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

3
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9
10 **ABSTRACT**

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

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

28 **1. INTRODUCTION**

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

38 Researchers investigating the fractionation of magmas (eg Schuessler et al., 2008; Teng et
39 al., 2008; Sossi et al., 2012) have found that the most evolved differentiates often have
40 heavy iron isotope enriched compositions. These studies demonstrate measurable Fe-

41 isotopic fractionation at magmatic temperatures. Although fractional crystallisation is now
42 clearly demonstrated as one mechanism that drives felsic differentiates towards heavy iron
43 isotopic compositions, it has also been proposed by Poitrasson and Freyrier, (2005) and
44 Heimann et al., (2008) that fluid exsolution from cooling siliceous plutons (>70% SiO₂) may
45 also lead to heavy isotopic enrichment; discharged Cl-bearing fluids preferentially stripped
46 these granites of isotopically light Fe²⁺ driving the residual magmas to heavy iron isotope
47 composition. A third mechanism of fractionating Fe isotopes, thermal diffusion, is
48 demonstrated in the experiment of Huang et al (2009), who melted the geostandard AGV-1
49 (a homogenous andesite powder) under hydrous conditions, with a steady temperature
50 gradient between 350 and 950°C. The run products showed that significant Fe-isotope
51 fractionation of 2.8‰ had occurred, with the hotter region being isotopically lighter than the
52 cold end.

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

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

75 Magmatic-hydrothermal fluids that are released from cooling and crystallising plutons may
76 carry high concentrations of economic metals such as Cu, Au, Mo, Sn and W (eg Heinrich
77 1990; Simon et al., 2004; Webster 2004; Cerny et al., 2005; Williams-Jones and Heinrich,
78 2005; Zajacz et al., 2007; Audetat et al., 2008; Frank et al., 2011;). Suites of economic
79 metals that occur together in magmatic-hydrothermal deposits have a well-known
80 association with magma oxidation state (Blevin and Chappell 1992; Blevin 2004; Cerny et
81 al., 2005; Vigneresse 2007). Tin and Sn-W deposits are often associated with weakly to
82 strongly peraluminous, reduced or ilmenite-series granites using the terminology of Ishihara
83 (1977), whilst Cu-Au±Mo±W are associated with oxidised, magnetite-series intermediate to
84 felsic intrusives often found in magmatic arc terranes (Cerny et al., 2005; Seedorf et al.,
85 2005; Sillitoe 2010 and references therein).

86 To date, published case studies of iron isotope systematics in magmatic-hydrothermal
87 deposits (eg Graham et al 2004, Li et al., 2010) do not have results for both magmatic suites
88 and associated Fe-bearing ore minerals. In this paper we present 50 iron isotopic
89 compositions of bulk granite (*sensu stricto*) and mineral separates, from different structural
90 and stratigraphic positions in the Renison Sn-W deposit. The Renison deposit is a world
91 class example of a stratabound carbonate replacement Sn deposit associated with reduced
92 S-type granitic intrusion, and therefore represents one end of the magma oxidation state
93 spectrum. Our results are compared to theoretical predictions for equilibrium mineral-mineral
94 fractionation. We also compare our results to published data from the Xinqiao Cu-Fe-S-Au
95 skarn, associated with a quartz-monzodiorite stock (Wang et al., 2011), to examine the effect
96 of magma oxidation state on the isotopic composition of fluids that later deposited the
97 magmatic-hydrothermal minerals. Our results contribute a large new empirical dataset to a
98 rapidly expanding field of research, and further illustrate the complex interplay of processes
99 that fractionate iron isotopes.

100 **2. GEOLOGY**

101 **2.1. Regional Geology**

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

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

111 The oldest sedimentary sequence in the mine area is the Upper Neoproterozoic Success
112 Creek Group (Fig. 1). The Success Creek Group comprises shallow water to subaerial
113 siliceous clastic sediments, shales and dolostones (Patterson et al., 1981). The Crimson
114 Creek Formation overlies and is in faulted contact with the Success Creek Group (Patterson
115 et al., 1981). The Crimson Creek formation comprises a shelf sequence of siltstones, shales
116 and volcanoclastics with minor dolostones. (Patterson et al 1981; Kitto, 1994).

