

Magmatic Fluids Implicated in the Formation of Propylitic Alteration: Oxygen, Hydrogen and Strontium Isotopic Constraints from the Northparkes Porphyry Cu-Au District, NSW, Australia

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Abstract

In porphyry ore deposit models, the propylitic facies is widely interpreted to be caused by convective circulation of meteoric waters. However, recent field-based and geochemical data suggest that magmatic-derived fluids are likely to contribute to development of the propylitic assemblage. In order to test this hypothesis, we determined the oxygen and hydrogen isotope compositions of propylitic mineral separates (epidote, chlorite and quartz), selected potassic mineral separates (quartz and magnetite) and quartz-hosted fluid inclusions from around the E48 and E26 deposits in the Northparkes porphyry Cu-Au district, NSW, Australia. In addition, the strontium isotope composition of epidote was determined to test for the potential contribution of seawater in the Northparkes system given the postulated island arc setting and submarine character of some country rocks.

Oxygen isotope geothermometry calculations indicate potassic alteration occurred between ~600-700°C in magmatic/mineralized centers, persisting to ~450°C upon lateral transition into propylitic alteration. Across the propylitic facies, temperature progressively decreased outwards to <250°C. These temperature estimates and additional data from chlorite geothermometry were utilized to calculate the oxygen and hydrogen isotopic composition of the fluid in equilibrium with the sampled minerals. Results show that propylitic fluids spanned a range of compositions with $\delta^{18}\text{O}$ between 0.5 and 3.7‰ and δD between -49 and -17‰, excluding the data from two fluid inclusion extractions which were markedly lower. Comparison of these results with the modeled compositions of meteoric and/or magmatic fluids during their evolution/isotopic exchange with local country rocks shows that a magmatic fluid component must exist

across the propylitic halo during its formation. Strontium isotope data from propylitic epidote provide initial (based on formation at ~450 Ma) $^{87}\text{Sr}/^{86}\text{Sr}$ values in the range of 0.704099 to 0.704354, ruling out the presence of seawater as a second fluid in the system. Although we cannot exclude magmatic-meteoric mixing, especially towards the fringes of the system, our results support a model in which magmatic-derived fluid is the primary driver of propylitic alteration as it undergoes cooling and chemical equilibration during outwards infiltration into country rocks. This is consistent with chemical mass transfer calculations for Northparkes and published chemical-thermodynamic models that only require a magmatic fluid for the production of propylitic assemblages. In view of this, and supporting data from other deposits, we suggest that magmatic fluids are essential drivers of propylitic alteration in porphyry systems.

Introduction

The spatial coincidence between porphyry-style mineralization, potassic alteration and porphyritic intrusions led to the early concept that heat, metals and the mineralizing fluids may be derived from the intrusions themselves (e.g., Lindgren, 1905; Ransome, 1919; Emmons, 1927). Subsequent pioneering studies, including experimental work (e.g., Burnham and Jahns, 1962; Jahns and Burnham, 1969; Shinohara, 1994; Burnham, 1997), fluid inclusion (e.g., Roedder, 1971 and compilations by Roedder, 1984; Bodnar et al. 2014) and isotopic investigations (e.g., Sheppard et al., 1971; Sheppard and Gustafson, 1976) established the presence of a magmatic fluid in porphyry systems. It is now universally accepted that mineralization and potassic alteration are driven by the focused, commonly periodic, release of large volumes of magmatic fluids into the shallow crust (e.g., Ulrich et al., 2002; Seedorff et al., 2005; Spencer et al., 2015).

Propylitic alteration in porphyry systems is generally thought to be contemporaneous with the potassic alteration zone it encloses (*"propylitic and K-silicate alteration assemblages are probably contemporaneous and zonally related"*: Gustafson and Hunt, 1975; propylitic alteration is the *"lateral equivalent of potassic"*: Sillitoe, 2010). Despite this, it is widely accepted that meteoric waters are predominant (Seedorff et al., 2005), or exclusive (Proffett, 2003; Sillitoe, 2010; Ridley, 2013; Halley et al., 2015) in the propylitic alteration facies. In this view, meteoric fluids generate propylitic assemblages as they are heated on convective flow paths toward thermal anomalies centered on porphyry intrusions, and there is limited addition of metals or sulfur from magmatic sources. Consequently, the boundary between magmatic and meteoric fluid regimes has been considered to be essentially at the transition between the potassic and propylitic alteration facies (e.g., Fig. 15 of Proffett, 2003; Fig. 19 of Yang et al., 2009; Fig. 1 of Halley et al., 2015). This interpretation of propylitic alteration is largely based on its occurrence at the periphery of systems and the common assumption that propylitic alteration is isochemical apart from the addition of volatiles.

Detailed chemical, mineralogical and isotopic studies of propylitic alteration that attempted to establish the relative roles of different fluid sources in its generation are remarkably few. The pioneering study of

68 Ballantyne (1981) was the first to establish systematic changes in mineral assemblage, mineral chemistry,
69 fluid inclusion and oxygen isotopic data across propylitic halos at North Silver Bell, Safford and Christmas
70 (USA). He concluded that potassic and propylitic alteration were cogenetic: *“the lack of any abrupt change*
71 *in the inferred isotopic composition of the fluid across the potassic-propylitic boundary is in accordance with*
72 *the lack of any abrupt discontinuity in mineralogy, mineral chemistry or fluid temperatures at this point.*
73 *Propylitic alteration and potassic alteration were probably coeval”*. With regard to the propylitic alteration
74 fluid, Ballantyne inferred that the $\delta^{18}\text{O}$ of propylitic fluids decreased across the halo at North Silver Bell and
75 that *“even at the most remote sample locations [~1600 m from the limit of the biotite zone] a fluid*
76 *component heavier than normal meteoric water was involved unless water to rock ratios were vanishingly*
77 *small”*. Significantly, Ballantyne concluded that the data were *“consistent with an increasing meteoric water*
78 *component outwards, but also that a minor component with magmatic affinities persisted into the*
79 *propylitic facies. Whole rock chemical analyses indicate that propylitization involved chemical modification*
80 *of the host rocks at Silver Bell for at least 1600 m beyond the biotite zone”*. Notwithstanding these
81 conclusions, it is important to note that the oxygen isotopic measurements were only made on 13 calcite
82 separates, one epidote-chlorite pair and 6 whole rock samples.

83 Subsequently, Bowman et al. (1987) and Norman et al. (1991) carried out similar studies in the Bingham
84 (Utah) and SW Tintic (Utah) districts, respectively, and extended the work to include hydrogen isotopes.
85 Based on oxygen and hydrogen isotopic analysis of biotite, amphibole, K-feldspar, quartz, 5 whole rock
86 samples and 5 vein selvage samples (only 13 *“propylitic”* mineral separates) combined with rough
87 temperature estimates from fluid inclusion data, Bowman et al. (1987) also showed that there was a
88 decrease in $\delta^{18}\text{O}$ of propylitic fluids outwards, coupled with an apparent increase in δD . They concluded
89 that the inferred trend could be explained by one of two models: (1) mixing of magmatic fluid with
90 increasingly large amounts of formation water (with 25-40% magmatic water in the outer propylitic zone);
91 or (2) the interaction of meteoric or formation water with igneous rocks at low water/rock ratios over the
92 temperature range 350-600°C, probably in a deep reaction zone. Norman et al. (1991) analyzed 5 epidote, 6
93 chlorite, 8 calcite and 5 vein quartz samples plus 9 whole rocks. Based on their estimated propylitic fluid
94 compositions they concluded that meteoric fluids mixed with highly evolved, igneous-interacted meteoric
95 waters at low water/rock ratios, or alternatively with a *“late incursion of magmatic water unlike many other*
96 *porphyry Cu systems”*.

97 Zaluski et al. (1994) analyzed around 100 samples but only 3 were propylitic mineral separates (chlorite) on
98 which δD was determined, and two of these contained biotite contamination. Based on the results, they
99 concluded that propylitic alteration was *“most likely dominated by meteoric ground waters evolved at low*
100 *water/rock ratios”* although they also suggested some magmatic mixing was possible. It is, however,
101 arguable that this interpretation is inconsistent with the data presented, which show that magmatic fluid
102 must be predominant on the proposed mixing trend.

103 Thus, despite permissive evidence of magmatic fluid involvement, or indeed potential dominance in all
104 datasets, models proposed in these early studies leaned towards meteoric or formation water as the
105 primary driver of propylitic alteration, perhaps influenced by the prevailing view at the time that ground
106 water circulation around and within intrusive centers was extensive (e.g., Sheppard et al., 1971; Taylor,
107 1974; Sheppard and Gustafson, 1976; Cathles, 1977; Norton and Knight, 1977). However, with hindsight, it
108 is now believed that these studies overemphasized the significance of meteoric fluids (Hedenquist and
109 Richards, 1998; Sillitoe, 2010), and later works have subsequently demonstrated that sericitic alteration can
110 also be, and is perhaps more often, driven by magmatic-hydrothermal fluids (Hedenquist et al., 1998;
111 Watanabe and Hedenquist, 2001; Harris and Golding, 2002; Skewes et al., 2003; Rusk et al., 2004; Seedorff
112 and Einaudi, 2004; Harris et al., 2005; Reed et al., 2013).

113 There is a growing body of evidence that challenges the isochemical character of propylitic alteration and
114 the predominance of non-magmatic water in its formation. Mass balance calculations reveal the alteration
115 facies is consistently associated with metasomatic addition of metals such as Fe, Mn, Zn and Pb (Ulrich and
116 Heinrich, 2002; Derakhshani and Abdolzadeh, 2009; Siahcheshm et al., 2014; Pacey, 2016), probably in the
117 form of trace sulfides. Net addition of other elements (e.g., K, Cu) can also occur in strong propylitic
118 alteration (Pacey, 2016). Indeed, the spatial coincidence between propylitic alteration and whole rock base
119 metal geochemical anomalies surrounding porphyry deposits has long been observed (e.g., Jerome, 1966;
120 Cox et al., 1975; Jones, 1992; Zaluski et al., 1994; Ulrich and Heinrich, 2002). Only recently though have
121 trace element studies shown that a range of elements are present at elevated concentrations in the
122 propylitic minerals themselves (Cooke et al., 2014; Wilkinson et al., 2015; Pacey et al., this volume). Some
123 of these elements are typical porphyry pathfinder elements (Mn, Zn, Pb, Cu, Sb, As and Bi) inferred to be
124 ultimately derived from magmatic fluids. This work has also demonstrated how the concentration of these
125 elements and others (e.g., Ti, V, Co, Al, Si, Fe, Mg, Ca, Li, Ba, Sr) within epidote and/or chlorite display a
126 remarkably systematic spatial variation around porphyry magmatic-hydrothermal centers. Such hypogene
127 mobility of ore-related and other elements and their incorporation directly within propylitic alteration
128 minerals is strong evidence that the alteration facies is a surprisingly dynamic environment, at least in
129 terms of fluid flux and trace element dispersion. Further permissive evidence for magmatic fluid
130 involvement is provided by $\delta^{13}\text{C}$ data from calcite from propylitically-altered rocks which are consistent
131 with the presence of magmatic CO_2 in the alteration fluid (Ramírez et al., 2006; Djouka-Fonkwé et al.,
132 2012).

133 Recognizing this disconnect between the emerging evidence and the widely accepted paradigm for
134 propylitic alteration, this study was conceived to revisit the isotope tracing approach to test the alternative
135 models for fluid sources. Advances in analytical methods and publication of a wider range of experimental
136 fractionation factors and geothermometers since the early work enable better constraints to be imposed.
137 We no longer need to rely on potentially unrelated secondary fluid inclusion homogenization temperatures

138 (only a minimum estimate of fluid trapping) for temperature estimation. Most significantly, in this work we
139 focused on high purity propylitic mineral separates that avoid the uncertainties inherent in whole rock
140 investigations. Our study is based on a suite of very well-constrained samples from the Northparkes
141 porphyry Cu-Au district of Central West NSW, Australia, principally around the Endeavour (E)48 deposit.
142 Details of the geology and alteration in this system are available in Pacey et al. (2019) and a study of the
143 zonation of propylitic mineral chemistry in the district is provided by Pacey et al. (this volume).

144 **Geological Setting**

145 The Northparkes district lies within the Ordovician to earliest Silurian Junee-Narrowmine volcanic belt, one
146 of several such belts that comprise the Macquarie Arc, located outboard of Gondwana and thought to
147 represent an island arc (Crawford et al., 2007; Glen et al., 2007; Glen et al., 2012). Country rocks in the
148 Northparkes region comprise an evolutionary sequence of basaltic to trachytic volcanic-volcaniclastic
149 packages with a high-K to shoshonitic affinity (Lickfold et al., 2003; Crawford et al., 2007; Lickfold et al.,
150 2007). Krynen et al. (1990) identified three major stratigraphic packages: the Nelungaloo, Goonumbla and
151 Wombin Volcanics. The Middle to Late Ordovician age Goonumbla Volcanics, dominated by
152 trachyandesites, are intercalated with rare marine carbonates and contain peperitic textures, indicating a
153 dominantly submarine environment (Simpson et al., 2005; Pacey et al., 2019). However, within the Late
154 Ordovician to earliest Silurian Wombin Volcanics, trachytic welded ignimbrites and volcanic agglomerates
155 are present (Kolkert, 1998; Simpson et al., 2005; Pacey et al., 2019), indicating volcanism was at least partly
156 subaerial by that time. Therefore, based solely on geological evidence, there is the possibility that both
157 meteoric water and seawater could have been present during alteration at Northparkes.

