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## Title

Epidote trace element chemistry as an exploration tool in the Collahuasi District, Northern Chile

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## **Bibliographic citation**

Baker, Michael; Wilkinson, Jamie; Wilkinson, CC; Cooke, David; Ireland, T (2020). Epidote trace element chemistry as an exploration tool in the Collahuasi District, Northern Chile. University Of Tasmania. Journal contribution.

https://figshare.utas.edu.au/articles/journal\_contribution/Epidote\_trace\_element\_chemistry\_as\_an\_exploration\_t

Is published in: 10.5382/econgeo.4739

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1	Epidote trace element chemistry as an exploration tool in the Collahuasi
2	district, northern Chile
3	
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19	
20	Abstract
21	
22	The Collahuasi district of northern Chile hosts several late Eocene-early Oligocene world-
23	class porphyry Cu-Mo deposits, including Rosario, Ujina and Quebrada Blanca deposits, and
24	associated high sulfidation epithermal mineralization at La Grande. Mineralization is hosted
25	by intermediate to felsic intrusive and volcanic rocks of the upper Paleozoic to Lower
26	Triassic Collahuasi Group, which experienced lower greenschist facies regional
27	metamorphism prior to mineralization. Extensive hydrothermal alteration zones surround the
28	porphyry and epithermal deposits, associated with hypogene ore-forming processes.
29	However, outside of the observed sulfide halo the limits of geochemical anomalism
30	associated with mineralization are difficult to define due to mineralogical similarities
31	between weak, distal propylitic alteration and regional metamorphism affecting the host
32	rocks.
33	

Recent advancements in laser ablation inductively-coupled plasma mass spectrometry 34 analysis (LA-ICP-MS) of epidote from hydrothermal alteration zones around porphyry and 35 skarn deposits have shown that low-level hypogene geochemical anomalies can be detected at 36 distances further from the center of mineralization than by conventional rock chip sampling. 37 Selective analysis of propylitic epidote from the Collahuasi district indicates that anomalous 38 39 concentrations of distal pathfinder elements in epidote, including As (>50 ppm), Sb (>25 ppm), Pb (>100 ppm), and Mn (>5,000 ppm) were detectable 1.5 to 4.0 km from deposit 40 centers. Significantly, the concentrations of these trace elements in epidote were obtained 41 42 from samples that contained whole rock concentrations of <25 ppm As, <2 ppm Sb, <100 ppm Pb, and <5,000 ppm Mn. Systematic increases in Cu, Mo and Sn concentrations in 43 epidote near deposit centers, and corresponding decreasing As, Sb and Pb concentrations, 44 also provide effective tools for assessing the fertility and locating the centers of porphyry 45 mineralization. In addition, anomalous concentrations in epidote of Cu (up to 1 wt %) and Zn 46 47 (up to 6,000 ppm) effectively discriminate epidote associated with high sulfidation epithermal veins in the Collahuasi district (e.g., La Grande, Poderosa-Rosario) from alteration associated 48 49 with porphyry mineralization. 50 51 Introduction 52 The ability to identify the location of concealed mineralization and assess the fertility 53 potential of districts from distal hydrothermal alteration halos is of paramount importance to 54 55 explorers, especially considering that the future of mineral exploration will involve searching for signs of mineralization and alteration at increasing depths (McIntosh, 2010). 56

57 Consequently, there is now a need for explorers to be able to maximize the information that

can be obtained from regional-scale geochemical sampling of prospective mineralized

59 districts. In mineralized porphyry districts, recent studies have sought to define the

60 geochemical footprint of propylitic alteration halos surrounding mineralized porphyry and

epithermal deposits (Cooke et al., 2014, 2017, this issue; Ahmed et al., this issue; Pacey et al.,

62 this issue; Wilkinson et al., this issue). New mass spectroscopy techniques developed to

analyze epidote mineral chemistry have been shown to record the subtle geochemical

64 footprints of porphyry mineralization at distances farther than can be achieved by

65 conventional geochemical analyses (Cooke et al., 2014; Wilkinson et al., this issue).

66 However, for this technique to be considered useful in mineral exploration, it must be

sufficiently robust as to be applicable to rocks from any mineralized porphyry district.

00	
69	We present a case study of epidote mineral chemistry from the Rosario-La Grande hybrid
70	porphyry-epithermal deposit and Ujina porphyry deposit from the Collahuasi district of
71	northern Chile. Our results show that the geochemical footprints of large porphyry and
72	epithermal deposits can be identified using epidote mineral chemistry, at distances greater
73	than using conventional geochemical analysis. Additionally, our results indicate that this
74	method of mineral chemical analysis can identify porphyry mineralization and vector towards
75	higher-grade zones in districts that have experienced regional metamorphism. This study
76	shows that analysis of epidote mineral chemistry from the propylitic alteration zone
77	surrounding porphyry deposits can provide critical vectoring and fertility information,
78	enabling the identification of prospective areas for exploration.
79	
80	District Geology
81	
82	The Collahuasi district is situated in Region I in northern Chile, on the western slope of the
83	Central Andean Cordillera at elevations between 4400 and 5000 m a.s.l., 5 km from the
84	border with Bolivia (Fig. 1). The district covers an area of approximately 1200 km <sup>2</sup> and lies
85	at the northern end of the major Eocene-Oligocene porphyry Cu-Mo belt of northern Chile
86	(Fig. 1). The district is centered on the world-class Rosario hybrid porphyry Cu-Mo and high-
87	sulfidation Cu-Ag deposit (3.11 Gt at 0.82% Cu, 0.024% Mo and 0.01 g/t Au; Masterman et
88	al., 2004; Djouka-Fonkwé et al., 2012), the Quebrada Blanca porphyry Cu-Mo deposit (1.43
89	Gt at 0.59% Cu; Ireland, 2010) and the Ujina porphyry Cu-Mo deposit (636 Mt at 1.06% Cu;
90	Camus, 2002; Fig. 2). To the south of Rosario, late-stage high sulfidation Cu-(Ag-Au) and
91	Ag-Au veins were localised along the Rosario and Monctezuma fault systems. They include
92	the La Grande, Poderosa, Condor, Esperanza, Cacique and Monctezuma vein systems (Fig. 2;
93	Masterman et al., 2004; Ireland, 2010; Djouka-Fonkwé et al., 2012). These late-stage
94	epithermal vein systems have overprinted low-grade porphyry Cu-Mo mineralization and
95	alteration and locally define zones of high copper grades (Masterman et al., 2004). Several
96	other mineral deposits, including the Huinquintipa gravel-hosted exotic Cu deposit, and La
97	Profunda prospect, are located within the district (Fig. 2). The geology, geochronology,
98	mineralization and hydrothermal alteration of the Collahuasi district have been detailed in a
99	number of recent studies (e.g., Munchmeyer et al., 1984; Vergara and Thomas, 1984;

100 Maksaev, 1990; Dick et al., 1994; Lee, 1994; Clark et al., 1998; Rowland, 1998; Masterman,

68

2003; Masterman et al., 2004, 2005; Maksaev et al., 2007; Munizaga et al., 2008; Urqueta et
al., 2009; Ireland, 2010; Djouka-Fonkwé et al., 2012).