117 The contact between the Success Creek Group and Crimson Creek Formation is marked by
118 the Red Rock Member (Fig. 2), a variably hematitic unit comprising siltstones and
119 volcanoclastics, conglomerates and greywackes, cherty ironstones and thin dolostones
120 (Patterson et al., 1981; Kitto, 1994). Strata comprising the upper Success Creek Group and
121 lower Crimson Creek Formation are termed the Mine Sequence by mine geologists

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

125 **2.1. Deposit Geology**

126 The Renison deposit is controlled by the NW striking, normal Federal Bassett Fault ('FBF'),
127 located on the north east limb of a south east plunging anticline (Fig. 1,2). Intrusion of the

128 Renison granite caused brittle fracturing and normal fault reactivation in the intruded Late
129 Neoproterozoic Success Creek and Crimson Creek Formations. This allowed magmatic
130 fluids accumulated in a probable cupola structure on the upper surface of the cooling
131 Meredith Granite pluton, to be tapped and ascend along the FBF and invade the
132 sedimentary strata depositing base metal and tin ores, as a result of replacement of
133 carbonate units. Stratabound, massive pyrrhotite-cassiterite with minor pyrite and base
134 metals (eg, galena sphalerite chalcopyrite) replaced 3 dolomite horizons within the Success
135 Creek Group and Crimson Creek Formation (Fig. 2). Although the bulk of the mineralisation
136 is replacement style, fault controlled veins are also economically exploited. Faulted blocks of
137 the Mine Sequence are mined within the FBF and are referred to as 'Stratafault' Ore.

138 Normal faults located within 1km of the mine area also provided a conduit for mineralising
139 fluids, as evidenced by the numerous historical workings that lie along them (Figs. 1, 2). The
140 stratabound ore surfaces are structurally complex (Fig 3), being controlled by structures both
141 sub-parallel and transverse to the FBF (Kitto, 1994).

142 **2.2. The Renison Granite**

143 The Renison granite is a fractionated, shallow (2-4 km) S-type intrusion, ranging in
144 composition from adamellite to alkali-feldspar granite (Sawka et al.,1990; Bajwah et al.,
145 1995; Black et al.,2005). Interpretation of gravity data by Richardson and Leaman (1989,
146 referenced in Kitto, 1994) shows that the Renison Granite forms part of the larger Meredith
147 Pluton which includes the Heemskirk intrusion to the west and Granite Tor to the east (Kitto,
148 1994; Fig. 1).

149 The Renison granite is a grey, medium to coarse grained biotite granite (Fig. 4). Bajwah et
150 al., (1995) describes four texturally distinct types; K-feldspar porphyry, fine-grained
151 porphyritic granite, fine grained non-porphyritic granite and medium to coarse grained
152 equigranular granite. Unaltered granite comprises quartz, K-feldspar, plagioclase and biotite,
153 with ilmenite, monazite, apatite, zircon, fluorite, topaz, tourmaline and rare allanite as
154 accessory phases. Phenocrysts in the porphyritic varieties are either quartz or K-feldspar up
155 to 1 cm across. Plagioclase phenocrysts are recorded in the quartz-feldspar porphyry..
156 These types are interpreted, on the basis of geochemistry and petrography (Bajwah et al.,
157 1995; Walshe et al., 2011) to be related by fractional crystallisation.

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

161 **2.3. Mineralogy and paragenesis**

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

166 *1) Oxide –Silicate stage*

167 Rare assemblages of carbonate and magnetite may represent the earliest
168 magmatic fluid (Kitto, 1994; Fig. 5), followed by quartz-arsenonopyrite ±
169 cassiterite ± wolframite ± pyrrhotite-pyrite-chalcopyrite-ilmenite-rutile (Fig. 6C)

170 This stage is interpreted by Kitto (1994) to be coincident with the onset of normal-
171 dextral movement along the FBF system. Fluid inclusion studies showed
172 minimum formation temperatures of 340-420°C, and salinity varied between 8-12
173 equivalent wt% NaCl.

174

175 2) *Main Sulphide stage*

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

187

188 3) *Late Base Metal Stage*

189 Crustiform rhodocrosite-lined veins are characteristic of this stage. Vein
190 mineralogy comprises sphalerite- galena- quartz- -pyrrhotite- pyrite-chalcopyrite-
191 fluorite-calcite-chlorite. The interpretation of this stage being associated with
192 brittle reactivation is based on textural features such as syntaxial crack-seal veins
193 and microfolding (Kitto, 1994 and references therein). Fluid inclusion studies
194 record lower temperatures (150° -210°C) and bimodal salinities (2 or
195 10wt%NaCl), suggesting mixing of magmatic-hydrothermal fluids with meteoric
196 groundwaters (Patterson et al., 1981; Kitto, 1994; Walshe et al., 1996).

