts (~48-60 wt% SiO$_2$) by Teng et al., (2013) report δ$^{57}$Fe ranging from -0.017±0.04‰ (95% confidence interval, CI) to 0.269±0.047‰ (95%CI).

4.2. Isotopic composition of minerals separates

Sulfides, magnetite and siderite results are detailed in Table 1 and Figure 7. The δ$^{57}$Fe of arsenopyrite (n=7) analyses vary between +0.85 ±0.06‰ (2σ) and +1.11±0.06‰ (2σ). Pyrite results (n=7), are very similar to arsenopyrite, varying between +0.89 ±0.01‰ (2σ) and +1.59±0.01‰ (2σ). The two magnetite samples returned +1.0±0.06‰ (2σ) and +1.01±0.04‰ (2σ), so are also isotopically heavy. Chalcopyrite analyses (n=6) vary between +0.28±0.1‰ (2σ) and +1.32±0.07‰ (2σ). Pyrrhotite analyses (n=16) are the isotopically lightest of all the minerals analysed, varying between -1.0 ±0.09‰ (2σ) and 0.00±0.10‰ (2σ). Siderite analyses (n=3) vary between -0.07±0.12‰ (2σ) and +0.05±0.02‰ (2σ). These results are very close to those reported for a skarn carbonate of -0.07‰ by Dideriksen et al., (2006).

5. DISCUSSION

5.1. Mineral-Mineral Fractionation

There are few published experimental measurements of mineral-mineral or mineral-fluid pairs that have formed at magmatic-hydrothermal temperatures, although the number of experimental bodies of work being published in the literature is increasing (eg Saunier et al., 2011, and Syverson et al., 2013). In the absence of empirical data, theoretical fractionation factors are calculated using the relationship:

$$\Delta A-B = \delta^{56}\text{Fe}_A - \delta^{56}\text{Fe}_B = 10^3 \ln \alpha^{56}\text{Fe}_{A-B}$$  (1)
where

\[ 10^3 \ln^{56} \text{Fe}_{A-B} = 10^3 \ln^{56} \text{Fe}_A - 10^3 \ln^{56} \text{Fe}_B, \]

The variable \(10^3 \ln^{56} \text{Fe}_{A-B}\) is termed the “reduced partition function”, and can be calculated by

Mössbauer Spectroscopy (eg Polyakov and Mineev, 2000; Polyakov et al. 2007; Polyakov and Soultanov, 2011). Other calculations of theoretical equilibrium Fe-isotope fractionation between minerals and fluids have been reported by researchers using a variety of methods such as Density Functional Theory (Blanchard et al., 2009; Rustad et al., 2010), infrared, Raman and vibrational spectroscopies (eg Polyakov and Mineev, 2000; Schauble et al., 2001) and inelastic nuclear resonant X-ray scattering (Polyakov et al. 2007). A review of these methods is contained in Schauble (2004).

At equilibrium, the fractionation of iron isotopes is governed by several factors. Heavy isotopes are incorporated into sites wherein vibrational energy is minimised ie short, strong chemical bonds (Schauble 2004). The formation of a stiff chemical bond is made more favourable by several parameters. To summarise from Schauble et al., (2001), these include (1) the oxidation state of Fe, so that Fe\(^{3+}\) compounds preferentially incorporate the heavy isotopes; (2) the ligand bond strength, for example chloride complexes have weaker bonds than CN\(^-\) or H\(_2\)O complexes so are isotopically lighter, and (3) and the coordination number of Fe in the compound in question, for example 4-fold coordination versus 6-fold coordination. Polyakov and Mineev (2000) also reported the effect of covalent bonds for pyrite, which has a high \(\beta\) factor, despite being a ferrous compound.

Theoretical Fe-isotopic fractionation between minerals as a function of temperature can be calculated using published reduced partition functions (eg Blanchard et al. 2009; Polyakov and Soultanov, 2000; Polyakov and Soultanov, 2011). For a typical magmatic-hydrothermal temperature of 350°C, it can be predicted that \(10^3 \ln^{56} \text{mgt-py}>\text{cpy-sid-po}\) (Fig.9A). The isotopic compositions of the different minerals we analysed form distinct and consistent groupings implying a relationship governed by coherent partitioning. Our data clearly are consistent with the prediction that pyrite, magnetite and chalcopyrite are isotopically heavier than siderite and pyrrhotite. The pyrrhotite and siderite data is also consistent with the prediction that ferrous minerals preferentially incorporate the light iron isotope. We also note that the Fe isotope compositions for pyrrhotite (Fig 7 and Table 1) cannot be distinguished on the basis of spatial position within the deposit, which suggests that equilibrium fractionation has been reached in part.