103

Basement rocks of the Collahuasi district are Ordovician metamorphosed mica schist, 104 amphibolites and minor migmatites of the Choja Formation (Ireland, 2010). The Choja 105 106 Formation is overlain by the Paleozoic to Permo-Triassic Collahuasi Formation (Fig. 2). The 107 Collahuasi Formation, also referred to as the Peine Group (Bahlburg and Breitkreuz, 1991; Ireland, 2010), is a sequence of rhyolitic, dacitic and andesitic flows with intercalated 108 109 immature volcaniclastic rocks and rare limestone lenses and is the main host to mineralization in the Collahuasi district (Masterman et al., 2004; Munizaga et al., 2008; 110 Urqueta et al., 2009; Djouka-Fonkwé et al., 2012). To the west of the Collahuasi district, the 111 Collahuasi Formation is unconformably overlain by deep- to shallow-marine Jurassic 112 sedimentary rocks of the Quehuita Formation. Overlying the Quehuita Formation are 113 114 Cretaceous continental volcanic and arenitic rocks of the Cerro Empexa Formation (Fig. 2; Masterman et al., 2004; Ireland, 2010). Extensive Cenozoic ignimbrite flows (Huasco and 115 116 Ujina Ignimbrites) cover basement rocks to the north and in the southeast part of the district

117 (Fig. 2).

118

Three pre-Middle Triassic intrusive phases that intruded the Collahuasi, Quehuita and Cerro 119 120 Empexa Formations have been recognised. These include ca. 270-260 Ma diorite to granodiorite plutons (e.g., Escorial Diorite, Ceucis Granodiorite; Huete et al., 1977; Damm et 121 122 al., 1986), the Permo-Triassic granodioritic Collahuasi Porphyry ( $245 \pm 12$  Ma; Masterman, 2003), and the ca. 238-237 Ma Cascasca dikes, a basaltic andesite dike swarm located 123 between the Ujina and Rosario porphyry deposits (Ireland, 2010; Fig. 3). The host sequences 124 were subsequently intruded by a series of calc-alkaline diorite to granite stocks and plutons of 125 Paleocene to Eocene age (Fig. 2; Masterman, 2003; Masterman et al., 2004; Ireland, 2010). 126 They include the upper Eocene Quebrada Blanca intrusive complex (Urqueta et al., 2009) 127 which hosts the Quebrada Blanca porphyry Cu-Mo deposit, the mineralized Rosario Porphyry 128  $(34.4 \pm 0.3 \text{ Ma}; \text{Masterman et al.}, 2004)$ , the syn-mineralization Ujina porphyry  $(35.0 \pm 0.3 \text{ m})$ 129 130 Ma; Masterman et al., 2004), and the syn- to late-mineralization Inca porphyry ( $34.8 \pm 0.3$ Ma; Masterman et al., 2004) that intrude the Ujina porphyry (Masterman, 2003; Urqueta et 131 al., 2009). 132

133

The host rocks of the Collahuasi district are separated into three stratigraphic domains by the 134 north-trending Domeyko and Loa fault systems (Fig. 2). In the west, the Quehuita and Cerro 135 Empexa Formations are separated from the Collahuasi Formation by the regional-scale 136 Domeyko Fault. In the east, the Loa fault system separates the Collahuasi Formation from a 137 chain of Miocene-Pliocene andesite stratovolcanoes (Fig. 2). The Quebrada Blanca, Rosario 138 139 and Ujina porphyry deposits define a broad east-west corridor between the West Fissure of the Domeyko fault system to the west and the Loa Fault to the east (Fig. 2; Dick et al., 1994). 140 141 142 **Rosario and Ujina porphyry Cu-Mo deposits** 143 Geologic setting 144 Rosario: The host rocks of the Rosario deposit are andesitic to rhyolitic flows and lesser 145 volcaniclastic rocks of the Collahuasi Formation (Fig. 2; Masterman et al., 2004; Ireland, 146 147 2010). The host sequence was intruded by several porphyritic dikes and stocks, beginning with the pre-mineralization granodiorite Collahuasi porphyry (Masterman, 2003). The 148 149 Collahuasi porphyry is a NW-trending, 50-300 m wide dike, with a strike length of 8 km (Munchmeyer et al., 1984; Masterman et al., 2004). The southeastern portion of the intrusion 150 151 is outside the hydrothermal alteration halo of the Rosario deposit (Masterman et al., 2004). The Collahuasi porphyry was intruded by the Rosario quartz monzonite porphyry 152 (Masterman et al., 2004). The Rosario porphyry is NW-trending, 300 to 500 m wide, up to 153 1500 m long and has been identified at depths of up to 1000 m at Rosario (Masterman et al., 154 155 2004). The intrusion is the primary host for low-grade, veinlet and disseminated porphyrystyle Cu-Mo mineralization (Masterman, 2003). A third intrusion, the sill-like, Triassic Inés 156 dacite porphyry has also been identified by previous workers (Clark et al., 1998; Masterman 157 et al., 2004). The Rosario fault system, a series of NW-striking, SW-dipping brittle faults, cut 158 the mineralized intrusions (Masterman et al., 2004). This fault system localised high-159 sulfidation Cu-Ag massive-sulfide veins and overprinting supergene mineralization (Fig. 3; 160 Dick et al., 1994; Masterman et al., 2004). 161 162 *Ujina:* Ujina is hosted by the Collahuasi Formation, which is composed of a thick basal 163 andesite sequence overlain by rhyolite and sedimentary breccia (Bisso et al., 1998; 164

165 Masterman et al., 2004). Two porphyritic intrusions, both K-feldspar-quartz-biotite-phyric,

166 have been identified at Ujina. The main host to porphyry-style mineralization is the Ujina