197

198 4) *Carbonate Stage*

199 Dolomite, fluorite, clear quartz, chalcopyrite and calcite comprise a carbonate-
200 dominant mineral assemblage infilling brecciated sediments or vugs and fault
201 cavities.

202 A hydrothermal magnesian siderite halo surrounds the stratabound ore surfaces (Patterson
203 1981; Kitto, 1994), and is interpreted to form via dissolution of the host dolomites by
204 magmatic fluid. The limit of the reaction front is usually very sharply defined as an abrupt
205 transition to largely unaltered sedimentary rock (Fig. 6A,D).

206 Sulfur isotope, oxygen and hydrogen isotope studies have been carried out by previous
207 workers (eg Patterson et al 1981; Kitto 1994 and references therein). The $\delta^{34}\text{S}$, $\delta^{18}\text{O}$ and δD
208 values of minerals from the Oxide-Silicate and Main Stages are 6‰, +10‰ and \sim -90‰,
209 respectively, interpreted to represent magmatic sulfur and water sources. However, Walshe
210 et al., (1996) present an alternative model of reduced, sedimentary sulfur-bearing meteoric
211 waters homogenizing at depth with magmatic fluids, prior to ascent through fault conduits .

212 3. ANALYTICAL METHOD

213 3.1. Sample Selection

214 Sample locations and descriptions are described in Table 1, and illustrated in Figures 1-3.
215 Samples of stratafault ore, which contain both arsenopyrite-pyrrhotite-chalcopyrite-pyrite
216 assemblages and massive pyrrhotite, were sampled from the Central Federal and Rendeeps
217 mine areas. Siderite alteration of host dolomite units was sampled from core drilled in the
218 North King mine area. Dolomite-hosted replacement ore was sampled from several historic
219 mines along the Black Face Fault, adjacent to the Blow Fault. Samples thus encompass a
220 strike length of approximately 1.2km, and vertical extent of about 1km from surface.

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

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

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

231 **3.2. Preparation for Fe-isotope analysis**

232 Fresh, unaltered, unmineralised granite samples were crushed and milled in their entirety, to
233 produce a whole rock powder. These were dissolved in a mixture of concentrated HNO₃-
234 HCl-HF overnight at 80°C. Sulfide mineral separates were dissolved in HNO₃-HCl only.
235 Samples were then dried, following further additions of concentrated HNO₃ to drive off the
236 HF. The samples were converted to chloride in 6M HCL, dried again, and finally taken up in
237 6M HCL and centrifuged to remove insoluble cassiterite or silicate mineral inclusions prior to
238 ion-exchange chromatography.

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

241 **3.3. Mass spectrometry**

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

247 Sample introduction was via a glass spray chamber and Scott double pass assembly,
248 together with a low flow, self-aspirating PFA nebulizer (between 50-70 ul/min). Samples were
249 analysed in a 0.05M HCl solution. Iron was set to a concentration of 3.5 ppm to give a
250 sensitivity of ~1V on ⁵⁷Fe. Ni spiking was set to a concentration of ~8 ppm, to give a signal of
251 ~1V on ⁶¹Ni.

252 Sample take-up time to achieve a stable signal was set at 45s. A measurement consisted of
253 35 cycles of 8s integration time in static mode. A baseline measurement was done before
254 each sample measurement. Each sample was run a minimum of 3 times.

255 Delta values were corrected for mass bias using the Ni-spiking method described by
256 Poitrasson and Freydier, 2005. Data quality control was assured through the running of a
257 hematite internal standard every 10th analysis, in addition to running replicates of
258 geostandard GSP2. Our long term average for GSP2 is 0.176 ±0.13‰ (2σ) for δ⁵⁶Fe and
259 0.29±0.17‰ (2σ) for δ⁵⁷Fe, which compare well with the published composition of 0.159
260 ±0.013‰ for δ⁵⁶Fe, and 0.23 ±0.021‰ for δ⁵⁷Fe (Craddock and Dauphas, 2011).