158 Porphyry-related intrusive rocks are constrained as latest Ordovician to earliest Silurian (Lickfold et al.,
159 2003; Lickfold et al., 2007), hosted within the Wombin Volcanics, with which they appear broadly
160 comagmatic (Lickfold et al., 2003; Pacey et al., 2019). A cluster of five Cu-Au orebodies (E22, E26, E27, E48
161 and GRP314), as well as numerous prospects, occur in the district. Mineralization largely comprises
162 disseminated and fracture-hosted Cu-sulfides associated with quartz vein stockworks, and is hosted in the
163 center of potassic alteration zones of K-feldspar $\pm$ biotite $\pm$ magnetite (Fig. 1). Such alteration-
164 mineralization is developed around the margins and apices of complex, multiphase quartz monzonite
165 porphyry intrusions. These intrusions are narrow (~50 to 100 m in diameter) but vertically elongate (>1.4
166 km) and were emplaced within and above a large (~12 km diameter) stock that underlies much of the
167 mining area (Pacey et al., 2019). The latter varies in composition between an equigranular biotite quartz
168 monzonite and plagioclase-phyric alkali feldspar granite. Magmatic-hydrothermal phenomena, such as UST
169 textures, are common in the quartz monzonite intrusions (Heithersay and Walshe, 1995; Lickfold et al.,
170 2003; Pacey et al., 2019).

171 The intrusion-centered zones of K-feldspar $\pm$ biotite $\pm$ magnetite alteration grade outwards, with increasing
172 distance from the quartz monzonite porphyry intrusive complexes, to an annulus of biotite $\pm$ magnetite and
173 then into widespread propylitic alteration (Fig. 1). The propylitic facies is dominated by chlorite-epidote-
174 albite $\pm$ phengite $\pm$ calcite $\pm$ quartz $\pm$ pyrite $\pm$ anhydrite assemblages and covers an area 20x greater than
175 the potassic alteration (Pacey et al., 2019). The intensity of propylitic alteration is very variable as it is
176 developed around fractures and becomes pervasive where vein and fracture networks are closely spaced.
177 There is a general decrease in propylitic alteration intensity away from the center of the deposits and it is
178 most pervasive in permeable volcanic or fractured igneous rocks.

179 At E48 and GRP314, potassic alteration is locally overprinted by intense and texturally-destructive white
180 “sericite” (specific mineralogy uncertain)-albite-quartz-alunite $\pm$ chlorite alteration. Further, at E26 and
181 GRP314, veins of quartz and/or anhydrite that are spatially and temporally linked to late-mineralization
182 quartz monzonite porphyry intrusions are surrounded by “sericite”-quartz $\pm$ pyrite alteration (Pacey et al.,
183 2019). Previous isotopic investigations of both these assemblages suggested the involvement of magmatic
184 fluid (Wolfe, 1996; Harris and Golding, 2002).

185 Outside the immediate vicinity of the Northparkes deposits, a low-grade regional metamorphic assemblage
186 of chlorite, calcite, prehnite and pumpellyite is observed. However, there is no evidence to suggest a
187 metamorphic overprint within the mineralized district (Pacey et al., 2019). Indeed, post-mineralization
188 structural deformation is remarkably limited, probably a result of the biotite quartz monzonite-dominated
189 pluton forming a strain-resistant crustal block (Scheibner, 1993). The only notable feature is the Altona
190 Fault, a planar structure with unknown displacement that truncates the top of the E48 and GRP314
191 deposits. This structure dips gently eastwards at $\sim 15^\circ$, and is considered a relatively minor thrust fault (H.
192 Dalstra and L. Oosterwijk, unpub. report, 2005).

193 **Approach and Methods**

194 Fourteen epidote and fourteen chlorite mineral separates from samples across the propylitic alteration
195 zone surrounding the E48 deposit were prepared to determine their oxygen and hydrogen isotopic
196 compositions (Fig. 1; Table 1). All samples are from below the level of the Altona Fault, to ensure an
197 undisturbed relationship with mineralized centers. One additional epidote and two chlorite separates were
198 obtained from deposit-distal, regional metamorphic samples for comparison. The major element
199 compositions of all epidote and chlorite separates (Table 1) were reported by Pacey et al. (2019).

200 The oxygen isotope compositions of a further nine quartz separates from propylitic veins, along with five
201 quartz and five magnetite separates from potassic veins (including two potassic veins from E26), were also
202 determined to facilitate isotope geothermometry, based on quartz-epidote, quartz-chlorite and quartz-
203 magnetite pairs (Fig. 1; Table 1). Where oxygen isotope geothermometry was not possible, the chlorite
204 geothermometer of Jowett (1991) was used to estimate sample formation temperatures. These data reveal

the thermal gradient associated with alteration. Such geothermometry was essential to define the temperature of crystallization of the potassic and propylitic assemblages and therefore enable calculation of $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$, i.e. the isotopic composition of the alteration fluids in equilibrium with the minerals. As the only viable means of obtaining constraints on the hydrogen isotope composition of the magmatic-derived potassic alteration fluids, $\delta\text{D}_{\text{H}_2\text{O}}$ was also determined directly by bulk decrepitation of fluid inclusions in quartz from two potassic veins. Alteration $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$ were then compared against the modelled range that might be expected for magmatic or meteoric waters undergoing progressive exchange with the host rocks. To inform the modelling, $\delta^{18}\text{O}$ and δD were also determined for several whole rock samples.

Further, Pacey et al. (2019) reported the $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{86}\text{Sr}$ ratios for fifteen epidote and ten whole rock samples of freshest composition, the latter representing the biotite quartz monzonite, alkali feldspar granite and trachyandesites. These data permitted calculation of the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the samples, facilitating a direct comparison of strontium in epidote with that of either intrusive or country rocks and to assess the potential role of seawater.

Alteration samples were collected based on three main considerations: (1) their ability to provide suitably coarse and clean grains of alteration minerals; (2) textural evidence of isotopic equilibrium, i.e. coexisting phases in veins/vugs and/or intergrown aggregates of quartz-epidote-chlorite; and (3) to provide spatial coverage around E48 (Fig. 1). Whole rock samples were collected from the freshest/least altered examples of the most homogeneous lithologies. Mineral separates were prepared according to the procedure outlined in Appendix 1. The high purity (>95% mineral of interest) of the separates was confirmed by XRD analysis on a subset of the samples. Oxygen and hydrogen isotope analytical methods are also reported in Appendix 1.

Results

Results of oxygen and hydrogen isotope analyses are provided in Table 2 and presented graphically in Figure 2. Based on 21 replicate oxygen isotope analyses and 5 replicate hydrogen isotope analyses (replicate data also provided in Table 2), standard errors (1σ) arising from a combination of both analytical uncertainty and within-sample variability are $\pm 0.2\text{‰}$ and $\pm 2\text{‰}$ respectively.

Whole rocks

Of an initial six whole rock samples, only two were analyzed successfully for oxygen isotope composition (NP13AP027 and NP13AP283), with an average oxygen yield of $11.0\text{ }\mu\text{mol/mg}$. Both were satisfactorily repeated, with duplicates $<0.6\text{‰}$ different from the initial results. The remaining samples produced anomalously high yields ($>30\text{ }\mu\text{mol/mg}$) indicating contamination by moisture from reactive phases, most probably clays. Consequently, data are only available for a sample of fresh biotite quartz monzonite with

238 average $\delta^{18}\text{O} = 5.8\text{‰}$ and hematite-reddened, but still relatively fresh, alkali feldspar granite with average
239 $\delta^{18}\text{O} = 9.2\text{‰}$.

240 The hydrogen yield from all six whole rock samples averaged $0.45 \mu\text{mol/mg}$, approximately equivalent to
241 $0.8 \text{ wt. \%}$ contained H_2O . Combined, the analyses give an average $\delta\text{D} = -74\text{‰}$, with trachyandesite
242 averaging -73‰ , alkali feldspar granite -80‰ and biotite quartz monzonite -69‰ . Although no repeat
243 analyses were conducted, each lithology was represented by two separate samples which differed in δD by
244 $\sim 20\text{‰}$. These differences, and variable yields and lack of reproducible oxygen isotope data for the same
245 samples, suggest whole rock analyses should be treated with caution.

246 *Quartz*

247 For all quartz separates, the oxygen yield averaged $15.9 \mu\text{mol/mg}$ ($n = 21$), compared to a theoretical 100%
248 yield of $16.6 \mu\text{mol/mg}$ for pure quartz. Five quartz separates were analyzed twice, and one separate
249 analyzed three times. Repeats showed natural internal variability up to $\pm 0.4\text{‰}$ (NP12AP044), but typically
250 around $\pm 0.2\text{‰}$. Quartz samples from propylitic veins displayed an average $\delta^{18}\text{O} = 9.0\text{‰}$ (ranging from
251 $7.4\text{--}10.8\text{‰}$), as did those from potassic veins ($8.1\text{--}10.6\text{‰}$).

252 Thermal decrepitation of fluid inclusions in two quartz samples from potassic veins both gave a hydrogen
253 yield of $0.09 \mu\text{mol/mg}$ with resulting δD of -73 and -48‰ .

254 *Magnetite*

255 Magnetite separates consistently gave a relatively low oxygen yield of $6.4 \mu\text{mol/mg}$ ($n = 8$), compared to a
256 theoretical yield of $8.6 \mu\text{mol/mg}$ for pure Fe_3O_4 . This is unlikely to be a result of impurities because XRD
257 data showed the separates were very clean and the presence of minor hematite and/or quartz would not
258 result in a lower yield. Rather, this is likely an intrinsic analytical problem related to the spinel structure of
259 magnetite which makes total liberation of oxygen difficult. Three separates were analyzed twice, suggesting
260 a typical standard error of $\pm 0.3\text{‰}$. The average $\delta^{18}\text{O}$ for potassic-stage magnetite was 1.7‰ , with a range
261 of $0.7\text{--}2.5\text{‰}$.

262 *Epidote*

263 The average oxygen yield from epidote was $12.6 \mu\text{mol/mg}$ ($n = 23$); the theoretical 100% yield (average =
264 $13.6 \mu\text{mol/mg}$) was calculated for each sample individually based on the SEM-EDS compositional data
265 (Table 1) and assumed 100% purity of the separate. The average yield of 93% is generally considered
266 excellent for epidote, because Ca may also react with ClF_3 during laser heating to form stable fluorite (CaF_2)
267 that can inhibit further liberation of O_2 from grain centers. Seven separates were analyzed twice and one
268 separate three times, indicating a typical standard error of $\pm 0.2\text{‰}$. Propylitic epidote gave an average $\delta^{18}\text{O}$
269 value of 3.2‰ , and a range of $1.9\text{--}4.3\text{‰}$. This contrasts with the metamorphic epidote separate for which
270 $\delta^{18}\text{O}$ was 7.6‰ .

271 On average, epidote separates yielded 0.94 $\mu\text{mol/mg H}_2$ ($n = 17$) compared to a theoretical yield of 1.04
272 $\mu\text{mol/mg}$ based on SEM-EDS compositional data and assuming 100% purity and perfect stoichiometric
273 quantities of OH. This average analytical yield corresponds to ~ 1.7 wt. % H_2O in epidote and analytical totals
274 of all 3,856 SEM-EDS analyses of epidote from the district (Pacey et al., 2019) average 98.5 wt. %, giving a
275 combined total of ~ 100 wt. %. These calculations imply hydrogen contributions from any fluid inclusions
276 present in epidote were negligible. Replicate analyses of two epidote separates produced δD values that
277 were 5.1‰ and 2.2‰ different to initial results, indicating a standard error of approximately ± 2 ‰.
278 Propylitic epidote samples gave an average δD of 67‰, with a range of 52‰ to 86‰. Metamorphic
279 epidote returned a δD value of 58‰.

280 *Chlorite*

281 Chlorite oxygen yields averaged 14.0 $\mu\text{mol/mg}$ ($n = 21$), compared to a theoretical average of 14.7
282 $\mu\text{mol/mg}$. Again, theoretical yields were calculated based on SEM-EDS compositional data (Table 1) for
283 each sample. The lowest yield was 74% for NP13AP249. However, a repeat of this sample with a 98% yield
284 gave a value only 0.2‰ different to the original. In total, five samples were repeated and yielded a typical
285 standard error of ± 0.2 ‰. Propylitic chlorite samples gave an average $\delta^{18}\text{O}$ of 2.1‰, and a range of 0.8-
286 3.1‰. By contrast, the two metamorphic chlorite samples returned significantly higher values of 5.7 and
287 6.5‰.

288 Out of necessity, chlorite separates were weighed prior to removal of adsorbed water so as to minimize the
289 time available for resorption of atmospheric moisture during later handling. Consequently, the calculated
290 yields of hydrogen from chlorite consistently appear slightly low, averaging only 4.5 $\mu\text{mol/mg}$ ($n = 18$),
291 compared to the average theoretical yield of 6.5 $\mu\text{mol/mg}$. Yield calculations also assume 100% purity and
292 stoichiometric OH; any substitution of the latter by F would also result in lowered yield. Regardless, yields
293 were relatively consistent, in the range 3.0-5.7 $\mu\text{mol/mg}$, and provided a useful check on the analytical
294 procedure. All propylitic chlorite separates returned δD values over a limited range of -50‰ to -66‰, with
295 an average of -59‰. The two metamorphic samples analyzed were isotopically lighter ($\delta\text{D} = -66$ and -72 ‰).
296 Replicate analysis of three separates provided repeat results only 4.6‰, 2.8‰ and 1.2‰ different from
297 initial results, suggesting typical standard errors around ± 1.4 ‰.