167 porphyry, a cylindrical 1200 m-diameter granodiorite stock (Masterman et al., 2004). It was

- intruded by a series of north- and northwest-trending granodiorite dikes collectively termed
  the Inca porphyry (Bisso et al., 1998; Masterman et al., 2004). Disseminated porphyry Cu-
- 170 Mo mineralization is concentrically zoned around the Ujina porphyry with the highest
- 171 hypogene grades occurring near the sulfide-poor, chalcopyrite-bornite-dominated
- potassically-altered core (DeBeer and Dick, 1994; Masterman et al., 2004; Urqueta et al.,
- 173 2009). The Inca porphyry is weakly mineralized in comparison to the Ujina porphyry, and
- 174 Masterman et al. (2004) interpreted this as evidence that the Inca porphyry was intruded late
- in the mineralization history. The host rocks and porphyry mineralization at Ujina are
- 176 partially overlain by the Miocene Ujina Ignimbrite (Fig. 2).
- 177

## 178 Mineralization and Alteration

Rosario: Multiple generations of mineralization and alteration have been identified at Rosario 179 (Lee, 1994; Masterman, 2003; Masterman et al., 2004, 2005; Ireland, 2010; Djouka-Fonkwé 180 et al., 2012). Detailed descriptions of the paragenesis are given by Lee (1994) and Masterman 181 (2003). At Rosario, porphyry-style mineralization is associated with early, transitional and 182 183 intermediate-stage veins, with at least seven vein stages documented (Masterman et al., 2005). High-sulfidation mineralization is associated with late-stage, structurally-controlled 184 185 massive sulfide veins, including the La Grande, Poderosa, Condor, and Rosario veins (Fig. 3; 186 Masterman et al., 2004).

187

Propylitic alteration assemblages across the Rosario-La Grande hydrothermal system were 188 189 mapped in detail by Ireland (2010) and are summarised in Figure 3. Ireland (2010) observed epidote-dominated replacement and vein alteration assemblages intermittently over an area of 190 ~15 km<sup>2</sup> surrounding Rosario. The most pervasive epidote-dominated alteration textures and 191 veining are generally restricted to highly fractured zones along the Monctezuma and Rosario 192 193 Fault systems proximal to Rosario (Fig. 3 and 4a). Outboard of these zones, alteration varies from selective epidote-chlorite-albite alteration around the La Grande epithermal system and 194 195 up to 2 km north of Rosario (Fig. 4b), to weakly developed chlorite-(carbonate) replacementstyle alteration that has been observed selectively altering host rocks of the Collahuasi 196 197 Formation, approximately 5 km from Rosario (Fig. 3; Ireland, 2010; Djouka-Fonkwé et al., 2012). 198

199

200 *Ujina:* A detailed description of the paragenesis of Ujina was provided by Masterman (2003).

201 At least two stages of hypogene mineralization and alteration have been identified

(Masterman, 2003; Masterman et al., 2004, 2005). The earliest stage of mineralization and 202 alteration is associated with potassic alteration, centered on the Ujina porphyry (Fig. 3). The 203 potassic alteration is characterised by a K-feldspar-dominated alteration adjacent to and 204 within the porphyry that passes outward to biotite-dominated alteration on the periphery of 205 the system (Masterman et al., 2004). Disseminated and veinlet-style chalcopyrite-bornite are 206 207 characteristic of this early-stage of mineralization. Intermediate-stage veins contain quartz and molybdenite, and do not have associated alteration halos (Masterman et al., 2004). These 208 veins are cut by late- or main-stage veins that contain pyrite, chalcopyrite and quartz, 209 210 surrounded by illite-chlorite alteration halos (Masterman et al., 2004). Overlying Ujina is an enriched supergene zone characterised by kaolinite and smectite (Masterman et al., 2004). 211 212 Propylitic alteration at Ujina comprises an inner zone of epidote-(chlorite)-dominated vein 213

and replacement-style alteration (Fig. 4c) and an outer zone of chlorite-(carbonate)-214 215 dominated alteration (Fig. 3; Ireland, 2010). It is associated with the earliest stage of mineralization and is inferred to have developed at the same time as the potassic alteration 216 217 that overprinted the Ujina porphyry (Masterman et al., 2004; Ireland, 2010). Felsic to intermediate host rocks of the Collahuasi Formation are weakly carbonate-chlorite-(sericite)-218 219 altered up to 2 km from the deposit, with the intensity of alteration decreasing away from the 220 center of mineralization. Chlorite-(epidote)-bearing replacement assemblages occur closer to 221 the deposit but are still observed over a kilometre away from the outer edge of observed potassic alteration (Fig. 3; Ireland, 2010). Weakly developed epidote-chlorite-(carbonate-222 223 hematite) alteration assemblages are found in outcrops of the mafic Cascasca dikes up to 3 km south of the deposit (Figs. 3 and 4d). 224

- 225
- 226

#### **Analytical Methods**

227

A total of 170 rock chip and drill core samples containing visible propylitic alteration 228 229 assemblages were collected from both Rosario and Ujina for use in this study (Fig. 3). Each sample was analyzed for its whole-rock geochemistry, and selected epidote grains from each 230 231 sample were analyzed by electron microprobe and laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS). Samples selected for epidote mineral chemical analyses 232 were prepared as epoxy-mounted 1-inch diameter round mounts. Epidote grains in each 233 sample suitable for LA-ICP-MS analysis were then selected via reflected light petrography. 234 In general, epidote grains less than  $\sim 80 \,\mu\text{m}$  were not selected for analysis, due to the 235

minimum required laser beam width and ablation pit formed during analysis. Depending on
the sample texture and abundance of the desired phase, up to five grains per sample were
analyzed, with typically three spot analyses from each grain. Where both vein and
replacement-style alteration were present in a sample, mineral chemical data were acquired

from each in order to test for textural influence on trace element substitutions.