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

$$262 \quad \delta^{56}\text{Fe} = \left[\left(\frac{{}^{56}\text{Fe}/{}^{54}\text{Fe}_{\text{sample}}}{({}^{56}\text{Fe}/{}^{54}\text{Fe}_{\text{IRMM14}})} - 1 \right) \times 10^3 \right]$$

263 4. RESULTS

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

266 4.1. Isotopic composition of whole rocks

267 The δ⁵⁷Fe of fresh Renison granite (n=4) vary between +0.27±0.09‰ (2σ) and +0.43±
268 0.01‰ (2σ) as shown in Table 1 and Fig. 7. They are similar in composition to isotopically
269 heavy felsic (>65-70 wt%SiO₂) igneous rocks reported by Poitrasson and Freydier (2005),
270 which ranged between 0.137±0.027‰ (2SE) and 0.584±0.034‰ (2SE). In comparison,
271 δ⁵⁷Fe of mafic igneous geostandards range from 0.074 ± 0.077‰ to 0.247 ±0.022‰
272 (Craddock and Dauphas, 2011), and a wide ranging study of oceanic basalts (~48-60 wt%
273 SiO₂) by Teng et al., (2013) report δ⁵⁷Fe ranging from -0.017±0.04‰ (95%confidence
274 interval, CI) to 0.269±0.047‰ (95%CI).

275 4.2. Isotopic composition of minerals separates

276 Sulfides, magnetite and siderite results are detailed in Table 1 and Figure 7. The δ⁵⁷Fe of
277 arsenopyrite (n=7) analyses vary between +0.85 ±0.06‰ (2σ) and +1.11±0.06‰ (2σ). Pyrite
278 results (n=7), are very similar to arsenopyrite, varying between +0.89 ±0.01‰ (2σ) and
279 +1.59±0.01‰ (2σ). The two magnetite samples returned +1.0±0.06‰ (2σ) and
280 +1.01±0.04‰ (2σ), so are also isotopically heavy. Chalcopyrite analyses (n=6) vary between
281 +0.28±0.1‰ (2σ) and +1.32±0.07‰ (2σ). Pyrrhotite analyses (n=16) are the isotopically
282 lightest of all the minerals analysed, varying between -1.0 ±0.09‰ (2σ) and 0.00±0.10‰
283 (2σ). Siderite analyses (n=3) vary between -0.07±0.12‰ (2σ) and +0.05±0.02‰ (2σ). These
284 results are very close to that those reported for a skarn carbonate of -0.07‰ by Dideriksen
285 et al., (2006).

286 5. DISCUSSION

287 5.1. Mineral-Mineral Fractionation

288 There are few published experimental measurements of mineral-mineral or mineral-fluid
289 pairs that have formed at magmatic-hydrothermal temperatures, although the number of
290 experimental bodies of work being published in the literature is increasing (eg Saunier et al.,
291 2011, and Syverson et al., 2013). In the absence of empirical data, theoretical fractionation
292 factors are calculated using the relationship:

$$293 \quad \Delta A-B = \delta^{56}\text{Fe}_A - \delta^{56}\text{Fe}_B \approx 10^3 \ln \alpha^{56}\text{Fe}_{A-B} \quad (1)$$

294 where

$$295 \quad 10^3 \ln \alpha^{56}\text{Fe}_{A-B} = 10^3 \ln \beta_A - 10^3 \ln \beta_B, \quad (2)$$

296 The variable $10^3 \ln \beta$ is termed the “reduced partition function”, and can be calculated by
297 Mössbauer Spectroscopy (eg Polyakov and Mineev, 2000; Polyakov et al. 2007; Polyakov
298 and Sultantov, 2011). Other calculations of theoretical equilibrium Fe-isotope fractionation
299 between minerals and fluids have been reported by researchers using a variety of methods
300 such as Density Functional Theory (Blanchard et al., 2009; Rustad et al., 2010), infrared,
301 Raman and vibrational spectroscopies (eg Polyakov and Mineev, 2000; Schauble et al.,
302 2001) and inelastic nuclear resonant X-ray scattering (Polyakov et al. 2007). A review of
303 these methods is contained in Schauble (2004).

304 At equilibrium, the fractionation of iron isotopes is governed by several factors. Heavy
305 isotopes are incorporated into sites wherein vibrational energy is minimised ie short, strong
306 chemical bonds (Schauble 2004). The formation of a stiff chemical bond is made more
307 favourable by several parameters. To summarise from Schauble et al., (2001), these include
308 (1) the oxidation state of Fe, so that Fe^{3+} compounds preferentially incorporate the heavy
309 isotopes; (2) the ligand bond strength, for example chloride complexes have weaker bonds
310 than CN^- or H_2O complexes so are isotopically lighter, and (3) and the coordination number
311 of Fe in the compound in question, for example 4-fold coordination versus 6-fold
312 coordination. Polyakov and Mineev (2000) also reported the effect of covalent bonds for
313 pyrite, which has a high β factor, despite being a ferrous compound.