298 **Discussion**

299 *Independent alteration temperature constraints*

300 To provide context in which to assess subsequent geothermometry results, we first provide an overview of
301 independent constraints on the temperatures expected during potassic and propylitic alteration.

302 *Potassic alteration:* The maximum temperature in the potassically-altered core of porphyry systems is
303 limited by the water-saturated solidus of the felsic melts from which the magmatic aqueous fluid exsolved.
304 For water-saturated granitic melts this implies temperatures of $\sim 750^\circ\text{C}$ at pressures of 100 MPa within the

305 shallow crust (e.g., Huang and Wyllie, 1973; Ebadi and Johannes, 1991; Johannes and Holtz, 1996).
306 However, the presence of certain species such as F and B may lower the solidus further (Manning, 1981). At
307 Northparkes, there is clear evidence for the coexistence of melt, high temperature magmatic fluids and
308 potassic alteration (Pacey et al., 2019).

309 Minimum temperatures of crystallization of quartz formed in the magmatic-hydrothermal transition at
310 Northparkes are constrained by fluid inclusion homogenization temperatures (T_h) averaging $\sim 500^\circ\text{C}$,
311 although several samples showed $T_h > 650^\circ\text{C}$ (Lickfold et al., 2003). Heithersay and Walshe (1995) obtained
312 higher values, with an average T_h for inclusions in aplitic vein dikes of $\sim 800^\circ\text{C}$, and in other magmatic-
313 hydrothermal features of $\sim 700^\circ\text{C}$. For the main-stage, sulfide-bearing, quartz-stockwork veins, Lickfold et al.
314 (2003) reported an average T_h of $\sim 500^\circ\text{C}$, but again several analyses were $> 650^\circ\text{C}$. For the same veins,
315 Heithersay and Walshe (1995) reported an average T_h of $\sim 600^\circ\text{C}$. In a review of fluid inclusions from
316 porphyry copper deposits, Bodnar et al. (2014) suggested T_h values $> 600^\circ\text{C}$ in veins associated with potassic
317 alteration should be much more common than often reported, simply because this is the upper
318 temperature limit of many fluid inclusion stages. Based on this information, a likely temperature range for
319 potassic alteration at Northparkes is $500\text{--}700^\circ\text{C}$.

320 *Propylitic alteration:* In a worldwide review of modern geothermal systems, Bird and Spieler (2004) showed
321 that epidote is typically only abundant above $\sim 250^\circ\text{C}$ and remains stable to $> 350^\circ\text{C}$. This same study
322 suggests chlorite is typically developed in the range of $\sim 120\text{--}400^\circ\text{C}$, although phase relationships indicate it
323 can be stable to $\sim 550^\circ\text{C}$ (Reed et al., 2013). Given that the formation of albite is often driven by conversion
324 of the plagioclase anorthite component into epidote, then phase relationships (assuming hematite
325 saturation at a pressure of 500 bars) suggest that coexisting high Fe epidote (i.e. $X_{\text{Ep}} > 0.9$), albite and
326 hematite define a lower temperature limit of $\sim 350^\circ\text{C}$ (Beane and Titley, 1981). To be stable at lower
327 temperatures, the Fe-content of epidote and/or anorthite component of plagioclase must decrease. The
328 upper temperature limit of this assemblage is $\sim 425^\circ\text{C}$, at which point coexisting Fe-rich garnet and
329 anorthite are thermodynamically more stable.

330 Only limited data are available for fluid inclusions from propylitic veins, but most T_h values are $100\text{--}500^\circ\text{C}$
331 (Bodnar et al., 2014). At North Silver Bell, Arizona, the highest T_h values of 375°C were documented in the
332 transition from potassic to propylitic alteration, and they progressively decreased outwards to 232°C ,
333 marked by the disappearance of epidote, and ultimately 193°C in the outer, chlorite-dominated zone
334 (Ballantyne, 1981). Similarly, Norman et al. (1991) recorded an outwards decrease in T_h from 351 to 160°C
335 across the propylitic zone at SW Tintic, Utah. At Bingham, Utah, the reported outwards decrease in T_h was
336 from $\sim 450^\circ\text{C}$ to 350°C (Bowman et al., 1987). At El Teniente, Chile, T_h values from two propylitic epidote-
337 quartz vein samples were between $247\text{--}338^\circ\text{C}$ (J.J. Wilkinson, pers. obs.). Assuming near-hydrostatic
338 conditions in the propylitic halo at depths of ≤ 5 km, the maximum temperature correction to T_h values due

339 to trapping pressure for low-to-moderate salinity fluids would be $\sim 30^{\circ}\text{C}$, assuming an isochoric dP/dT of
340 $\sim 1.8 \text{ MPa}/^{\circ}\text{C}$. Based on these data, it is likely that temperatures across propylitic halos are typically ~ 400 to
341 $< 200^{\circ}\text{C}$ but range from the lower limit of potassic alteration ($\sim 500^{\circ}\text{C}$) to $< 160^{\circ}\text{C}$.

342 *Oxygen isotope geothermometry*

343 A brief review of available mineral-water oxygen isotope calibrations is provided in Appendix 2, to provide
344 background and justification for our choice of preferred calibrations used in the geothermometry
345 calculations. In summary, we utilize the experimentally-based fractionation equations of Zhang et al. (1989)
346 and Cole and Ripley (1999) for the quartz-water and chlorite-water systems respectively, and the
347 theoretically-calculated fractionation equations of Zheng (1991) and Zheng (1993) for the magnetite-water
348 and epidote-water systems respectively.

349 Results of magnetite-quartz, epidote-quartz and chlorite-quartz oxygen isotope geothermometry are given
350 in Table 3. When plotted as a function of distance from the E48 center (Fig. 3), isotope equilibrium
351 temperatures can be approximated by a power law decrease.

352 Magnetite-quartz equilibrium suggests temperatures in the range $600\text{--}700^{\circ}\text{C}$, consistent with previous fluid
353 inclusion data from potassic alteration at Northparkes. It is worth highlighting that temperatures calculated
354 using other fractionation equations are within $\pm 13^{\circ}\text{C}$ of our preferred estimates (Appendix 2).

355 For epidote-quartz and chlorite-quartz assemblages, equilibrium temperatures are in the range $420\text{--}240^{\circ}\text{C}$,
356 consistent with data from other systems. For two samples, temperatures were estimated independently by
357 both epidote-quartz and chlorite-quartz mineral pairs. Results differ by only 2°C for NP13AP249, an
358 epidote-quartz vein (sample pictured in fig. 22j of Pacey et al. 2019), and only 8°C for NP13AP016, a vug
359 containing epidote, chlorite and quartz. Further, it is notable that temperatures obtained using other
360 available fractionation equations are all within $\pm 19^{\circ}\text{C}$ and $\pm 16^{\circ}\text{C}$ of our preferred estimates for epidote-
361 quartz and chlorite-quartz pairs respectively (Appendix 2).

362 *Chlorite geothermometry*

363 Alteration temperatures were also estimated by chlorite geothermometry based on the SEM-EDS
364 compositional data (Table 1) of Pacey et al. (2019). Several empirical and theoretical chlorite
365 geothermometers have been previously proposed (Cathelineau and Nieva, 1985; Walshe, 1986; Kranidiotis
366 and MacLean, 1987; Jowett, 1991) with some disagreement between results. To establish which
367 geothermometer appears most reliable in the Northparkes context, they were first applied to samples for
368 which chlorite-quartz oxygen isotope temperatures had been determined. This shows that the equation of
369 Jowett (1991) produces chlorite thermometry results that are most consistent with the oxygen isotope
370 temperatures (Table 3), hence results from this equation are used to extend temperature estimates to
371 samples where mineral pairs for oxygen isotope thermometry could not be separated (Table 4). However,

372 given the approximate discrepancy of $\pm 50^{\circ}\text{C}$ between the thermometry approaches, results from chlorite
373 geothermometry can only be considered rough estimates of average temperatures at different positions
374 within the propylitic halo during its formation. For this reason, preference is given to results which utilize
375 formation temperatures based on isotope geothermometry.

376 *Estimation of alteration $\delta^{18}\text{O}_{\text{H}_2\text{O}}$*

377 The $\delta^{18}\text{O}$ value of the alteration fluid in equilibrium with analyzed mineral pairs was obtained directly via
378 the isotope thermometry approach (Table 4). For all other samples, the formation temperature calculated
379 via the Jowett (1991) chlorite geothermometry equation was used in conjunction with the appropriate
380 mineral-water fractionation equation to estimate $\delta^{18}\text{O}_{\text{H}_2\text{O}}$. Clearly, when the chlorite temperature was
381 combined with epidote mineral data, this approach assumes that chlorite and epidote were coeval. In eight
382 samples, both coexisting epidote and chlorite were analyzed (Table 4), allowing paired estimates of
383 alteration $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ to be calculated. On average, these independent estimates for a given sample are within
384 0.6‰ of one another, although $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values obtained from chlorite are generally slightly lower than
385 those from epidote, particularly for the lower $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ samples (Fig. 4A).

386 Results show that fluids associated with the potassic-stage quartz-magnetite assemblage have significantly
387 higher $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (7.6-9.0‰) than propylitic fluids (0.5-3.7‰). The metamorphic samples yielded distinct
388 compositions between these two groups (5.1-6.8‰). Comparison between estimated formation
389 temperature and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (Fig. 5A) shows that the majority of data correlate positively, as would be
390 expected where fluids were equilibrating with similar rocks over a range of temperatures. Spatially, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$
391 is seen to broadly decrease across the propylitic zone with progression away from the E48 center,
392 particularly when considering only results based on more reliable estimates of formation temperature from
393 isotope geothermometry (Fig. 5B).

394 *Estimation of alteration $\delta\text{D}_{\text{H}_2\text{O}}$*

395 A review of the available mineral-water hydrogen isotope calibrations is provided in Appendix 2. In
396 summary, we utilize the experimentally-derived calibrations of Chacko et al. (1999) and Graham et al.,
397 (1984) to calculate alteration $\delta\text{D}_{\text{H}_2\text{O}}$ in the epidote-water and chlorite-water systems respectively.

398 Epidote: Based on epidote data, propylitic fluids appear to have had δD in the range -20 to -49‰, with a
399 comparable range for compositions calculated using epidote-quartz isotope thermometry and chlorite
400 geothermometry (Table 4).

401 *Chlorite:* Results from calculations based on chlorite hydrogen data suggest propylitic fluids with $\delta\text{D}_{\text{H}_2\text{O}}$
402 values in the range -17 to -33‰ (Table 4). These values are consistent with the higher end of the range
403 estimated from epidote. However, it is stressed that hydrogen isotope fractionation in the chlorite-water

404 system is currently poorly understood, partly owing to the slow nature of isotopic exchange below ~500°C
405 (Appendix 2). Consequently, the calibration of Graham et al., (1984) used to calculate these δD_{H_2O} values is
406 the only one which has been published and is based on experimental data between 500-700°C. Although
407 this is outside the range of temperatures determined in this study, it is used here in the absence of a more
408 appropriate alternative and is reliant on the assumption that fractionation remains not strongly
409 temperature-dependent below 500°C. However, preliminary data reported by Heijboer and Vennemann
410 (2008) actually suggest a strong temperature-dependency of hydrogen fractionation in the chlorite-water
411 system between 200-300°C.

412 Therefore, our chlorite-based δD_{H_2O} values are clearly associated with significant unconstrained uncertainty
413 and, where data are available for coexisting epidote and chlorite in the same sample, four of the δD_{H_2O}
414 results are not in good agreement (Fig. 4B). We consider it most likely this is because the chlorite-water
415 hydrogen calibration of Graham et al., (1984) is inappropriate for the conditions in question. However, it
416 remains a possibility such disagreement is also owing to errors in the chosen epidote-water hydrogen
417 calibration, inaccurate crystallization temperature estimates and/or that epidote and chlorite in these
418 samples were not formed in isotopic equilibrium with each other. Therefore, given the lack of confidence in
419 these results, preference should be given to alteration δD_{H_2O} estimates derived from epidote data.

420 As observed for $\delta^{18}O_{H_2O}$, there is a broad correlation between alteration temperature and δD_{H_2O} (Fig. 5C),
421 albeit with more scatter. Notably there is also an apparent systematic increase in δD_{H_2O} from potassic to
422 propylitic alteration, as well as across the propylitic zone (Fig. 5D). Again, this is particularly true when
423 considering only results based on more reliable estimates of formation temperature from isotope
424 geothermometry.

425 *Fluid inclusions:* The amount of hydrogen present in quartz is principally a function of the abundance of
426 fluid inclusions, although some structurally-bound OH can exist. Although fluid inclusion extraction by
427 thermal decrepitation is prone to generating artificially low δD (Faure, 2003), it has been shown that
428 heating at $\leq 750^\circ C$ (as per our methodology, see Appendix 1) may be reliable, particularly where hydrogen
429 yields are greater than $\sim 0.05 \mu\text{mol/mg}$ quartz (e.g., Gleeson et al., 2008). In our study, yields were above
430 this value ($0.09 \mu\text{mol/mg}$; Table 2) suggesting that the results might be reliable. The δD_{H_2O} of potassic fluids
431 determined by this method (-48 and -73‰) is consistent with previous studies (see review by Hedenquist
432 and Lowenstern, 1994) and, in combination with the obtained $\delta^{18}O_{H_2O}$ of 7.1-9.0‰, suggests a magmatic
433 water origin.

434 *Modelling potential fluid sources*

435 In the Northparkes system, three major fluid sources could have potentially contributed to propylitic
436 alteration: (1) spent porphyry ore/potassic alteration fluids of magmatic origin as they cooled and migrated

437 away from thermal centers; (2) meteoric waters which were heated as they flowed in toward thermal
438 centers, during convective circulation around the intrusive system; and (3) heated seawater which could
439 have been present in the local environment.