241

## 242 Whole-rock geochemistry

Whole rock geochemical analyses were completed on the same samples used for epidote 243 244 trace element analysis to allow direct comparison of mineral chemistry and whole rock compositions. We did not analyze weathered samples. Whole rock major and trace element 245 data were generated at Acme Analytical Laboratories Ltd. in Vancouver, Canada. Samples 246 were jaw crushed to 70% passing 10 mesh (2 mm), a 250 g aliquot was riffle split and 247 pulverized to 95% passing 150 mesh (100 µm) in a mild-steel ring-and-puck mill. A 0.2 g 248 249 powdered sample was fused in a graphite crucible with 1.5 g of LiBO<sub>2</sub>/LiB<sub>4</sub>O<sub>7</sub> flux at 980°C for 30 min and then dissolved in 5% HNO<sub>3</sub>. Major elements were determined using a Jarrel 250 251 Ash AtomComp Model 975/Spectro Ciros Vision inductively coupled plasma emission spectrograph. Trace elements were analyzed using a Perkin-Elmer Elan 6000 or 9000 252 253 inductively coupled plasma mass spectrometer. For major and trace elements, calibration standards, verification standards, and reagent blanks were included in the sample sequence. 254 255 Reported detection limits are 0.04 wt % for the major elements and 0.5 ppm for the majority of the trace elements, excluding the REE (0.05 ppm). Whole rock major and trace element 256 257 data for selected samples from the Collahuasi district are listed in Table 1. Whole rock major and trace element data for all samples are listed in Appendix A. 258

259

## 260 Electron microprobe analysis of epidote

The concentration of Ca and other major elements in each epidote grain was confirmed by 261 281 electron microprobe analyses of epidote grains following the method of Cooke et al. 262 (2014). Compositional analyses were acquired on a Cameca SX100 electron microprobe 263 located at the Central Science Laboratory, University of Tasmania, on five tuneable 264 wavelength dispersive spectrometers at a take-off angle of 40°. The analyses were performed 265 at an accelerating voltage of 15 kV, a beam current of 10 nA, and a beam diameter of 10 µm, 266 using Cameca's PeakSight software (version 3.4). Elements were acquired using analyzing 267 crystals LLIF for Fe Ka, and Mn Ka, PET for K Ka, Ca Ka, and Ti Ka, LPET for P Ka, S 268 Ka, and Cl K. All standards were from Astimex Scientific Ltd. The background correction 269

- 270 method was linear for all elements except for Fe and Mn, where only a high background was
- used with a slope factor. Unknown and standard intensities were corrected for deadtime.
- 272 Matrix correction was done using the Cameca PAP program (Pouchou and Pichoir, 1984)
- 273 mass absorption coefficients.
- 274
- 275 X<sub>Fe</sub> values used to quantify the solid solution series between epidote
- 276  $(Ca_2Al_2Fe^{3+}[Si_2O_7][SiO_4]O(OH))$  and clinozoisite  $(Ca_2Al_3[Si_2O_7][SiO_4]O(OH))$  were
- 277 calculated from electron microprobe data using the formula  $X_{Fe} = Fe^{3+}/(Fe^{3+} + Al)$
- 278 (Armbruster et al., 2006). Electron microprobe data for all samples are listed in Appendix B.
- 279

## 280 Quantitative LA-ICP-MS multielement analysis of epidote

A total of 629 laser ablation analyses were collected from epidote veins and altered wall 281 rocks in 107 samples from both the Rosario and Ujina deposits. The laser ablation analyses 282 were collected using two instruments housed at the CODES LA-ICP-MS analytical facility, 283 University of Tasmania, including: (1) a New Wave 213 nm solid-state laser microprobe 284 coupled to an Agilent 4500 quadrupole ICP-MS; and (2) a New Wave 193 nm solid-state 285 laser coupled to an Agilent 7500cs quadrupole ICP-MS. Both laser microprobes were 286 equipped with in-house, small volume (~2.5 cm<sup>3</sup>) sample chambers. A total of 43 elements 287 were analyzed from each spot. Ablation was performed in an atmosphere of pure He ( $\sim 0.7$ 288 1/min). Quantitative analyses of epidote were performed by ablating spots 30  $\mu$ m in size , 289 with a laser repetition rate of 10 Hz. For the 193 nm laser, the beam fluence at the sample 290 was  $\sim 3 \text{ J/cm}^2$  and for the 213 nm laser  $\sim 5 \text{ J/cm}^2$ . The analysis time for each sample was 90 s, 291 with 30 s for measurement of the gas background (with the laser off) and 60 s of signal 292 293 analysis with the laser on (Appendix D). The signal analysis time of ~60 s was necessary to minimise the analytical uncertainty for each spot analysis and therefore lower the detection 294 limits for analyte elements. Isotopes measured were <sup>43</sup>Ca, <sup>52</sup>V, <sup>55</sup>Mn, <sup>57</sup>Fe, <sup>65</sup>Cu, <sup>66</sup>Zn, <sup>69</sup>Ga, 295 <sup>75</sup>As, <sup>88</sup>Sr, <sup>89</sup>Y, <sup>90</sup>Zr, <sup>95</sup>Mo, <sup>118</sup>Sn, <sup>121</sup>Sb, <sup>125</sup>Te, <sup>137</sup>Ba, <sup>139</sup>La, <sup>140</sup>Ce, <sup>141</sup>Pr, <sup>146</sup>Nd, <sup>147</sup>Sm, <sup>153</sup>Eu, 296 <sup>163</sup>Dy, <sup>172</sup>Yb, <sup>175</sup>Lu, <sup>197</sup>Au, <sup>205</sup>Tl, <sup>208</sup>Pb, <sup>209</sup>Bi, <sup>232</sup>Th, and <sup>238</sup>U. No corrections for interfering 297 molecular or isobaric species were required due to the selection of appropriate analytical 298 isotopes and minimized molecular species formation. Acquisition time for each mass was set 299 300 to 0.02 s, with a total sweep time to analyze all masses of ~0.65 s. The NIST-612 glass standard (NIST, USA) was used for calibration, analyzed with a 100 µm diameter beam at a 301 laser repetition rate of 10 Hz. It was analyzed twice every 1.5 h to correct for drift in 302 instrument sensitivity with time. The secondary standard GSD-1G, run at a 30 µm spot size, 303