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

326 Our results are consistent with results reported by Graham et al., (2004), Markl et al., (2006)
327 and Wang et al., (2011) who also found magnetite and pyrite to be isotopically heavier than
328 siderite and chalcopyrite. In contrast, pyrite deposited from rapidly quenched sea floor
329 hydrothermal fluids is isotopically light (eg Rouxel et al., 2004; Rouxel et al, 2008), with
330 fractionation dominated by kinetic processes. Another possibility is that pyrite is preserving
331 the isotopic composition of a FeS precursor, where fractionation is dominated by kinetic
332 processes (Rouxel et al, 2008). Syverson et al’s (2013) precipitation experiments, conducted
333 at hydrothermal conditions ($300\text{--}350^\circ\text{C}$, 500 bars) resulted in fractionation of the light
334 isotope first, perhaps as a result of kinetic or Rayleigh processes, with deposited minerals
335 getting isotopically heavier with time. We observe fractionation between pyrite and pyrrhotite
336 of up to $\sim 2\%$, which suggests that pyrite at Renison does not preserve the isotopic

337 composition of a lighter precursor so perhaps kinetic processes are not the dominant
338 process in longer lived magmatic-hydrothermal systems.

339 **5.2. Mineral-Fluid Fractionation**

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

359 **5.3. Fe- isotopes as a geothermometer**

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

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

376 Furthermore, mineral pairs from the same sample give very different temperatures. For
377 example, RB013 yield temperatures from 70°C to 510°C, for siderite, pyrite and pyrrhotite
378 from the same paragenetic stage. The 70°C result is not supported by other evidence; the

379 lowest temperatures recorded in fluid inclusions at Renison is ~100°C for the Late Base
380 Metal and Carbonate stages of mineralisation.

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

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

393 **5.4. Comparison of Renison mineral compositions with Xinqiao skarn and the** 394 **effect of magma oxidation state on magmatic-hydrothermal minerals**

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

403 The Xinqiao Cu-Fe-S-Au deposit is associated with the Jitou quartz-monzodiorite ('QMD')
404 stock, emplaced during Mesozoic late syn- to post-orogenic high-K, calc-alkaline magmatism
405 (Xu and Zhou 2001; Wu et al., 2008). The mineralogy of plagioclase-alkali feldspar-
406 amphibole-quartz with accessory magnetite (Wu et al., 2008) indicates a hydrous, oxidised
407 magma. The deposit comprises a carbonate replacement skarn and a stratiform sulphide
408 deposit. We consider only the minerals reported to be sourced from the skarn at Xinqiao, so
409 as to compare only higher temperature magmatic-hydrothermal minerals between the two
410 deposits. Xu et al (2001) report 2 populations of fluid inclusion homogenisation
411 temperatures; one group formed at temperatures of 380-420°C and a second population at
412 220-300°C. Thus the temperatures of formation of sulphides in both Renison and Xinqiao
413 are very similar.

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

418 The Jitou QMD, hosting the skarn deposit (Wang et al., 2011), has $\delta^{57}\text{Fe}$ compositions of
419 -0.15‰ to 0.29‰ , and is therefore isotopically lighter than the Renison granite (0.27‰ -
420 0.43‰). The difference in isotopic composition between the two intrusions can be explained
421 qualitatively by the control exerted by the crystallisation of magnetite, as follows:

422 The behaviour of iron isotopes is governed in part by the redox state of the iron; Fe (III)
423 bearing phases fractionate the heavier isotopes, and Fe (II) bearing phases fractionate the
424 lighter isotope (Schauble, 2004). We therefore expect that an oxidised magma crystallising
425 magnetite—which has 2x Fe(III) and 1xFe(II)—will remove more ^{56}Fe and ^{57}Fe from the melt
426 than ^{54}Fe , resulting in a melt with isotopically light composition. Sossi et al., (2012), have
427 demonstrated this control that magnetite crystallisation exerts on the Fe-isotope composition
428 of a melt, in their study of a differentiating dolerite sill acting as a closed system. It is also
429 likely that lack of differentiation also plays a part, as monzodiorites have significantly less
430 SiO_2 (<70 wt%) than that of highly fractionated felsic magmas (70-77wt%)