440 *Strontium isotopes:* Strontium isotopes are not significantly fractionated between mineral and fluid phases,
441 hence the initial strontium isotopic composition ($^{87}\text{Sr}/^{86}\text{Sr}_i$) of an alteration mineral essentially records the
442 composition of the fluid from which it precipitated. The strontium isotope ratio of a fluid is controlled by
443 the dissolution of, and/or ion exchange with, rubidium- and strontium-bearing minerals in its source region
444 and along its flow path (e.g., Peterman and Stuckless, 1992; Banner, 1995; McNutt, 2000; Frost and Toner,
445 2004). Therefore, $^{87}\text{Sr}/^{86}\text{Sr}_i$ of an alteration mineral reflects the source of the alteration fluid and the rocks
446 with which it has equilibrated.

447 Results of rubidium and strontium isotope analyses of volcanic and plutonic rocks, along with epidote
448 separates from Northparkes were used by Pacey et al. (2019) to establish an estimated formation date of
449 450 ± 11 Ma for the system, in agreement with other available age estimates (Lickfold et al., 2003; Lickfold
450 et al., 2007). This date was used to calculate the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the samples (Table 5; Fig. 6).
451 Average initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for volcanic country rocks, plutonic rocks (biotite quartz monzonite and alkali
452 feldspar granite) and propylitic epidote were 0.704206 ± 0.000032 ($n = 4$, 1σ), 0.704174 ± 0.000044 ($n = 6$,
453 1σ) and 0.704212 ± 0.000090 ($n = 14$, 1σ) respectively. One sample of metamorphic epidote, although of
454 unknown age, gave a distinct initial $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.704616 assuming formation at 450 Ma. These results are
455 in good agreement with those reported by Cooke et al. (2007) who analyzed five intrusive rocks from
456 Northparkes (biotite quartz monzonite and quartz monzonite porphyry intrusions) that gave an average
457 initial $^{87}\text{Sr}/^{86}\text{Sr}$ 0.70406 ± 0.00031 (1σ) and one epidote sample from the E27 deposit with an initial $^{87}\text{Sr}/^{86}\text{Sr}$
458 of 0.70424, based on an assumed formation age of 440 Ma.

459 Both intrusive and country rock lithologies at Northparkes have overlapping strontium isotopic
460 compositions (Fig. 6A), likely owing to their broadly similar age and magma genesis. The average $^{87}\text{Sr}/^{86}\text{Sr}_i$
461 of 0.7042 is in good agreement with the presumed island arc tectonic setting (e.g., Simpson et al., 2005),
462 indicating limited or no crustal contamination with ratios close to the bulk silicate earth value of 0.7045
463 (e.g., Salters and Stracke, 2004; Workman and Hart, 2005).

464 Propylitic epidote shows a wider, but still relatively limited range in its strontium isotopic composition,
465 encompassing the full range of whole rock values (Fig. 6A). An increase in epidote $^{87}\text{Sr}/^{86}\text{Sr}_i$ away from the
466 E48 deposit is apparent (Fig. 6B), although there is a lot of scatter. This could be interpreted in terms of
467 outward equilibration between fluids initially containing magmatic strontium and the country rocks that
468 have slightly higher $^{87}\text{Sr}/^{86}\text{Sr}_i$, or by progressive mixing with external (meteoric) fluids that had equilibrated
469 with the country rocks. Irrespective of the veracity of either of these models, given that the most proximal
470 epidotes (<600 m) yield $^{87}\text{Sr}/^{86}\text{Sr}_i$ values that are inconsistent with country rock equilibration, it is concluded

471 that these samples at least are likely to be dominated by magmatic fluid-derived strontium. Seawater
472 $^{87}\text{Sr}/^{86}\text{Sr}$ has remained at >0.7065 throughout the Phanerozoic, and during the Late Ordovician/Early
473 Silurian was approximately 0.708-0.709 (e.g., Burke et al., 1982; Qing et al., 1998; Veizer et al., 1999).
474 Because of these very high values relative to the data reported here, we consider that there was no
475 significant ($<5\%$) involvement of seawater either directly or via interaction with phases precipitated from
476 seawater (e.g., calcite) in the Northparkes system.

477 *Oxygen and hydrogen isotopes:* At the time of formation, broadly constrained to 435-455 Ma (Perkins et al.,
478 1990; Lickfold et al., 2003; Lickfold et al., 2007; Pacey et al., 2019), paleogeographic reconstructions
479 indicate that Northparkes was located at a latitude of approximately 20°N , outboard of eastern Gondwana
480 (Glen et al., 1998; Scotese, 2001; van Hinsbergen et al., 2015). Further, the submarine character of all
481 country rocks, including those broadly coeval with mineralization, suggests a low altitude environment.
482 Therefore, based on the global meteoric water line of Craig (1961) and observations of modern
483 precipitation (Bowen and Revenaugh, 2003), meteoric fluids would be expected to have an initial isotopic
484 composition of $\delta^{18}\text{O} \approx -3\text{‰}$ and $\delta\text{D} \approx -15\text{‰}$. This assumes the bulk oxygen and hydrogen isotopic
485 composition of seawater has remained constant since the Late Ordovician, which, although still uncertain,
486 is broadly in agreement with studies that suggest Phanerozoic values have remained in a narrow range
487 close to the present day composition (Veizer et al., 1997; Lécuyer et al., 1998; Jaffrés et al., 2007). In
488 contrast, the composition of magmatic-derived fluids responsible for potassic alteration in porphyry
489 systems is thought to be in the range of $\delta^{18}\text{O} = 6$ to 9‰ and $\delta\text{D} = -35$ to -75‰ (Sheppard et al., 1971;
490 Taylor, 1979; Hedenquist and Lowenstern, 1994). This is in good agreement with our results from potassic
491 veins which average $\delta^{18}\text{O}_{\text{H}_2\text{O}} = 8\text{‰}$ and $\delta\text{D}_{\text{H}_2\text{O}} = -60\text{‰}$ (Table 4).

492 The principal lithologies hosting the magmatic-hydrothermal system at Northparkes are the biotite quartz
493 monzonite pluton and trachyandesite volcanics. Based on global compilations of oxygen and hydrogen
494 isotope data for unaltered whole rock samples (Taylor, 1968; Taylor, 1974; Taylor, 1978), basalts, gabbros,
495 syenites and andesites have an average $\delta^{18}\text{O} \approx 6\text{‰}$ (mostly in the range of 5 to 8‰) and $\delta\text{D} \approx -70\text{‰}$ (mostly
496 in the range of -50 to -100‰). Although data from fresh, unaltered whole rock samples from Northparkes
497 are scarce, available results are in good agreement with these values, with the biotite quartz monzonite
498 yielding an average $\delta^{18}\text{O}$ of 5.8‰ , and analyses of all biotite quartz monzonite and trachyandesite samples
499 yielding an average δD of -71‰ .

500 These constraints on the initial isotopic composition of end-member fluids and the rocks with which they
501 may have interacted are the basis for our isotopic exchange modelling approach (Fig. 7). The isotopic
502 evolution paths of meteoric and magmatic-derived potassic alteration fluids were calculated over a range
503 of fixed temperatures during progressive equilibration with the country rock (i.e. toward progressively
504 lower effective water/rock ratios) using the equation of Ohmoto and Rye (1974). In this approach, it is

505 reasonably assumed that water-rock oxygen isotope equilibration is controlled by orthoclase and
506 plagioclase feldspars, and hydrogen isotope equilibration is controlled by biotite, as these are the most
507 abundant phases in the host rocks. At infinitely small water/rock ratios (<0.001) both fluids approach the
508 same range of temperature-dependent compositions which represent the line of full equilibration/rock
509 buffering (dashed line in Fig. 7), beyond which each end-member fluid cannot pass. This boundary is
510 independent of the starting composition of the fluids, being controlled by the ambient temperature, rock
511 composition and mineral-fluid fractionation factors for the minerals that dominate isotopic exchange. It
512 defines two domains: above the line any fluid composition must have a meteoric component and below the
513 line, fluids must have a magmatic-derived component. Given the uncertainties in input parameters and the
514 simplicity of the approach the exact positions of modelled curves should not be interpreted too literally.
515 Nonetheless, the model provides a useful framework within which the calculated $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$ for the
516 fluids at Northparkes can be interpreted.

517 The calculated $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$ data are compared with the model results in Figure 7. Metamorphic
518 fluids, although represented by only three data points, are distinct from fluids involved in
519 mineralization/alteration having relatively high $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$. It is noteworthy that the chlorite-derived
520 data plot adjacent to the line of full equilibration: suggesting full rock buffering, as would be expected for
521 metamorphic water. Propylitic fluid data plot in an array between magmatic-derived potassic alteration
522 fluids and meteoric waters. Broadly, there is a decrease in estimated temperature moving to lower $\delta^{18}\text{O}_{\text{H}_2\text{O}}$
523 and higher $\delta\text{D}_{\text{H}_2\text{O}}$ which generally correlates with increasing distance (see data labels in Fig. 7). This is
524 indicative of a relatively systematic behavior, as previously noted if plotting $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$ as a function
525 of distance from the porphyry center, with $\delta\text{D}_{\text{H}_2\text{O}}$ producing a curved trend in comparison to $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ which
526 shows a fairly flat trend with a sharp increase into the potassic samples (Fig. 5B,D). These spatial
527 relationships are entirely consistent with isotopic equilibration of fluids with rock where the oxygen
528 exchange proceeds faster than the hydrogen exchange because of the difference in the ratio of oxygen and
529 hydrogen in fluids to oxygen and hydrogen in the rock (Ohmoto and Rye, 1974).

530 Similar trends in $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$ were reported by Bowman et al. (1987) at Bingham, Utah and by
531 Parsapoor et al. (2014) at Darreh-Zar, Iran, and at North Silver Bell, Ballantyne (1981) also documented an
532 outwards decrease in $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ of the alteration fluid. Thus, the behavior we have established here has been
533 observed in a number of systems.

534 On its own, a trend of decreasing $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and increasing $\delta\text{D}_{\text{H}_2\text{O}}$ outwards at Northparkes does not
535 distinguish between a cooling-equilibrating magmatic-derived fluid, increasingly meteoric-dominated
536 mixtures with distance or warming-equilibrating meteoric waters. However, it is important to emphasize
537 that all but six of the data fall well-below the line of full equilibration and so the majority of the fluids

involved must contain a magmatic component, even in some of the most distal samples (e.g., NP12AP003, 1710 m from E48 and NP12AP036, 1630 m from E48). Five of the remaining six samples plot on or very near the line of full equilibration and only one sample must contain a meteoric component according to the model. Thus, the data appear to rule out warming meteoric fluids as the principal driver of propylitic alteration and implicate magmatic-derived fluid involvement to distances of at least 1.6 km. Notably, the relatively systematic behavior of calculated propylitic $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$ data (with temperature and distance from deposit centers) is also a remarkably good fit to the isotopic evolution that might be envisaged for a magmatic-derived, potassic alteration fluid that progressively cools and equilibrates during further outwards infiltration into country rocks (red arrow in Fig. 7).

Additional evidence for magmatic fluid predominance: Based on the oxygen and hydrogen isotope results presented it is not possible to easily distinguish between a propylitic alteration zone principally driven by cooling magmatic fluids or one in which mixing between partially equilibrated magmatic and meteoric fluids occurred. In the latter case, there are many hypothetical mixing paths that could be constructed to account for the results. However, the strontium data suggest that magmatic fluids were predominant in the inner 600 m and chlorite chemistry data define a proximal depletion zone for Li, Ca, Ba, Pb and Cu out to 3-4 km from E48 with an increase in concentrations beyond that (Pacey et al., this volume) which is difficult to account for by models invoking inflowing meteoric water. Furthermore, an enrichment in elements such as Mn and Zn in chlorite and Mn and Bi in epidote are observed in a well-defined halo around E48 that peaks at ~800 m (Pacey et al., this volume). Mass transfer analysis shows that these elements (plus As) are very likely to be metasomatically added by magmatic fluids (Pacey 2016), with enrichment appearing to extend to 2-3 km. Similar metasomatic addition of metals such as Fe, Mn, Zn and Pb to the propylitic halo has also been reported in other porphyry systems (Ulrich and Heinrich, 2002; Derakhshani and Abdolzadeh, 2009; Siahcheshm et al., 2014) which can be most easily explained by a magmatic origin. Igneous carbon also appears to be predominant in propylitic halos as evidenced by carbon isotope systematics in the Collahuasi district, Chile (Djouka-Fonkwé et al., 2012) and at Mantos Blancos, Chile (Ramírez et al., 2006). In the former study, mass transfer analysis concluded net addition of (igneous) carbon occurred, as also observed at Northparkes (Pacey, 2016).