Our results are consistent with results reported by Graham et al., (2004), Markl et al., (2006) and Wang et al., (2011) who also found magnetite and pyrite to be isotopically heavier than siderite and chalcopyrite. In contrast, pyrite deposited from rapidly quenched sea floor hydrothermal fluids is isotopically light (eg Rouxel et al., 2004; Rouxel et al, 2008), with fractionation dominated by kinetic processes. Another possibility is that pyrite is preserving the isotopic composition of a FeS precursor, where fractionation is dominated by kinetic processes (Rouxel et al, 2008). Syverson et al’s (2013) precipitation experiments, conducted at hydrothermal conditions (300–350°C, 500 bars) resulted in fractionation of the light isotope first, perhaps as a result of kinetic or Rayleigh processes, with deposited minerals getting isotopically heavier with time. We observe fractionation between pyrite and pyrrhotite of up to ~2‰, which suggests that pyrite at Renison does not preserve the isotopic
composition of a lighter precursor so perhaps kinetic processes are not the dominant process in longer lived magmatic-hydrothermal systems.

5.2. Mineral-Fluid Fractionation

Figure 9B illustrates theoretical Fe fractionation between minerals and an Fe(II)-bearing fluid using the reduced partition function for the species $[\text{Fe(II)}\text{Cl}_2]^0$, calculated by. Experimental work (eg Simon et al., 2004; Saunier et al., 2011 and references therein), show that this is the predominant complex at magmatic-hydrothermal conditions. This diagram shows that we would predict magnetite and pyrite to be isotopically heavier than the fluid, and siderite and pyrrhotite to be lighter. However, this diagram shows the complications that can arise when choosing which theoretical fractionation factor to use for the fluid. The difference between possible values for $10^3\ln{\beta}$ arises owing to the choice of basis sets (see Hill et al 2010 for details) used in the computation, and indeed, the choice of computational approach (see Saunier et al 2011 for more detailed discussion about sources of uncertainty). Two dashed lines are plotted for theoretical chalcopyrite-fluid fractionation. The shaded wedge between the two possible lines shows the range of fractionation that could be expected, depending on whether $10^3\ln{\beta}$-factor 1 is used, or whether $10^3\ln{\beta}$-factor 2 is used. In this case the choice clearly affects whether we would predict chalcopyrite to be isotopically heavy or light compared to a fluid, with the impact being greater at lower temperatures. Although not plotted in the figure, similar differences in fractionation factors were observed for all our analysed minerals, depending on the choice of $10^3\ln{\beta}$ for ferrous fluid species. Continuing research to gather experimental and empirical data will be important for refining theoretical models.

5.3. Fe- isotopes as a geothermometer

The theoretical curves in Figure 9 imply that if isotopic equilibrium is achieved between minerals during precipitation, then any pair of minerals could be used to calculate the temperature of their formation. From our mineral pairs listed in Table 2, we have calculated an apparent fractionation factor, according to Equation (1), then estimated the temperature of formation from Figure 9A. It must be stated that although we have used mineral pairs that have co-precipitated, we have not observed any unequivocal equilibrium textures. The apparent fractionation factors for each pair give results that are consistent overall with fluid inclusion work for formation temperatures (Kitto, 1994), there are two clear inconsistencies:

Fluid inclusion isotope work by Kitto (1994) demonstrate that the fluid temperatures in the Main Sulfide Stage cooled from 350°C at depth to 200°C, at upper levels of the mine. However, our pyrite-pyrrhotite pairs from the Central Federal Mine Area (RB027) yield temperatures 180°C cooler than those from historic open-pits (40612-17 and 40612-21) which are further away from the intrusion at a stratigraphically higher position; the opposite of that indicated by fluid inclusion work. The sample from deepest in the mine (RB017) from the Rendeeps yields a temperature of 160°C from co-precipitated chalcopyrite-pyrrhotite pairs, again about 200°C lower than homogenisation temperatures of fluid inclusions.

Furthermore, mineral pairs from the same sample give very different temperatures. For example, RB013 yield temperatures from 70°C to 510°C, for siderite, pyrite and pyrrhotite from the same paragenetic stage. The 70°C result is not supported by other evidence; the
lowest temperatures recorded in fluid inclusions at Renison is ~100°C for the Late Base Metal and Carbonate stages of mineralisation.

This raises an interesting dichotomy of results, that at the deposit-scale, Fe isotopes fractionate between magmatic hydrothermal minerals and fluids in a distribution predicted by theoretical equilibrium factors, yet natural mineral-mineral pairs yield highly variable results (eg Dziony et al., 2014), limiting the use of Fe-isotopes as a geothermometer at the present time. It is possible that other mineral deposition processes, for example, wall rock reaction, may overprint the fractionation controlled by temperature.