was used to assess and correct for plasma-loading effects, if present. Time intervals for data 304 reduction were selected by visual inspection of each spectrum. Parts of a spectrum that were 305 contaminated by mineral inclusions (i.e., spikes in trace element data) were not integrated, 306 nor were parts where concentrations changed markedly (e.g., at the commencement and 307 conclusion of ablation; Appendix D). Data reduction was undertaken according to standard 308 309 methods (Longerich et al., 1996) using Ca as the internal standard. An additional ~200 epidote LA-ICP-MS analyses were discarded due to poor-quality spectra that resulted from 310 ablation of inclusions or grain boundaries. The discarded analyses included the filtering of 311 312 processed data to remove analyses with major element concentrations that were not consistent with epidote sensu stricto (Franz and Liebscher, 2004). This included analyses with Ca 313 concentrations below 143,000 ppm or above 185,000 ppm, Al concentrations below 75,000 314 ppm and Fe concentrations below 25,000 ppm. Representative epidote LA-ICP-MS data from 315 the Collahuasi district are listed in Table 2. A full list of epidote LA-ICP-MS analyses for all 316 317 samples is given in Appendix C. 318 319 **Results** 320 321 Electron microprobe analyses of epidote from the Collahuasi district yielded X<sub>Fe</sub> values ranging from 0.11 to 0.44, with mean and median values of 0.28. Both electron microprobe 322 and laser ablation analyses show that Mn is the most abundant trace element, with 323 microprobe analyses detecting up to 0.13 wt. % Mn, and LA-ICP-MS spot analyses detecting 324 325 up to 2.5 wt. % Mn. Maximum values of key trace elements that have been shown to preferentially partition into epidote group minerals (Armbruster et al., 2006; Cooke et al., 326 2014), as detected by LA-ICP-MS spot analyses in this study include: 5,210 ppm Ce, 17,710 327

328 ppm Sr, 1,570 ppm V, 2,470 ppm La, 1,330 ppm Nd, 1,170 ppm Y, and 640 ppm Pb

329 (Appendix C). Trace element concentrations in several laser ablation analyses trend towards

330 clinozoisite (Al end-member) and piemontite (Mn end-member) compositions as defined by

Armbruster et al. (2006). However, most of the analyses can be classified as epidote *sensu stricto* (Table 2).

333

334 *Whole rock geochemistry* 

Figures 5, 6, and 7 show the spatial distribution of geochemical anomalies for key pathfinder

elements from rock-chip sampling around the Rosario and Ujina porphyry deposits and the

La Grande high sulfidation epithermal deposit. Although most of the analyzed rock types

range from mafic to felsic intrusive and extrusive rocks, no correlation between rock type and 338 pathfinder element anomalism was identified. Maximum concentrations of the trace metals 339 Cu, Au, Mo, and Sn are recorded in intermediate intrusive (diorite and granodiorite) and 340 extrusive (andesite and dacite) host rocks in and adjacent to the potassic alteration zones of 341 Rosario and Ujina, as well as in samples associated with the La Grande and Rosario high 342 sulfidation epithermal vein systems (Fig. 5; Appendix A). The highest Cu concentrations 343 were detected from samples within the potassic alteration zone at Ujina, and from a sample 344 from the La Grande epithermal deposit (Fig. 5). The trace elements As, Sb, Pb, Zn, and Mn 345 346 are strongly enriched 1-4 km from the centers of mineralization, with Pb, Sb, Zn, and Mn anomalism also spatially associated with the Rosario and La Grande high sulfidation vein 347 systems (Fig. 6 and 7). Other trace elements of interest, including La, Y, and Zr, show higher 348 concentrations within the pyrite halo surrounding Rosario and Ujina, and are anomalous up to 349 2 km from the center of the porphyry deposits (Fig. 7). 350

351

### 352 Epidote LA-ICP-MS mineral chemistry

Figures 8, 9, and 10 illustrate the spatial distribution of trace element concentrations in 353 epidote as determined by LA-ICP-MS analysis from the Rosario and Ujina porphyry 354 355 deposits. Proximal to centers of mineralization, metals with elevated concentrations detected in whole rock geochemical analyses (e.g., Cu, Au, Mo, and Sn) also show elevated 356 concentrations in epidote (Fig. 8). However, the concentrations of Cu, Au, and Mo in epidote 357 are typically lower than their corresponding whole rock compositions (cf. Fig. 5). Notable 358 359 exceptions are epidote analyses from two samples from the Rosario-Poderosa high sulfidation vein system to the southeast of the Rosario porphyry deposit (Fig. 8a). These returned Cu 360 concentrations up to 8,400 ppm (Table 2). Gold concentrations in epidote are mostly below 361 LA-ICP-MS detection limits; however, three samples from the Rosario high sulfidation 362 epithermal vein system contained trace amounts of Au in epidote (Fig. 8b). Elevated 363 concentrations of As, Sb, Pb, and Zn in epidote extends up to 4 km from the porphyry deposit 364 centers, beyond the mapped extent of the pyrite halos associated with both Rosario and Ujina 365 (Fig. 9). Around the Ujina deposit, As and Sb concentrations in epidote are generally greater 366 than 200 ppm and 10 ppm respectively and are detectable 1 to 4 km from the inferred center 367 of mineralization (Fig. 9). Significantly, peak concentrations of these trace elements in 368 epidote were obtained from rock chip samples that contain less than 50 ppm As and less than 369 3 ppm Sb (Fig. 6; Table 1). Several other rare earth and trace elements, including Mn, La, Y, 370

Sr, V, and Ce are also enriched in epidote analyses up to an order of magnitude greater than
their corresponding whole rock analyses (Fig. 10 and 11).

373

Anomalously high Cu concentrations in epidote surrounding Rosario (Fig. 8a) are associated 374 with samples proximal to high sulfidation epithermal mineralization along the Poderosa-375 376 Rosario and La Grande vein systems (Fig. 3). In particular, two samples from the Poderosa vein system are responsible for nearly all epidote analyses from this study that have Cu 377 concentrations >1,000 ppm, with individual analyses containing Cu concentrations up to 378 379 8,370 ppm (Fig. 12a). Anomalously high concentrations of Zn were also recorded in these samples and are over an order of magnitude greater than for analyses of other epidote grains 380 associated with the Rosario and Ujina porphyry hydrothermal systems (Fig. 12 and 13). The 381 high concentration of these elements in epidote associated with high sulfidation 382 mineralization, relative to the levels observed in epidote associated with the porphyry 383 mineralization (e.g., Cooke et al., 2014; Ahmed et al., this issue; Wilkinson et al., this issue), 384 may provide a means for discriminating between propylitic alteration associated with 385 386 porphyry and high sulfidation epithermal systems. 387

388 Anomalous concentrations of Cu (>1,000 ppm) in epidote were also recorded in two samples from the Casa de Piedra area, ~4 km north of Rosario (Fig. 3 and 8a). Propylitic alteration in 389 390 this area was noted by Ireland (2010) as being dominated by discrete fault-fill and wall rock alteration comprising pervasive quartz-epidote-(chlorite) replacement and cementation of 391 392 fault breccias, with narrow halos of pervasive epidotization of wall rocks where epidote has replaced plagioclase. The epidote-rich assemblages in this area were also observed to contain 393 394 native Cu, which was inferred to be a rare primary component (Ireland, 2010). Consequently, it is possible that the high Cu concentrations in epidote from Casa de Piedra may be due to 395 the incorporation of Cu nanoparticles into the epidote crystal structure. 396