Taken together, we believe there is convincing evidence that the propylitic alteration zone in porphyry systems is the lateral equivalent of the potassic zone, driven principally by magmatic-derived fluids undergoing cooling and progressive outward equilibration with their host rocks. This is consistent with thermodynamic models which demonstrate that a single magmatic fluid can create the transition from potassic to propylitic mineral assemblages by following evolutionary pathways of progressive fluid-rock interaction (decreasing water/rock ratio) under a relatively shallow thermal gradient, with the transition from potassic to propylitic occurring at ~450°C (Fig. 8, Reed et al., 2013). Based on observations of the development of propylitic assemblages in vein halos at Northparkes (Pacey et al., 2019), it is evident that

573 alteration can proceed with an important structural control. In this way, more “proximal” alteration
574 assemblages can be superimposed on more distal ones where fluids have been channeled outward by
575 significant structures (representing different evolutionary pathways, c.f. pathways A and B in Fig. 8). This
576 would maintain lower fluid/rock ratios and higher temperatures to greater distances, clearly impacting the
577 distribution of isotopic signatures, and can explain much of the heterogeneity we observe in the isotope
578 data reported here. It is assumed that a mixing interface with external ground waters must occur at some
579 point but we conclude this is located at edge of the zone of mineral chemical anomalism, now known to
580 extend several km away from porphyry centers (e.g., Cooke et al., 2014; Wilkinson et al., 2015; Pacey et al.,
581 this volume).

582 **Conclusions**

583 Based on our detailed isotopic study of mineral separates and whole rocks from the Northparkes porphyry
584 system we conclude the following:

- 585 1. There is a broad decrease in $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and increase in $\delta\text{D}_{\text{H}_2\text{O}}$ of alteration fluids with increasing
586 distance and decreasing temperature across the propylitic halo.
- 587 2. Warming and equilibrating meteoric water alone cannot have generated the observed fluid
588 characteristics and therefore was not solely responsible for propylitic alteration.
- 589 3. Fluids containing a magmatic component must have been present throughout much of the
590 propylitic halo, to distances of at least 1.6 km from E48.
- 591 4. All of the data, bar one measurement, can be accounted for by magmatic fluid infiltration alone.
- 592 5. Seawater was not involved in the system.
- 593 6. The most likely scenario is one involving expulsion, cooling and equilibration of magmatic fluid
594 around the porphyry system to distances of ~2.5-3 km, beyond which a mixing interface with
595 external meteoric waters developed.
- 596 7. Meteoric water therefore had no influence on ore depositional processes by fluid mixing or by
597 modifying the thermal structure in the porphyry centers; ore formation was purely an
598 orthomagmatic process driven by thermal and chemical gradients around the quartz monzonite
599 porphyry intrusions.

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Sample ID	Sample coordinates (m)			Lith.	Material	Mineral composition (apfu); average of <i>n</i> SEM-EDS spectra:										Analyzed for:
	East	North	Elev.			Si	ivAl	viAl	Ca	Fe ²⁺	Fe ³⁺	Mg	Mn	<i>n</i>		
NP12AP031	596505	6355925	-401	BQM	Chl Qtz	2.84 -	1.16 -	1.23 -	0.00 -	1.59 -	0.04 -	3.01 -	0.08 -	31 -	O, H O	
NP12AP033	596484	6355934	-368	AND	Chl	2.96	1.04	1.14	0.00	1.40	0.05	3.22	0.12	25	-	
					Epi	2.99	-	2.18	1.98	-	0.81	0.00	0.04	64	O, H, Sr	
NP12AP036	596591	6355887	-527	BQM	Chl	2.88	1.12	1.22	0.00	1.55	0.05	3.02	0.09	37	O, H	
					Epi	3.00	-	2.00	2.00	-	0.99	0.00	0.02	54	Sr	
NP12AP040	596726	6355819	-749	SST	Chl	2.93	1.07	1.19	0.00	1.42	0.06	3.19	0.05	46	-	
					Epi	3.00	-	2.15	1.99	-	0.82	0.00	0.05	37	O, H, Sr	
					Qtz	-	-	-	-	-	-	-	-	-	O	
NP12AP044	596697	6355834	-699	AND	<i>Chl^I</i>	2.90	1.10	1.23	0.00	1.43	0.07	3.11	0.07	73	-	
					<i>Epi^I</i>	3.00	-	2.21	1.98	-	0.77	0.00	0.05	82	O, H	
					Qtz	-	-	-	-	-	-	-	-	-	O	
NP12AP045	596687	6355840	-680	BQM	Chl	2.84	1.16	1.30	0.00	1.46	0.08	2.98	0.08	28	O, H	
					Epi	3.00	-	2.26	1.96	-	0.73	0.00	0.05	45	O, H, Sr	
NP12AP073	597172	6355894	-239	BQM	Chl	2.87	1.13	1.29	0.00	1.48	0.09	2.85	0.18	56	O, H	
					Epi	3.01	-	2.19	1.97	-	0.80	0.00	0.03	58	Sr	
NP12AP079	597411	6355910	-231	AFG	WR	-	-	-	-	-	-	-	-	-	H	
NP12AP093	598365	6356882	-60	AND	Epi	3.00	-	2.17	2.00	-	0.82	0.00	0.01	44	Sr	
NP12AP096	598338	6356858	-117	CON	Chl	2.95	1.05	1.18	0.00	1.68	0.07	2.90	0.09	64	O, H	
					Epi	3.00	-	2.11	1.99	-	0.87	0.00	0.03	40	O, H	
					Qtz	-	-	-	-	-	-	-	-	-	O	
NP12AP097	598333	6356854	-128	AND	<i>Epi^P</i>	3.00	-	2.12	1.99	-	0.86	0.00	0.03	59	O, H, Sr	
NP12AP101	598268	6356804	-261	AND	Mag	-	-	-	-	-	-	-	-	-	O	
					Qtz	-	-	-	-	-	-	-	-	-	O	
NP12AP102	598264	6356801	-269	AND	Mag	-	-	-	-	-	-	-	-	-	O	
					Qtz	-	-	-	-	-	-	-	-	-	O, H	
NP12AP105	598227	6356776	-345	SST	Mag	-	-	-	-	-	-	-	-	-	O	
					Qtz	-	-	-	-	-	-	-	-	-	O	
NP12AP115	598428	6356941	77	AND	Chl	2.90	1.10	1.27	0.00	1.69	0.10	2.61	0.19	3	-	
					Epi	3.01	-	2.11	2.00	-	0.87	0.00	0.00	68	O, H, Sr	
NP13AP016	598446	6356958	116	CON	Chl	2.86	1.14	1.33	0.00	1.67	0.10	2.64	0.12	32	O, H	
					Epi	3.00	-	2.20	2.01	-	0.78	0.00	0.01	52	O, H, Sr	
					Qtz	-	-	-	-	-	-	-	-	-	O	
NP13AP026	597648	6356237	-526	AFG	Chl Qtz	2.86 -	1.14 -	1.23 -	0.00 -	1.73 -	0.05 -	2.80 -	0.12 -	25 -	O, H O	
NP13AP027	597647	6356236	-527	AFG	WR	-	-	-	-	-	-	-	-	-	O, H	
NP13AP033	597568	6356168	-618	BQM	<i>Chl^B</i>	2.83	1.17	1.28	0.00	1.59	0.07	2.75	0.24	85	O, H	
					Qtz	-	-	-	-	-	-	-	-	-	O	
NP13AP037	597584	6356182	-600	BQM	Chl	2.84	1.16	1.28	0.00	1.51	0.07	2.73	0.32	37	O, H	
NP13AP040	597515	6356124	-672	BQM	Epi	3.00	-	2.27	1.96	-	0.72	0.00	0.06	49	Sr	
NP13AP049	597475	6356091	-713	BQM	Chl	2.91	1.09	1.20	0.00	1.60	0.06	2.82	0.24	32	O, H	
					Epi	3.00	-	2.19	1.97	-	0.80	0.00	0.06	34	O, H, Sr	
NP13AP057	597384	6356018	-805	BQM	Chl	2.86	1.14	1.26	0.00	1.86	0.06	2.51	0.23	43	O, H	
NP13AP061	597379	6356015	-810	BQM	Chl	2.80	1.20	1.30	0.00	1.57	0.06	2.55	0.45	28	O, H	
					Epi	3.01	-	2.24	1.94	-	0.73	0.00	0.09	2	O, H	
NP13AP102	597268	6354921	-1065	BQM	WR	-	-	-	-	-	-	-	-	-	H	
NP13AP160	598360	6354710	-568	BQM	Mag	-	-	-	-	-	-	-	-	-	O	
					Qtz	-	-	-	-	-	-	-	-	-	O	
NP13AP168	598358	6354709	-569	BQM	Mag	-	-	-	-	-	-	-	-	-	O	
					Qtz	-	-	-	-	-	-	-	-	-	O, H	
NP13AP244	597074	6356909	-57	AND	WR	-	-	-	-	-	-	-	-	-	H	
NP13AP248	597059	6356935	-7	AND	<i>Chl^I</i>	2.94	1.06	1.19	0.00	1.70	0.07	2.87	0.08	39	-	
					<i>Epi^I</i>	3.00	-	2.11	1.99	-	0.88	0.00	0.02	58	O, H	
					Qtz	-	-	-	-	-	-	-	-	-	O	
NP13AP249	597050	6356950	22	AND	<i>Chl^I</i>	2.94	1.06	1.19	0.00	1.70	0.07	2.87	0.08	39	O, H	
					<i>Epi^I</i>	3.00	-	2.11	1.99	-	0.88	0.00	0.02	58	O, H, Sr	
					Qtz	-	-	-	-	-	-	-	-	-	O	
NP13AP258	599063	6337512	302	MON	Chl	2.84	1.16	1.23	0.00	1.59	0.04	3.01	0.08	31	O, H	
NP13AP275	597104	6356855	-155	AND	<i>Epi^B</i>	3.00	-	2.11	1.99	-	0.88	0.00	0.02	92	Sr	
NP13AP283	597891	6355760	-957	BQM	WR	-	-	-	-	-	-	-	-	-	O, H	
NP13AP294	605860	6344416	324	MON	Chl	3.06	0.94	1.16	0.00	2.13	0.13	2.38	0.04	9	O, H	

NP13AP311	597165	6356739	-337	AND	WR	-	-	-	-	-	-	-	-	-	H
NP13AP312	597168	6356737	-348	AND	Chl	2.87	1.13	1.23	0.00	1.69	0.06	2.86	0.10	43	O, H
					Epi	3.00	-	2.09	1.97	-	0.89	0.00	0.05	34	O, H, Sr
NP13AP318	593865	6335983	286	BSLT	Chl	2.85	1.15	1.26	0.00	1.87	0.06	2.50	0.23	1	-
					Epi	3.00	-	2.15	1.96	-	0.87	0.00	0.01	64	O, H, Sr

Table 1– Sample location, lithology and, where applicable, mineral chemistry data for epidote and chlorite from Pacey et al. (this volume). Sample coordinates are relative to UTM Zone MGA55 (GDA94); elevation in meters above sea level. Lith. is the lithology for whole rock samples (WR) or host lithology from which mineral separates (chlorite, epidote, quartz or magnetite) were extracted: AFG = alkali feldspar granite; AND = trachyandesite; BQM = biotite quartz monzonite; BSLT = basalt; CON = volcanic conglomerate; MON = monzonite; SST = volcanic sandstone. Major element compositions are based on averages of *n* number of SEM-EDS spectra, with atoms per formula unit (apfu) calculated using 28 oxygen equivalents for chlorite and 12.5 for epidote. For the latter, all Fe is assumed to be Fe³⁺ in accordance with mineralogical preference; for the former, ^{iv}Al/^{vi}Al and Fe²⁺/Fe³⁺ are calculated based on stoichiometry. The composition of minerals shown in italics was not directly determined, rather their composition is given as the average of spatially adjacent sample(s), these were, as denoted in superscript: 1 = NP12AP040 and NP12AP045; 2 = NP12AP096 and NP12AP098; 3 = NP13AP032 and NP13AP037; 4 = NP13AP250 and NP13AP317 and 5 = NP13AP250, NP13AP312. Note, data are provided for some chlorite samples which were not analyzed for isotopic composition, as their chemistry is used to estimate formation temperatures (via chlorite geothermometry) for coexisting epidote.