Detailed in-situ studies using micro-drilling (eg Gagnevin et al., 2012), UV femtosecond laser (eg Horn et al., 2006; Dziony et al., 2014), and Secondary Ion mass Spectrometry (SIMS; eg Marin-Carbonne et al., 2011) have shown variability of >1‰ within individual zoned minerals. Studies with high degrees of spatial resolution may be needed to resolve fractionation at the mineral scale as a result of processes such as wall-rock interaction, and repeated dissolution-precipitation reactions.

### 5.4. Comparison of Renison mineral compositions with Xinqiao skarn and the effect of magma oxidation state on magmatic-hydrothermal minerals

The literature contains other case studies of Fe isotope data from magmatic-hydrothermal ore deposits as diverse as seafloor hydrothermal vents (eg Rouxel et al., 2004), hydrothermal iron oxide (Markl et al., 2006) and base metal deposits (Gagnevin et al., 2012), porphyry coppers and skarns (eg Graham et al., 2004; Wang et al., 2011) and magmatic Ni-Cu sulphides (Fiorentini et al., 2012). Of these case studies, Xinqiao is the only case study where both the source/host plutons and magmatic-hydrothermal minerals have been analysed. This deposit provides an interesting contrast with Renison, because of the different petrology and geochemistry of the associated plutons.

The Xinqiao Cu-Fe-S-Au deposit is associated with the Jitou quartz-monzodiorite (‘QMD’) stock, emplaced during Mesozoic late syn- to post-orogenic high-K, calc-alkaline magmatism (Xu and Zhou 2001; Wu et al.,2008). The mineralogy of plagioclase-alkali feldspar-amphibole-quartz with accessory magnetite (Wu et al., 2008) indicates a hydrous, oxidised magma. The deposit comprises a carbonate replacement skarn and a stratiform sulphide deposit. We consider only the minerals reported to be sourced from the skarn at Xinqiao, so as to compare only higher temperature magmatic-hydrothermal minerals between the two deposits. Xu et al (2001) report 2 populations of fluid inclusion homogenisation temperatures; one group formed at temperatures of 380-420°C and a second population at 220-300°C. Thus the temperatures of formation of sulphides in both Renison and Xinqiao are very similar.

Figure 10 illustrates comparison of our Renison data for magnetite, chalcopyrite and pyrite with the Xinqiao data. There are clear differences in iron isotope compositions between minerals from each deposit, with chalcopyrite, pyrite and magnetite from Renison being isotopically heavier than those from Xinqiao.

The Jitou QMD, hosting the skarn deposit (Wang et al., 2011), has δ57Fe compositions of −0.15‰ to 0.29‰, and is therefore isotopically lighter than the Renison granite (0.27‰-0.43‰). The difference in isotopic composition between the two intrusions can be explained qualitatively by the control exerted by the crystallisation of magnetite, as follows:
The behaviour of iron isotopes is governed in part by the redox state of the iron; Fe (III) bearing phases fractionate the heavier isotope, and Fe (II) bearing phases fractionate the lighter isotope (Schauble, 2004). We therefore expect that an oxidised magma crystallising magnetite—which has 2x Fe(III) and 1xFe(II)—will remove more $^{56}$Fe and $^{57}$Fe from the melt than $^{54}$Fe, resulting in a melt with isotopically light composition. Sossi et al., (2012), have demonstrated this control that magnetite crystallisation exerts on the Fe-isotope composition of a melt, in their study of a differentiating dolerite sill acting as a closed system. It is also likely that lack of differentiation also plays a part, as monzodiorites have significantly less SiO$_2$ (<70 wt%) than that of highly fractionated felsic magmas (70-77 wt%).

In contrast, in an S-type granite, both anatexis and fractional crystallisation mechanisms may control the isotopic composition; these have been examined by Foden et al (2014, submitted). The petrogenesis of S-type granites is dominated by partial melting of protoliths containing reduced minerals such as sulphides or graphite (eg Clemens, 2003). Telus et al. (2012) have shown the effects of partial melting by their analyses (reported as $\delta^{56}$Fe) of leucosomes (+0.246 ± 0.031‰ to +0.480 ± 0.029‰) in migmatites which are systematically heavier than the melanosome (+0.077 ± 0.029‰ to +0.302 ± 0.028‰). The difference between melanosome-leucosome pairs ranges from +0.038 ± 0.056‰ to +0.196 ± 0.058‰. If such a melt is transported to shallow levels and undergoes fractional crystallisation, then we would expect the melt to remain isotopically heavy because the main Fe-bearing minerals are Fe(II)-bearing minerals such as biotite (Paveseti et al., 2007; Vigneresse, 2007), garnet and ilmenite, which preferentially incorporate the light isotope. Although thermal diffusion cannot be discounted, given the models of pluton assembly by discrete additions of magma (eg Petford et al., 2000, Vigneresse, 2007), the vast bulk of the Renison granite is unexposed, which precludes detailed examination of contacts and relationships of any discrete magma batches which may be present.