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#### Discussion

Behaviour of key trace elements in epidote – implications for deposit type identification
Figure 11 shows the behaviour of key major and trace elements that substitute into propylitic
epidote from the Collahuasi district, relative to their corresponding whole rock geochemical
analyses. The rationale behind the behaviour of these elements was previously outlined by
Cooke et al. (2014), who showed that for the propylitic alteration zone surrounding a small
porphyry Cu-Au deposit, several key elements were preferentially enriched in the host rock

relative to epidote, including Na, Mg, K, Ti, Ba, Zr, Zn, Cu, Ce, Y, Nd, La, Yb, Mo, and Lu 405 (Fig. 11a). Conversely, a series of elements are significantly enriched in epidote relative to 406 the host rock, including Al, Fe, Mn, Sr, V, As, Pb, Sb, Sn, Eu, and Bi (Fig. 11b). Of the 407 elements that preferentially partition into epidote, both Al and Fe are essential trivalent cation 408 components (Armbruster et al., 2006). Manganese and Sr are the most abundant trace 409 410 elements, typically with concentrations between 1,000 ppm and 1 wt % (Table 2; Cooke et al., 2014; Wilkinson et al., this issue). Vanadium is the next most abundant trace element, 411 with concentrations typically between 100 and 1,000 ppm (Table 2). Other trace elements 412 413 that preferentially partition into epidote require LA-ICP-MS analysis to be detected, as their typical concentrations are below the detection limits of the electron microprobe. Of these 414 elements, the most important in this study are the proximal pathfinder elements (Cu, Mo, Au, 415

and Sn) and the distal pathfinder elements (As, Sb, Pb, Mn, and Zn).

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418 Based on analyses of epidote grains obtained from a sampling traverse across the Black Mountain porphyry deposit, Philippines, Cooke et al. (2014) demonstrated that the proximal 419 420 pathfinder elements are generally enriched in epidote that formed within the pyrite halo and close to centers of mineralization, whereas the distal pathfinder elements typically contain 421 422 higher concentrations further away from the deposit center, particularly outside of the pyrite halo. They postulated that this behaviour was a consequence of the combination of lateral 423 migration, cooling, and depletion of H<sub>2</sub>S in magmatic-hydrothermal fluids away from the 424 core of the porphyry deposit. Furthermore, enrichment of Cu, Au, and Mo in propylitic 425 426 epidote occurring within the pyrite halo suggests that either the concentrations of these metals in the mineralising fluids were high enough that they were incorporated into the epidote 427 crystal structure, or that sulfides of these metals were precipitated as nanoparticles and 428 trapped within crystallizing epidote grains (Cooke et al., 2014). Conversely, the 429 430 concentrations of As, Sb, and Pb in propylitic epidote are depleted within the pyrite halo, due to preferential scavenging by sulfides. However, at lower temperatures and low H<sub>2</sub>S activity 431 where sulfide phases are no longer stable these elements remain soluble and can then 432 433 substitute into epidote (Cooke et al., 2014).

434

435 Strong similarities in the behaviour of key trace elements in epidote from the Collahuasi

district (Fig. 11) and propylitic epidote from other porphyry deposits (Cooke at al., 2014,

437 2017, this issue; Ahmed et al., this issue; Pacey et al., this issue; Wilkinson et al., this issue),

438 suggest that there are consistent trends in the chemical composition of epidote formed from

hydrothermal alteration around porphyritic intrusions. Similarities in behaviour of the key 439 proximal (Cu, Mo, and Sn) and distal (As, Sb, Pb, and Zn) pathfinder elements in epidote 440 may reflect the style of mineralization that is associated with epidote alteration, as well as the 441 potential size of the deposit. Propylitic epidote from the Collahuasi district returned 442 concentrations of 0.2-8,370 ppm Cu (Table 2; Fig. 12 and 13), extending to much higher 443 444 values than reported for epidote from the Black Mountain deposit (0.1-100 ppm Cu). Concentrations of As (up to 343 ppm), Sb (up to 258 ppm), and Pb (up to 640 ppm) in 445 epidote from the Rosario and Ujina deposits (Table 2; Fig. 12 and 13) are also significantly 446 447 higher than for the epidote analyses from Black Mountain, which contained up to 180 ppm As, 65 ppm Sb, and 120 ppm Pb (Cooke et al., 2014). These results are consistent with the 448 suggestion that highly productive porphyry systems are likely to flux greater volumes of 449 mineralising fluid, which could lead to greater trace metal enrichment in epidote (Cooke et 450 al., 2014; Wilkinson et al., this issue). 451

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Extending the lateral footprint of geochemical anomalism associated with porphyry deposits 453 454 The lateral extents of mappable propylitic alteration, sulfide mineralization, and geochemical anomalism determined from conventional rock-chip assaying have traditionally formed the 455 456 identifiable footprints around porphyry deposits in volcanic-hosted terranes (Lowell, 1968; Lowell and Guilbert, 1970; Holliday and Cooke, 2007; Halley et al., 2015). This is contrary 457 to the early recognition that propylitic alteration may extend to the limits of pre-458 mineralization rock exposure, to at least 4 km (Ballantyne, 1981). However, the presence of 459 460 lower-greenschist facies regional metamorphism in districts hosting porphyry mineralization, such as the Collahuasi district (Ireland, 2010; Djouka-Fonkwé et al., 2012), can prove 461 problematic for explorers aiming to recognize the edge of a hydrothermal alteration system. 462 For example, epidote can form in a number of geologic environments, including in the 463 alteration halos surrounding porphyry and skarn deposits, in regional and contact 464 metamorphic terranes, and under certain magmatic conditions (Schmidt and Poli, 2004). 465 466 Recent studies within the Collahuasi district have sought to address this issue (Urqueta et al., 467

468 2009; Djouka-Fonkwé et al., 2012). Urqueta et al. (2009) used Pearce element ratio analysis 469 of intermediate and felsic rocks from the Collahuasi district to discriminate between fresh and 470 hydrothermally-altered samples. However, their results demonstrated that this method could 471 not distinguish lower greenschist facies metamorphism from distal propylitic alteration, as 472 neither process involves the gain or loss of major chemical components (Djouka-Fonkwé et 473 neither process involves the gain or loss of major chemical components (Djouka-Fonkwé et 474 neither process involves the gain or loss of major chemical components (Djouka-Fonkwé et 473 al., 2012). Djouka-Fonkwé et al. (2012) used a combination of petrographic and stable carbon 474 isotope analysis to demonstrate that propylitically-altered rocks of the Collahuasi district in 475 general contain higher magmatic CO<sub>2</sub> concentrations, as suggested by elevated  $\delta^{13}$ C values, 476 than regional metamorphic rocks.