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Sample ID	Dist. to E48 (m)	Material	Oxygen				Hydrogen				
			Wt. (mg)	Yield (μmol/mg)	Yield (% O ₂)	δ ¹⁸ O (‰ VSMOW)	Wt. (mg)	NC yield (μmol/mg)	H ₂ yield (μmol/mg)	Wt. % H ₂ O	δD (‰ VSMOW)
NP12AP079	-	WR (AFG)	-	-	-	-	32.8	0.03	0.22	0.40	-70
NP13AP027	-	WR (AFG)	3.3	10.5	-	9.5	148.7	0.06	0.19	0.34	-90
			3.2	10.5	-	8.8					
NP13AP102	-	WR (BQM)	-	-	-	-	94.5	0.00	0.53	0.95	-60
NP13AP283	-	WR (BQM)	3.4	11.6	-	5.6	103.7	0.07	0.36	0.65	-77
			3.4	11.3	-	5.9					
NP13AP244	-	WR (AND)	-	-	-	-	110.7	0.00	0.80	1.45	-62
NP13AP311	-	WR (AND)	-	-	-	-	105.9	0.05	0.58	1.05	-84
NP12AP101	320	Mag	6.8	6.6	77	1.6	-	-	-	-	-
			6.9	7.2	84	1.8					
		Qtz	2.4	15.4	93	9.2	-	-	-	-	-
			2.4	16.6	100	9.7					
NP12AP102	320	Mag	5.9	6.8	80	2.5	-	-	-	-	-
		Qtz	2.3	15.4	93	10.6	1580	0.00	0.09	0.17	-73
NP12AP105	280	Mag	6.4	6.3	73	2.1	-	-	-	-	-
		Qtz	2.5	16.3	98	9.0	-	-	-	-	-
NP13AP160	350 (E26)	Mag	7.2	6.3	74	1.6	-	-	-	-	-
			6.8	6.5	76	2.1					
		Qtz	2.6	16.8	101	8.3	-	-	-	-	-
			2.3	17.6	106	8.1					
NP13AP168	350 (E26)	Mag	6.6	5.7	67	0.7	-	-	-	-	-
			7.7	5.9	69	1.4					
		Qtz	3.0	16.6	100	8.5	990	0.00	0.09	0.16	-48
			2.5	16.6	100	8.9					
NP12AP031	1690	Chl	2.7	14.2	96	2.7	35.2	0.19	5.69	10.26	-56
			2.6	14.6	99	2.4	27.8	0.17	5.51	9.92	-59
		Qtz	2.1	14.4	87	10.8	-	-	-	-	-
NP12AP033	1710	Epi	2.4	12.0	89	4.3	78.3	0.02	1.29	2.32	-73
NP12AP036	1630	Chl	2.8	14.4	97	1.1	26.5	0.10	5.22	9.41	-57
		Epi	2.4	13.5	100	3.2	70.4	0.04	0.62	1.12	-68
			2.8	13.8	102	3.7					
NP12AP040	1540	Epi	2.5	12.2	90	2.9	59.5	0.17	0.93	1.68	-62
			3.0	13.8	102	2.8					

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		Qtz	2.7	15.3	92	9.3	-	-	-	-	-
NP12AP044	1560	Epi	2.7	12.0	89	2.5	72.0	0.00	0.95	1.70	-56
			2.8	12.1	89	1.9					
			2.9	12.7	93	2.6					
		Qtz	2.3	14.7	89	8.3	-	-	-	-	-
			2.2	14.9	89	9.1					
NP12AP045	1560	Chl	2.6	14.2	96	2.4	32.6	0.42	4.59	8.27	-59
		Epi	2.7	13.3	97	3.3	70.4	0.03	0.54	0.98	-59
							69.0	0.10	0.75	1.36	-54
NP12AP073	1120	Chl	2.6	17.6	119	1.8	32.5	0.17	4.90	8.83	-61
NP12AP096	410	Chl	2.6	14.0	95	1.7	34.2	0.28	5.51	9.93	-56
		Epi	3.0	11.0	81	3.4	77.6	0.16	0.84	1.52	-86
			2.9	12.8	95	3.3					
		Qtz	2.7	17.2	104	8.9	-	-	-	-	-
NP12AP097	400	Epi	2.8	12.7	94	2.6	73.6	0.05	0.92	1.65	-78
NP12AP115	500	Epi	2.8	13.6	101	3.7	72.5	0.01	1.18	2.12	-61
NP13AP016	560	Chl	2.7	14.4	98	2.5	35.9	0.27	4.17	7.51	-61
		Epi	2.6	11.2	82	3.0	70.5	0.04	1.11	2.01	-84
		Qtz	2.6	16.4	99	8.6	-	-	-	-	-
NP13AP026	530	Chl	3.0	12.8	88	1.4	28.4	0.19	3.48	6.26	-66
			2.6	13.7	94	1.7					
		Qtz	2.3	16.8	101	7.9	-	-	-	-	-
NP13AP033	640	Chl	2.6	14.3	98	2.8	26.8	0.31	4.02	7.25	-65
			2.9	14.5	99	2.1					
		Qtz	2.5	15.4	93	7.4	-	-	-	-	-
			2.6	16.7	100	7.6					
NP13AP037	610	Chl	2.5	15.5	106	1.5	37.5	0.18	4.90	8.82	-60
NP13AP049	760	Chl	2.7	14.8	101	0.8	26.6	0.49	4.73	8.53	-61
		Epi	2.8	13.4	99	2.7	75.4	0.08	1.03	1.86	-52
NP13AP057	870	Chl	2.7	13.1	90	2.9	25.9	0.02	3.01	5.41	-62

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Sample ID	Dist. to E48 (m)	Material	Oxygen				Hydrogen				
			Wt. (mg)	Yield (μmol/mg)	Yield (% O ₂)	δ ¹⁸ O (‰ VSMOW)	Wt. (mg)	NC yield (μmol/mg)	H ₂ yield (μmol/mg)	Wt. % H ₂ O	δD (‰ VSMOW)
NP13AP061	880	Chl	2.6	11.0	76	1.7	26.4	0.26	4.50	8.12	-61
			2.8	14.4	99	1.5					
		Epi	2.5	11.8	87	3.2	54.7	0.12	0.90	1.62	-60
			2.7	14.3	105	2.5					
NP13AP248	1100	Epi	2.9	10.7	79	3.7	78.3	0.04	1.16	2.10	-66
		Qtz	2.4	16.2	98	9.1	-	-	-	-	-
NP13AP249	1110	Chl	2.9	10.9	74	3.1	26.7	0.05	4.04	7.27	-54
			2.9	14.3	98	2.9	26.4	-	-	-	-50
		Epi	2.4	9.7	72	3.8	71.2	0.10	0.88	1.58	-57

--META--		Qtz	2.4	13.0	78	9.9	-	-	-	-	-	
			2.6	15.1	91	9.8						
			-	-	-	9.9						
	NP13AP312	940	Chl	2.7	14.8	101	2.2	35.6	0.17	4.40	7.92	-60
				26.3	0.23	4.07	7.34	-62				
		Epi	2.5	12.4	92	3.8	70.2	0.07	1.24	2.23	-83	
			2.9	12.9	96	3.3						
	NP13AP258	-	Chl	2.8	12.9	87	5.7	26.0	0.26	4.25	7.66	-66
	NP13AP294	-	Chl	2.6	13.4	93	6.5	37.4	0.26	4.48	8.08	-72
	NP13AP318	-	Epi	2.7	13.6	100	7.7	68.1	0.00	0.83	1.50	-59
2.7				13.7	101	7.4	67.0	0.00	0.81	1.46	-57	

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922 **Table 2** – Sample information and oxygen- and hydrogen-isotopic results. Multiple results for one sample represent
923 repeat analyses. The shortest lateral distance to the center of E48 is provided for all mineral separates, except those
924 indicated (E26), which are samples of potassic alteration from a porphyry intrusion of that system (Fig. 1) and thus
925 distances are to the E26 center. The latter were collected as the potassic alteration at E48 is strongly overprinted by
926 white mica alteration. The O₂ yield is the % of oxygen produced in comparison to a theoretical maximum calculated
927 from mineral stoichiometry. For quartz and magnetite, pure SiO₂ and Fe₃O₄ is assumed respectively; for chlorite and
928 epidote, yield calculations were based on known mineral composition from SEM-EDS data (Table 1). H₂ yield is
929 calculated as the weight % of H₂O present in the sample. Note H₂ and O₂ yield information are missing for one
930 replicate chlorite and one replicate quartz analysis of NP13AP249 respectively owing to a laboratory measurement
931 issue. Meta. = sample of regional metamorphic chlorite/epidote; NC = non-condensable gases, i.e. those which did
932 not condense within the liquid nitrogen cold trap during dehydration/decrepitation of the sample; other
933 abbreviations as per Table 1.

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Sample ID	Oxygen isotope geothermometry	Chlorite geothermometry temperature (°C)
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	Mineral pair	Temp. (°C)	Kranidiotis and MacLean (1987)	Jowett (1991)	Walshe (1986)
NP12AP101	Qtz-mag	619	-	-	-
NP12AP102	Qtz-mag	599	-	-	-
NP12AP105	Qtz-mag	677	-	-	-
NP13AP160	Qtz-mag	724	-	-	-
NP13AP168	Qtz-mag	698	-	-	-
NP12AP040	Qtz-epi	292	155	282	226
NP12AP044	Qtz-epi	294	159	292	237
NP12AP096	Qtz-epi	353	157	278	214
NP13AP248	Qtz-epi	364	159	281	240
NP13AP016	Qtz-epi	348	169	307	238
	Qtz-chl	356			
NP13AP249	Qtz-epi	315	159	281	240
	Qtz-chl	317			
NP12AP031	Qtz-chl	239	167	312	266
NP13AP026	Qtz-chl	345	168	307	246
NP13AP033	Qtz-chl	422	170	316	254

Table 3 – Formation temperatures calculated based on oxygen isotope geothermometry for the mineral pair indicated, and from several chlorite geothermometers using compositions provided in Table 1. Mineral $\delta^{18}\text{O}$ compositions used for isotope geothermometry are given in Table 2 and where repeat analyses were made, an average value was used. Temperatures were calculated based on the quartz-water calibration of Zhang et al. (1989) combined with the magnetite-water calibration of Zheng (1991), epidote-water calibration of Zheng (1993) and chlorite-water calibration of Cole and Ripley (1999).

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	Sample ID	Temp. (°C)	Mineral	$\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (‰ VSMOW)	$\delta\text{D}_{\text{H}_2\text{O}}$ (‰ VSMOW)
	NP12AP101	619	Qtz-Mag	8.0	-
	NP12AP102	599	Qtz-Mag	9.0	-73 ^q
	NP12AP105	677	Qtz-Mag	8.1	-
	NP13AP160	724	Qtz-Mag	7.6	-
	NP13AP168	698	Qtz-Mag	7.9	-48 ^q
	NP12AP040	292	Qtz-Epi	1.7	-30
	NP12AP044	294	Qtz-Epi	1.2	-23
	NP13AP248	364	Qtz-Epi	3.7	-27
	NP13AP016	348	Qtz-Epi	2.8	-46
		356	Qtz-Chl	3.0	-28
	NP12AP096	353	Qtz-Epi	3.2	-48
			Chl	2.2	-23
	NP13AP249	315	Qtz-Epi	3.1	-22
		317	Qtz-Chl	3.1	-17
	NP12AP033	273	Epi	2.7	-42
	NP12AP097	278	Epi	1.1	-47
	NP12AP115	295	Epi	2.6	-27
	NP12AP036	299	Epi	2.5	-35
			Chl	0.9	-22
	NP12AP045	312	Epi	2.5	-22
			Chl	2.4	-24
	NP13AP049	291	Epi	1.5	-20
			Chl	0.5	-25
	NP13AP061	326	Epi	2.3	-24
			Chl	1.8	-26
	NP13AP312	304	Epi	2.6	-49
			Chl	2.1	-26
	NP12AP031	239	Qtz-Chl	0.9	-20
	NP13AP026	345	Qtz-Chl	2.0	-32
	NP13AP033	422	Qtz-Chl	3.3	-33
	NP12AP073	303	Chl	1.7	-26
	NP13AP037	313	Chl	1.5	-25
	NP13AP057	308	Chl	2.8	-27
META	NP13AP318	312	Epi	6.8	-23
	NP13AP258	312	Chl	5.7	-31
	NP13AP294	246	Chl	5.1	-34

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976 **Table 4** – Alteration $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$ values calculated using the measured isotopic composition of mineral(s)
977 (Table 2) and formation temperatures as shown. Where repeat analyses of minerals were made, an average
978 composition was used in calculations. Temperatures in **bold** are from isotope geothermometry (Table 3) using the
979 mineral pair shown; all others are from chlorite geothermometry using the equation of Jowett (1991) and
980 compositional data (Table 1). $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ was calculated using the calibrations noted in Table 3. $\delta\text{D}_{\text{H}_2\text{O}}$ was calculated
981 using the calibrations of Chacko et al. (1999) for epidote-water and Graham et al., (1984) for chlorite-water. ^q Denotes
982 direct values from thermal decrepitation of fluid inclusions in quartz.

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Sample ID	Dist. to E48 (m)	Material	$^{87}\text{Sr}/^{86}\text{Sr}$	$\pm 2\sigma$ $\times 10^{-5}$	$^{87}\text{Sr}/^{86}\text{Sr}$ at 450 Ma
NP12AP033	1710	Epi	0.704318	0.7	0.704178
NP12AP036	1630	Epi	0.704303	0.8	0.704250
NP12AP040	1540	Epi	0.704631	0.9	0.704331
NP12AP045	1560	Epi	0.704308	0.9	0.704296
NP12AP073	1120	Epi	0.704352	0.7	0.704131
NP12AP093	440	Epi	0.704222	0.9	0.704104
NP12AP097	400	Epi	0.704234	0.7	0.704099
NP12AP115	500	Epi	0.704249	0.9	0.704131
NP13AP016	560	Epi	0.704379	0.7	0.704118
NP13AP040	700	Epi	0.704417	0.9	0.704180
NP13AP049	760	Epi	0.704536	1.0	0.704303
NP13AP249	1110	Epi	0.705055	0.6	0.704354
NP13AP275	1030	Epi	0.707759	0.5	0.704171
NP13AP312	940	Epi	0.705481	0.6	0.704324
NP13AP318	Meta.	Epi	0.704617	0.7	0.704616
NP12AP079	-	WR (AFG)	0.709530	0.6	0.704159
NP13AP013	-	WR (AND)	0.705209	0.8	0.704246
NP13AP027	-	WR (AFG)	0.708535	2.7	0.704261
NP13AP063	-	WR (BQM)	0.705344	0.7	0.704184
NP13AP100	-	WR (BQM)	0.705373	0.6	0.704178
NP13AP102	-	WR (BQM)	0.705291	0.7	0.704142
NP13AP244	-	WR (AND)	0.704759	0.8	0.704158
NP13AP282	-	WR (AND)	0.704804	0.9	0.704212
NP13AP283	-	WR (BQM)	0.705085	0.7	0.704123
NP13AP311	-	WR (AND)	0.704896	0.7	0.704207

Table 5 – Strontium-isotope sample information from Pacey et al. (2019) and the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio calculated here based on an age of 450 Ma using the ^{87}Rb (λ_{87}) decay constant provided by Rotenberg et al. (2012). Meta. denotes sample of regional metamorphic epidote not associated with mineralization. Material abbreviations as defined in Table 1.