431 In contrast, in an S-type granite, both anatexis and fractional crystallisation mechanisms may
432 control the isotopic composition; these have been examined by Foden et al (2014,
433 submitted). The petrogenesis of S-type granites is dominated by partial melting of protoliths
434 containing reduced minerals such as sulphides or graphite (eg Clemens, 2003). Telus et al
435 (2012) have shown the effects of partial melting by their analyses (reported as $\delta^{56}\text{Fe}$) of
436 leucosomes ($+0.246 \pm 0.031\text{‰}$ to $+0.480 \pm 0.029\text{‰}$) in migmatites which are systematically
437 heavier than the melanosomes ($+0.077 \pm 0.029\text{‰}$ to $+0.302 \pm 0.028\text{‰}$). The difference
438 between melanosome-leucosome pairs ranges from $+0.038 \pm 0.056\text{‰}$ to $+0.196 \pm 0.058\text{‰}$.
439 If such a melt is transported to shallow levels and undergoes fractional crystallisation, then
440 we would expect the melt to remain isotopically heavy because the main Fe-bearing
441 minerals are Fe(II)- bearing minerals such as biotite (Paveseti et al., 2007; Vigneresse,
442 2007), garnet and ilmenite, which preferentially incorporate the light isotope. Although
443 thermal diffusion cannot be discounted, given the models of pluton assembly by discrete
444 additions of magma (eg Petford et al., 2000, Vigneresse, 2007), the vast bulk of the Renison
445 granite is unexposed, which precludes detailed examination of contacts and relationships of
446 any discrete magma batches which may be present.

447 Our interpretation is that the Renison ore minerals are isotopically heavier than those from
448 Xinqiao because the magmatic fluid exsolved from an isotopically heavy, reduced S-type
449 magma, rather than an isotopically light, less differentiated oxidised I-type magma. The
450 range of isotopic ratios within our data is $-1.0 \pm 0.09\text{‰}$ for the lightest pyrrhotite to
451 $+1.59 \pm 0.01\text{‰}$ for the heaviest pyrite, which is much larger than the range in granites (0.0 to
452 $+0.6\text{‰}$; Foden et al, submitted; Poitrasson and Freydier, 2005), so it is likely that additional
453 mechanisms have operated.

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

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

462 However, at Renison, the isotopic composition of the granite is located midway between the
463 heavy minerals (pyrite-arsenopyrite-magnetite) and the light minerals (siderite-pyrrhotite; Fig.
464 7). Our data clearly do not support the hypothesis that the first minerals in a paragenetic
465 sequence will be isotopically lighter than the granite, although mass balance calculations to

466 assess the contribution of host rocks, and all mineral phases to the isotopic signature of the
467 analysed minerals, and to compute a composition of ore fluids is necessary to provide a
468 more quantitative discussion. There is evidence from the $\delta\text{H/D}$ and $\delta^{18}\text{O}$ work of Patterson et
469 al., (1981) that the earliest fluids equilibrated with the granite at $\sim 600\text{C}$, and a review of tin
470 deposits by Heinrich (1990) shows that this is often the case. At least on a qualitative basis,
471 reduced melts crystallise ferrous Fe-bearing phases, leaving the heavy isotope behind in the
472 melt. Therefore isotopic equilibration with the melt would result in an initially isotopically
473 heavy ore fluid.

474 The isotopic composition of hydrothermal fluids has been measured at seafloor conditions
475 (eg Sharma et al., 2001; Rouxel, et al., 2008) and experimentally at hydrothermal conditions
476 (Syverson et al, 2013; Saunier et al 2011). However, techniques that can routinely measure
477 the iron isotope ratios of ore fluids contained in fluid inclusions in natural magmatic-
478 hydrothermal minerals are still undeveloped. In-situ measurement of iron isotope
479 compositions in fluid inclusions and zoned minerals will shed light on processes that are
480 difficult to unravel using an average composition of the hand-picked sample.

481 **6. CONCLUSION**

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

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

498 Magmatic-hydrothermal ore deposits result from complex physicochemical interactions
499 between magmas, fluids, and host rocks. The rapidly developing capability to measure
500 isotope ratios at the nanometer scale may help to unravel processes at the mineral scale.
501 More experimental data exploring mineral deposition processes at high temperatures
502 ($>300\text{C}$) such as wall-rock reaction and mineral dissolution-precipitation are also needed to
503 calibrate theoretical fractionation curves.

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