477

Analysis of the systematic spatial variation of key trace elements in propylitic epidote has the 478 potential to be used in place of, or to complement, other methods for detecting the distal 479 480 geochemical signatures of mineralized magmatic-hydrothermal systems. LA-ICP-MS 481 analysis of epidote has revealed that trace element chemistry broadly varies with increasing lateral distance from the center of porphyry mineralization (Cooke et al., 2014). Selective 482 analysis of both vein and disseminated epidote grains shows that anomalous concentrations of 483 the key distal pathfinder elements As, Sb, and Pb, can be detected at distances further from 484 the center of mineralization compared to conventional rock chip sampling (Fig. 12 and 13; 485 486 Cooke et al., 2014). The concentrations of these elements generally increase outwards from the center of mineralization, reaching peak concentrations near the limits of sulfide 487 488 precipitation. They then decrease to apparent background levels with increasing distance from the deposit, where their concentrations are virtually indistinguishable from those of 489 490 regionally metamorphosed samples. In Figures 12 and 13, whole rock concentrations of As and Sb show no notable anomalism (e.g., <40 ppm As and <5 ppm Sb). Additionally, whole 491 492 rock concentrations of Pb are above 'background' levels of <50 ppm between 1-3 km from the deposit center at Rosario-La Grande (Fig. 12) and 1-2 km from the deposit center at Ujina 493 494 (Fig. 13). In contrast, anomalous concentrations of As (>50 ppm), Sb (>25 ppm), and Pb (>50 ppm) were detected in epidote analyses between 0.5-4.0 km and 1-4 km from the centers of 495 Rosario-La Grande and Ujina, respectively (Figs. 12 and 13). At distances greater than 4 km 496 from the centers of porphyry mineralization, the concentrations of these trace elements either 497 498 return to background levels comparable with whole rock concentrations, or epidote was no longer present as a stable alteration phase. Peak concentrations of these elements are 499 generally reached  $\geq 1$  km outboard of the limit of sulfide deposition (Figs. 12 and 13). 500 501

502 In assessing the background concentrations of pathfinder trace elements in propylitic epidote,

it is useful to consider the ability to chemically discriminate epidote formed in this

environment from epidote formed by regional metamorphic processes. The ability to

505 discriminate between these modes of occurrence is also critical for demonstrating the

applicability of alteration mineral chemistry as an exploration tool. Although the Peine Group

host rocks to the Rosario-La Grande and Ujina deposits have undergone lower greenschist 507 facies regional metamorphism (Ireland, 2010; Djouka-Fonkwé et al., 2012), regional 508 metamorphic rocks from the Collahuasi district were not analyzed in this study. 509 Consequently, to determine if the anomalous concentrations of trace elements in epidote are 510 unique to the Collahuasi district, or are present in other terranes, we have compared the 511 512 propylitic epidote analyses from this study to epidote from three suites of greenschist to amphibolite facies regionally metamorphosed rocks that have no known association with 513 hydrothermal mineralization (Fig. 14; Baker et al., 2017; Wilkinson et al., 2017). The 514 515 proximal (e.g., Cu, Bi, Sn) and distal (e.g., As, Sb, Pb, Zn) pathfinder metals in propylitic epidote all have higher concentrations when compared to the regional metamorphic epidote 516 analyses (Fig. 14a and b). This feature is most noticeable for the distal pathfinder elements, 517 which can have concentrations over an order of magnitude higher in propylitic epidote (Fig. 518 14c and d). This contrast has important exploration implications, as it effectively allows for 519 520 the screening of propylitic epidote in regionally metamorphosed terranes, particularly where other indications of hydrothermal mineralization (e.g., presence of sulfides) or alteration 521 522 textures (e.g., hydrothermal veins and chemical reaction fronts) are absent. 523 524 Conclusions 525 The use of LA-ICP-MS analysis of epidote can effectively detect the subtle geochemical 526 halos of mineralized porphyry and high sulfidation epithermal deposits of the Collahuasi 527 528 district, extends the geochemical footprint beyond the limits resolvable by conventional

529 whole rock assaying. Propylitic epidote from the alteration halos surrounding the Rosario and 530 Ujina porphyry deposits contains anomalous and spatially-variable concentrations of As, Sb,

Pb, La, and Y up to 4 km from the centers of mineralization. The anomalous concentrations

532 of these elements extend 1-2 km beyond zones of sulfide mineralization at both deposits. In 533 addition, epidote that formed as fine-grained disseminations and in veins associated with the

La Grande and Rosario-Poderosa high sulfidation epithermal vein systems are enriched in Cu

and Zn, in some samples over an order of magnitude greater than epidote alteration
associated with the Rosario and Ujina porphyry deposits. The anomalous concentrations of

537 these elements in epidote also effectively discriminate propylitic alteration associated with

538 porphyry Cu-Mo mineralization from similar mineral assemblages associated with regional

539 metamorphism and have the potential to be applied to alteration halos surrounding similar

540 deposit styles in other districts.

541

Concentrations of several key trace elements, including Sn, As, Sb, Pb, and Y, in epidote 542 from the Collahuasi district are similar to or higher than in propylitic epidote from smaller 543 porphyry deposits (Baker et al., 2017; Pacey et al., 2019; Wilkinson et al., 2019). This 544 supports the premise that the hydrothermal fluids forming larger and more strongly 545 mineralized porphyry systems flux more metals, leading to higher levels of metal enrichment 546 in propylitic epidote. Coupled with conventional exploration tools, including mapping the 547 intensity, variation and extent of propylitic alteration, LA-ICP-MS analysis of epidote 548 549 mineral chemistry has the capacity to assist explorers in discriminating between the magmatic hydrothermal alteration halos formed by mineralized porphyry systems and high sulfidation 550 epithermal deposits. It also has the ability to differentiate these modes of occurrence from 551 similar mineral assemblages formed through regional metamorphic processes, particularly in 552 the distal alteration halos to mineralized systems where other signs of mineralization (e.g., 553 554 presence of sulfides) are absent.