998 **Fig. 1** – Sample distribution map showing the mineral type, and elements for which isotopic composition was
 999 determined, relative to the E48, E26 and GRP314 deposits at Northparkes. Drillholes from which samples were
 1000 collected are annotated. Geology and alteration features are shown below the level of the Altona Fault (i.e. a
 1001 plan view at ~780 m below surface). Based on GDA94 MGA55, latitude and longitude values are provided as a
 1002 general guide only.

1003 **Fig. 2** – Raw results of (A) oxygen and (B) hydrogen isotopic analyses of all mineral and rock samples, as per
 1004 legend. Note only mineral data from alteration samples are plotted against lateral distance to the applicable
 1005 deposit center (E48 or E26). Analytical errors are encapsulated within the size of the symbols.

1006 **Fig. 3** – Estimated alteration temperatures from oxygen isotope and chlorite geothermometry plotted against
 1007 lateral distance to the applicable deposit center (E48 or E26). Power regression line shown is based only on the
 1008 oxygen isotope geothermometry results. Note the E26 potassic quartz-magnetite samples, despite being
 1009 located ~350 m from the center of the Cu orebody, were collected from, and intergrown with, a mineralized
 1010 porphyry intrusion. As such, they represent the highest temperature conditions which must be prevalent
 1011 across deposit centers.

1012 **Fig. 4** – Comparison of calculated alteration (A) $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and (B) $\delta\text{D}_{\text{H}_2\text{O}}$ based on the same samples, but derived
 1013 independently based on epidote-water and chlorite-water fractionation calibrations. Ideally both estimates
 1014 would show a 1:1 agreement. Generally, there is excellent agreement for $\delta^{18}\text{O}_{\text{H}_2\text{O}}$, but the relationship is far
 1015 from perfect for $\delta\text{D}_{\text{H}_2\text{O}}$, likely owing to uncertainties regarding hydrogen fractionation in the chlorite-water
 1016 system.

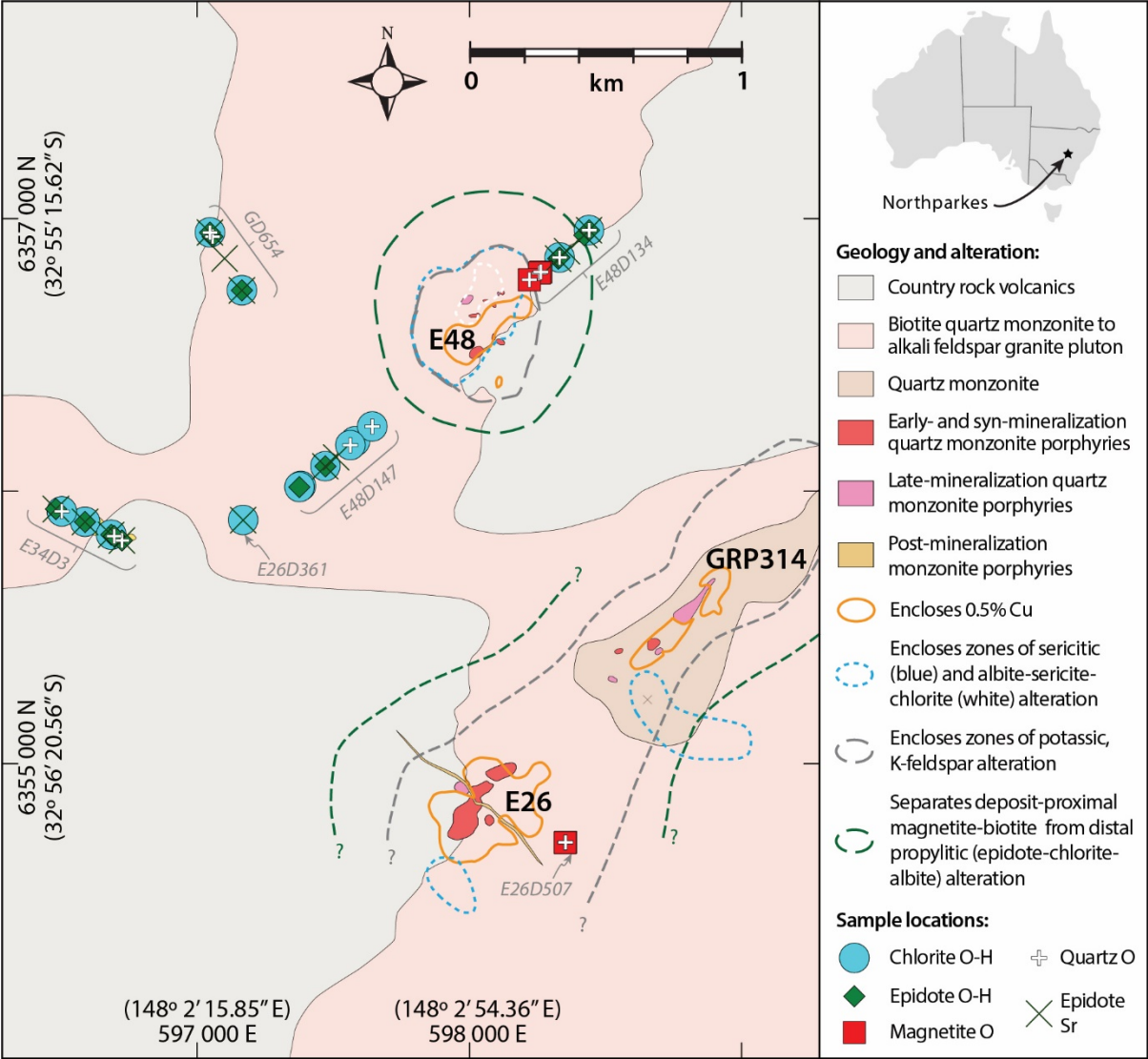
1017 **Fig. 5** - Alteration $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$ plotted against (A, C) estimated formation temperatures and (B, D) lateral
 1018 distance to the applicable deposit center. Note results derived from equilibrium with chlorite or epidote only
 1019 are reliant on formation temperatures from chlorite geothermometry. As this introduces higher,
 1020 unconstrained uncertainty, such results for propylitic samples are denoted with smaller symbols so that trends
 1021 underpinned by data from isotope geothermometry are more obvious. However, power regression lines
 1022 shown are based on all data.

1023 **Fig. 6** – Initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of propylitic epidote samples: (A) compared against the initial isotopic
 1024 composition of plutonic/magmatic and country rocks; (B) as a function of linear distance to the center of the
 1025 E48 orebody. Boxes in (A) represent the $\pm 1\sigma$ compositional variability of n samples, with whiskers at $\pm 2\sigma$;
 1026 circles are outliers $>2\sigma$ and horizontal lines show the mean value.

1027 **Fig. 7** - Modelled O-H equilibration paths of Northparkes meteoric water (black) and average magmatic-
 1028 derived potassic alteration fluids (orange) during isotopic exchange with country rock at fixed temperatures
 1029 (as labelled), toward progressively lower water:rock ratios. Water:rock ratios are indicated in italics and
 1030 marked on two equilibration paths as dark circles. The global meteoric water line (GMWL; Craig, 1961) and
 1031 field of magmatic-derived potassic alteration fluids (from Henenquist and Lowenstern, 1994, after Sheppard et
 1032 al., 1971 and Taylor, 1979) are also shown for reference. Modelling is based on the equation of Ohmoto and
 1033 Rye (1974) and assumes country rock monzonite has typical $\delta^{18}\text{O}_{\text{VSMOW}} \approx 6\text{‰}$ and $\delta\text{D}_{\text{VSMOW}} \approx -70\text{‰}$, with
 1034 exchange controlled by orthoclase and plagioclase feldspars and biotite. Black and red arrows represent the
 1035 approximate equilibration paths which might be expected for either inflowing, heating meteoric waters or
 1036 outflowing, cooling magmatic waters respectively. Both fluids develop toward a fixed composition at very low
 1037 water:rock ratios, at which point they are in equilibrium with the reservoir rock. This equilibrium composition
 1038 is temperature sensitive and its position is indicated across the temperature range by the grey dashed line of
 1039 full equilibration. Any alteration fluid data plotting below this line requires a magmatic water input, and any
 1040 above it a meteoric water input. Alteration $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$ (Table 4) are plotted and those data that are
 1041 underpinned by more robust isotope geothermometry are enlarged for clarity and labelled with formation
 1042 temperatures and distance from the applicable deposit. The data cannot exclude a meteoric fluid component
 1043 in propylitic alteration with numerous mixing scenarios possible. However, they necessitate the involvement

1044 of a magmatic component and show a remarkably good fit (in isotopic composition, temperature and
 1045 distance) to the envisaged equilibration path of an outflowing, cooling magmatic-derived fluid.
 1046 **Fig. 8** – Alteration mineral phase diagram simplified from Reed et al. (2013) showing the temperature
 1047 conditions and reaction ratio of magmatic fluid to granite (based on data from Butte, MT, USA) that controls
 1048 the presence or absence of alteration minerals. Lines on the diagram are labelled on the side where the
 1049 relevant mineral exists, being absent on the opposite side. Numerous evolutionary pathways (e.g., paths A and
 1050 B shown) exist that allow a magmatic fluid to initially generate potassic alteration (feldspar and/or biotite) and
 1051 transition, upon cooling and rock interaction, into generation of propylitic alteration (epidote-chlorite) –
 1052 without the need for any meteoric fluid input. Pathways A and B shown are based broadly on the Northparkes
 1053 data, both beginning with potassic alteration at 600-700°C and transitioning into propylitic alteration at
 1054 ~450°C. Path A is most representative of structurally-focused fluid flow where, for any given temperature,
 1055 water:rock ratios are higher than in path B. Pathway A matches observations that the innermost selvages to
 1056 large propylitic veins (P1 veins of Pacey et al. 2019) are characterized by dominant chlorite and phengitic
 1057 muscovite before transitioning into a vein-distal chlorite-epidote assemblage. Path B is most representative of
 1058 fluid infiltration via fine fracture networks and exploitation of permeable country rocks, it matches
 1059 observations of pervasive potassic alteration transitioning into pervasive propylitic alteration around the
 1060 Northparkes deposits (Fig. 1; Pacey et al. 2019).

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1063 **Figure 1**

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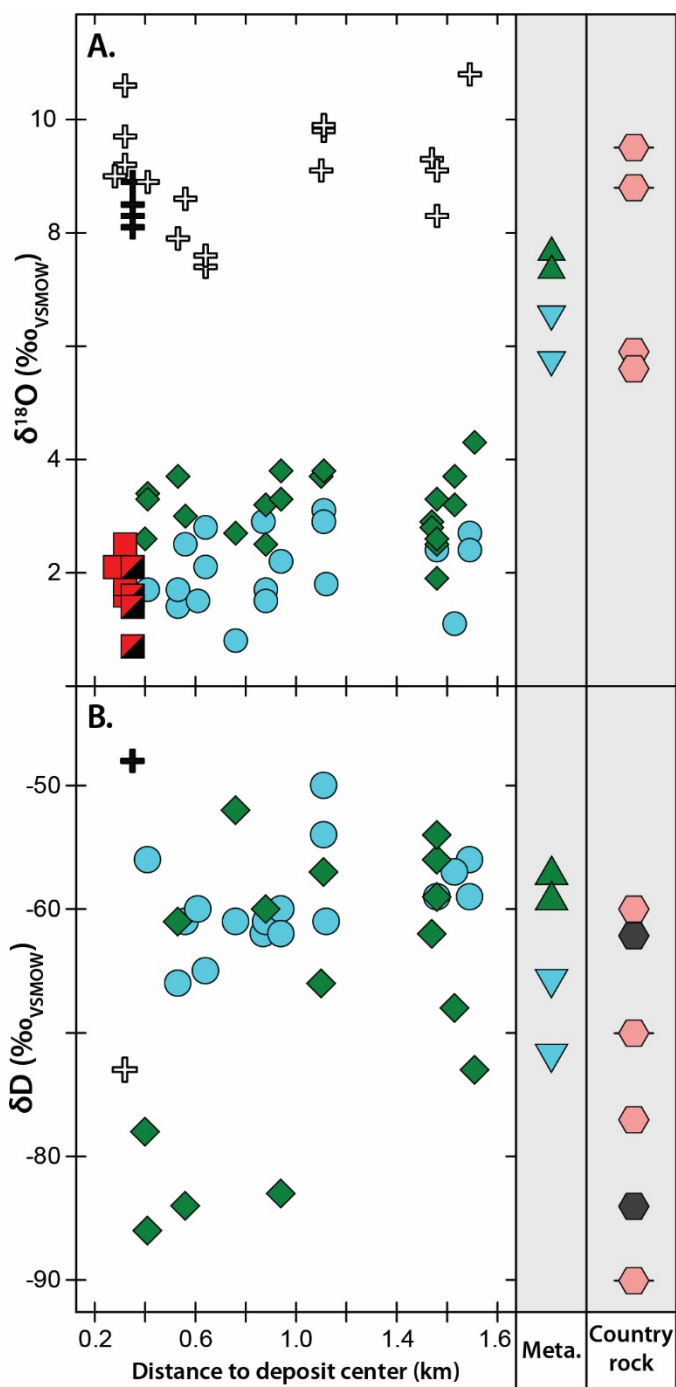