Our interpretation is that the Renison ore minerals are isotopically heavier than those from Xinqiao because the magmatic fluid exsolved from an isotopically heavy, reduced S-type magma, rather than an isotopically light, less differentiated oxidised I-type magma. The range of isotope ratios within our data is -1.0±0.09‰ for the lightest pyrrhotite to +1.59±0.01‰ for the heaviest pyrite, which is much larger than the range in granites (0.0 to +0.6‰; Foden et al, submitted; Poitrasson and Freydier, 2005), so it is likely that additional mechanisms have operated.

**Ore fluids as reservoirs of isotopically light iron isotopes**

The Jitou QMD, hosting the skarn deposit, is isotopically heavier than chalcopyrite-pyrite and magnetite. Wang et al., (2011) used these data to support the “light fluid” hypothesis put forward by Poitrasson and Freydier (2005) and Heimann et al., (2008), that Fe(II)-Cl rich fluids exsolved by magmas are isotopically lighter than the melt, because the valence state of Fe in Fe-Cl fluids is almost always Fe(II) (Simon et al., 2004; Saunier et al., 2011 and references therein), therefore will preferentially fractionate the light isotope. Minerals deposited from such a fluid would be isotopically lighter than the source granite.

However, at Renison, the isotopic composition of the granite is located midway between the heavy minerals (pyrite-arsenopyrite-magnetite) and the light minerals (siderite-pyrrhotite; Fig. 7). Our data clearly do not support the hypothesis that the first minerals in a paragenetic sequence will be isotopically lighter than the granite, although mass balance calculations to
assess the contribution of host rocks, and all mineral phases to the isotopic signature of the analysed minerals, and to compute a composition of ore fluids is necessary to provide a more quantitative discussion. There is evidence from the $\delta$H/D and $\delta^{18}O$ work of Patterson et al., (1981) that the earliest fluids equilibrated with the granite at ~600°C, and a review of tin deposits by Heinrich (1990) shows that this is often the case. At least on a qualitative basis, reduced melts crystallise ferrous Fe-bearing phases, leaving the heavy isotope behind in the melt. Therefore isotopic equilibration with the melt would result in an initially isotopically heavy ore fluid. The isotopic composition of hydrothermal fluids has been measured at seafloor conditions (eg Sharma et al., 2001; Rouxel, et al., 2008) and experimentally at hydrothermal conditions (Syverson et al, 2013; Saunier et al 2011). However, techniques that can routinely measure the iron isotope ratios of ore fluids contained in fluid inclusions in natural magmatic-hydrothermal minerals are still undeveloped. In-situ measurement of iron isotope compositions in fluid inclusions and zoned minerals will shed light on processes that are difficult to unravel using an average composition of the hand-picked sample.

6. CONCLUSION

We have analysed magmatic-hydrothermal minerals and bulk granite from the Renison Sn-W deposit to characterise the Fe isotopic composition of minerals associated with a reduced, S-type granite. Pyrite, magnetite and chalcopyrite are isotopically heavier than pyrrhotite and siderite, results which are consistent with theoretical equilibrium fractionation factors. However, the use of iron isotopes as a geothermometer is complicated by the variability of results within single samples, and that calculated temperatures of formation are spatially inconsistent with the results from detailed fluid inclusion work.

Pyrite, chalcopyrite and magnetite from the Renison deposit, are isotopically heavier than those from the Xinqiao skarn. These results are consistent with the hypothesis that a magmatic-hydrothermal fluid exsolved from, or equilibrated with, an isotopically heavy, reduced magma could deposit isotopically heavy ore minerals. In contrast, oxidised magmas crystallise magmatic magnetite which sequesters heavy Fe, resulting in an isotopically lighter melt, and hence a lighter magmatic-hydrothermal fluid. Our results also contradict the hypothesis magmatic-hydrothermal minerals should be isotopically lighter than the source intrusion, although the overall range of isotopic compositions suggests that other mechanisms may overprint and/or enhance fractionation controlled solely by temperature.

Magmatic-hydrothermal ore deposits result from complex physicochemical interactions between magmas, fluids, and host rocks. The rapidly developing capability to measure isotope ratios at the nanometer scale may help to unravel processes at the mineral scale. More experimental data exploring mineral deposition processes at high temperatures ($>300^{\circ}C$) such as wall-rock reaction and mineral dissolution-precipitation are also needed to calibrate theoretical fractionation curves.

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