Figure 2

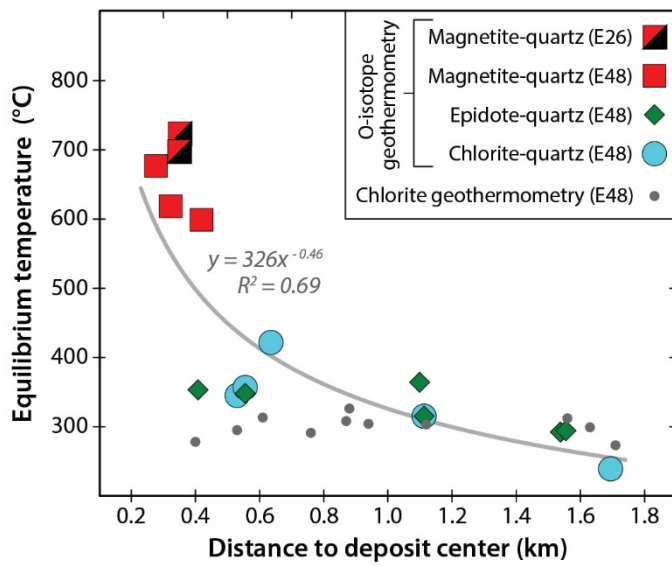


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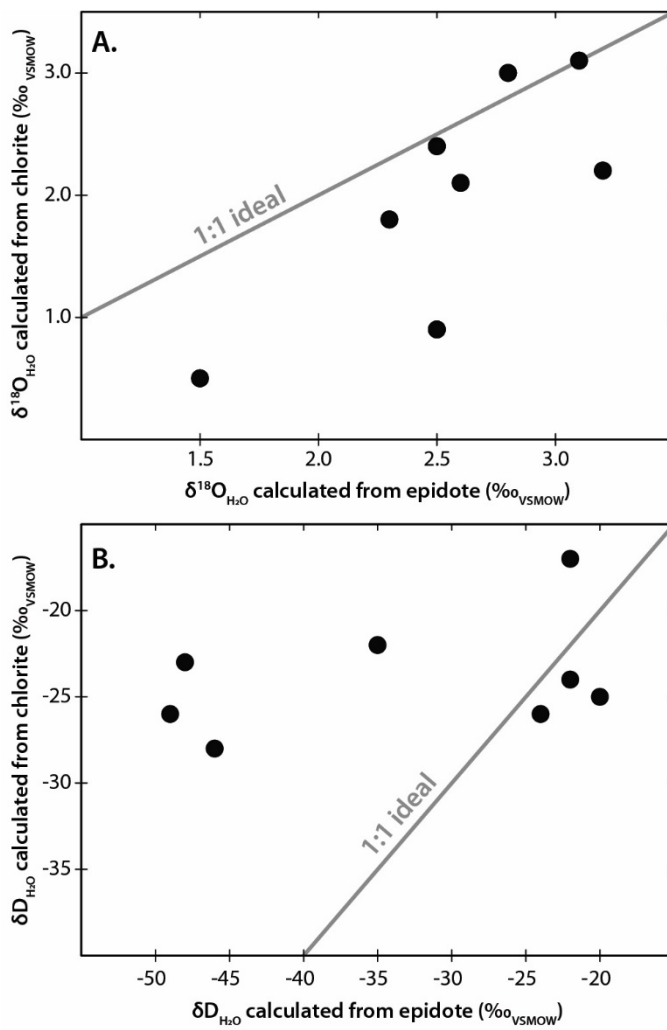


Figure 4

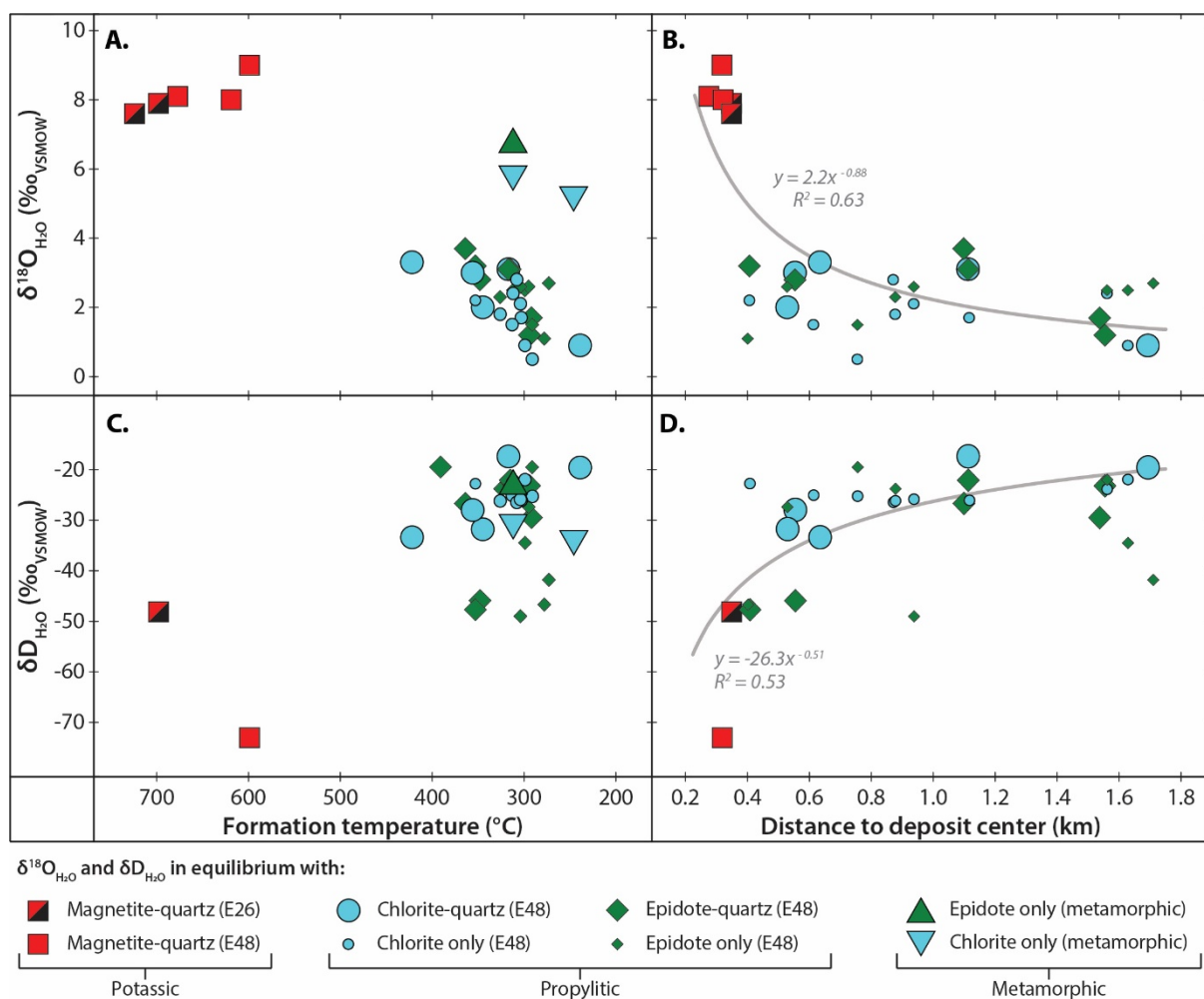


Figure 5

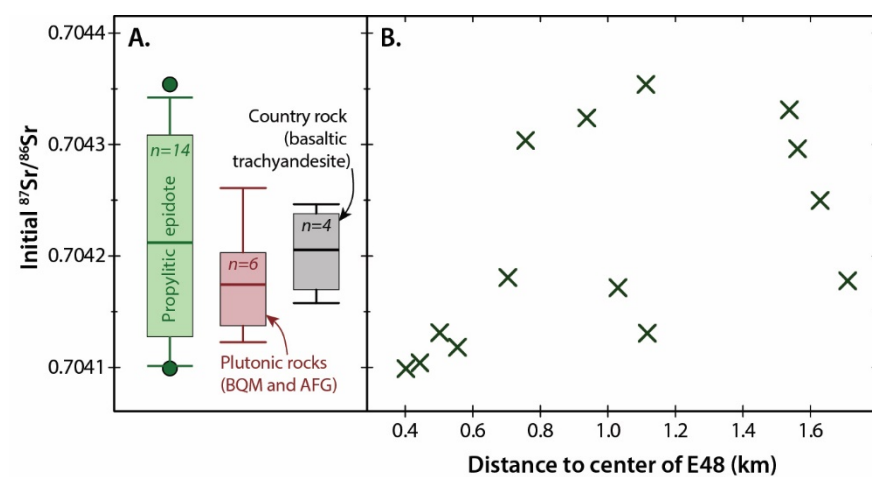


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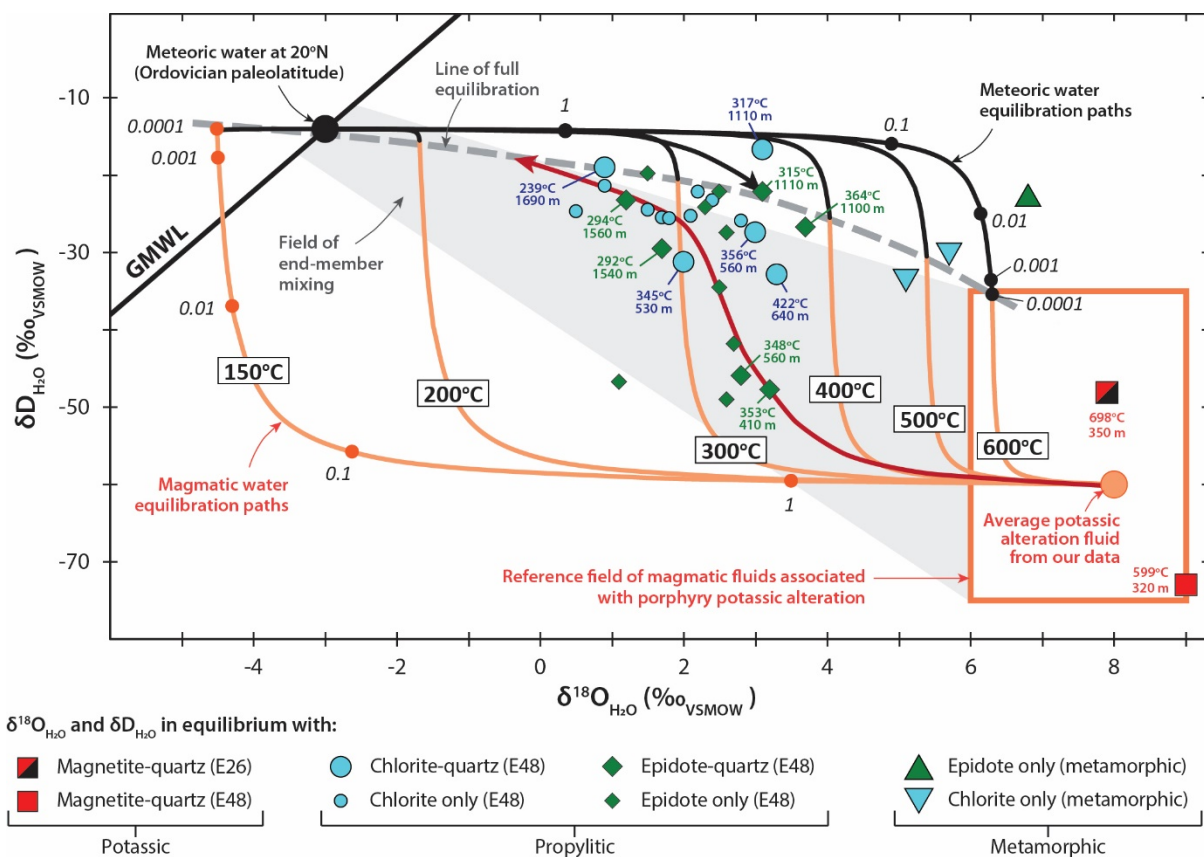
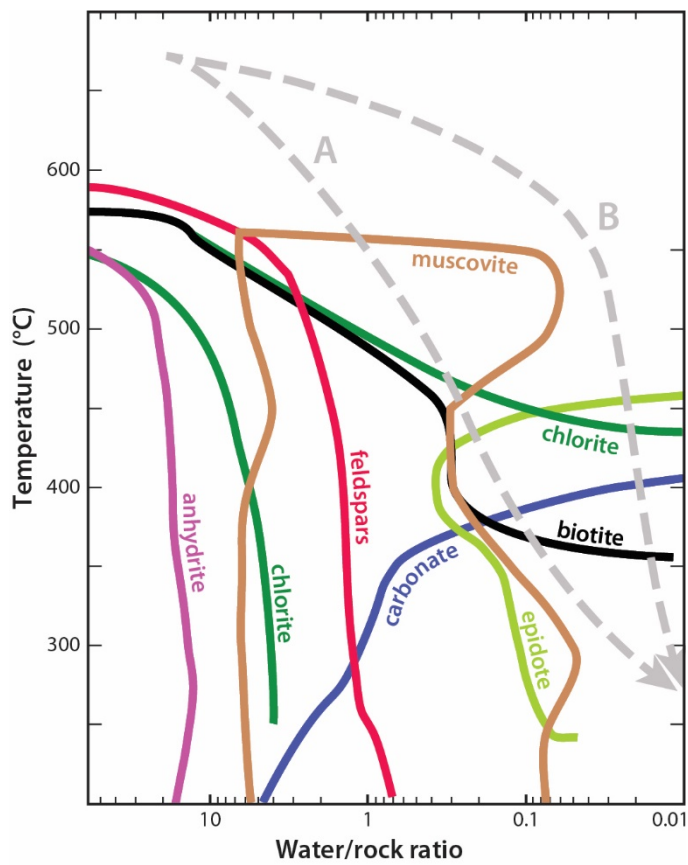


Figure 7



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1098 **Figure 8**

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