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Acknowledgments

558 We wish to thank editor Peter Hollings, and reviewers Farhad Bouzari and Glen Masterman for their valuable comments and corrections that have greatly improved the final version of 559 this manuscript. This research was supported by AMIRA International projects P765 (2004-560 2006): Transitions and Zoning in Porphyry-Epithermal Districts: Indicators, Discriminators 561 562 and Vectors (seven industry sponsors); and P765A (2008-2010): Geochemical and Geological Halos in Green Rocks and Lithocaps: The explorer's toolbox for porphyry and 563 epithermal districts (18 industry sponsors). We thank all our industry sponsors, collaborators 564 and research team members of those projects, in particular Alan Goode, J. Bruce Gemmell, 565 Cari Devell, Noel White, and Jeff Hedenquist. We also thank Alan Wilson, Alejandro 566 Sanhueza, Rodrigo Castagno, Rodrigo Gallo, Cristian Sprohnle, and support staff of Anglo 567 American plc for providing additional logistical support through their partly owned 568 subsidiary and operator of the Rosario and Ujina mines, Compañía Minera Doña Inés de 569 570 Collahuasi (CMDIC). Finally, we thank Karsten Goemann and colleagues at the Central Science Laboratory, University of Tasmania, and Sarah Gilbert for their assistance with 571 mineral chemistry analyses. 572

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752	in porphyry Cu systems using propylitic mineral chemistry: a case study of the El Teniente
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754	
755	Figure Captions
756	
757	Figure 1. Location map of northern Chile, southern Peru and northwestern Argentina
758	highlighting the location of the Collahuasi district and other major copper and gold deposits.
759	Metallogenic belts for major copper provinces of northern Chile-southern Peru are also
760	shown. Modified after Muntean and Einaudi (2000) and Masterman et al. (2005).
761	
762	Figure 2. Simplified geology map of the Collahuasi district, northern Chile. Approximate
763	outlines of copper mineralization at the Quebrada Blanca, Rosario, and Ujina porphyry
764	deposits is shown by dashed lines, as well as vein-hosted Cu-Ag-(Au) mineralization at La
765	Grande and Rosario-Poderosa (thin black lines). Modified after Dick et al. (1994) and
766	Masterman et al. (2004).
767	
768	Figure 3. Whole rock geochemistry and epidote LA-ICP-MS sample distribution and
769	observed hydrothermal alteration zones at the Rosario and Ujina porphyry deposits. Samples
770	associated with areas of epithermal mineralization or alteration are shown with red symbols.
771	Fault locations after Ireland (2010). Alteration zones and andesite dike locations modified
772	after Ireland (2010).
773	

Figure 4. Representative examples of hydrothermally-altered rocks from the Rosario, La 774 Grande and Ujina deposits. (A) CL005 – pink quartz-(feldspar)-phyric rhyolite containing 775 network of thin epidote-(chlorite)-bearing veins, Rosario deposit. (B) CL023 – dacite cut by 776 thin to mm-wide epidote-albite-(chlorite) veins (right side of photo) and spotty, disseminated 777 epidote-albite alteration, La Grande deposit. (C) CL039 – grey quartz-plagioclase-phyric 778 779 rhyolite containing thin epidote-calcite-(chlorite) veins, Ujina deposit. (D) CL140 – finegrained diabase dike containing pervasive disseminated chlorite alteration with rare epidote 780 crystals, Cascasa dike swarm approximately 3 km south of Ujina. Mineral abbreviations: alb 781 782 – albite; chl – chlorite; epi – epidote; qtz – quartz.

783

Figure 5. Assay results for proximal pathfinder elements for 170 rock chip samples from the

785 Collahuasi district. A. Cu (ppm). B. Au (ppb). C. Mo (ppm). D. Sn (ppm). Samples

associated with areas of epithermal mineralization or alteration are shown using unfilled

circles. Also shown are the locations of major porphyry and epithermal vein deposits,

788 potassic alteration zones (pink stipple), zones of anomalous metal concentration (red dashed

789lines) and pyrite halos (black dashed lines). Data are subdivided into equal tails, six groups

(3%, 20%, 50%, 80%, 97%, 100%). Whole-rock assay results for selected samples listed in

Table 1. Abbreviations: BDL = below detection limit.

792

Figure 6. Assay results for distal pathfinder elements for 170 rock chip samples from the
Collahuasi district. A. As (ppm). B. Sb (ppm). C. Pb (ppm). D. Zn (ppm). Symbols as
described in Figure 5. Whole-rock assay results for selected samples listed in Table 1. See
Figure 5 for abbreviations.

797

Figure 7. Assay results for 170 rock chip samples from the Collahuasi district. A. Mn (ppm).
B. La (ppm). C. Y (ppm). D. Zr (ppm). Symbols as described in Figure 5. Whole-rock assay
results for selected samples listed in Table 1. See Figure 5 for abbreviations.

801

Figure 8. Median concentrations of proximal pathfinder elements obtained from 629 epidote

LA-ICP-MS spot analyses of 107 samples from the Collahuasi district. A. Cu (ppm). B. Au

804 (ppm). C. Mo (ppm). D. Sn (ppm). Samples associated with areas of epithermal

- 805 mineralization or alteration are shown using unfilled circles. Also shown are the locations of
- 806 major porphyry and epithermal vein deposits, potassic alteration zones (pink stipple), zones
- of anomalous metal concentration (red dashed lines) and pyrite halos (black dashed lines).

- Data subdivided into equal tails, six groups (3%, 20%, 50%, 80%, 97%, 100%). Epidote data
- are summarized in Table 2. Corresponding rock chip assays are listed in Table 1.
- 810 Abbreviations: BDL = below detection limit.
- 811
- Figure 9. Median concentrations of distal pathfinder elements obtained from 629 epidote LA-

813 ICP-MS spot analyses of 107 samples from the Collahuasi district. A. As (ppm). B. Sb

814 (ppm). C. Pb (ppm). D. Zn (ppm). Symbols described in Figure 8. Epidote data are

summarized in Table 2. Corresponding rock chip assays are listed in Table 1. See Figure 8 forabbreviations.

817

818 Figure 10. Median concentrations of selected elements obtained from 629 epidote LA-ICP-

MS spot analyses of 107 samples from the Central Baguio district. A. Mn (ppm). B. La

820 (ppm). C. Y (ppm). D. Zr (ppm). Symbols described in Figure 8. Epidote data are

summarized in Table 2. Corresponding rock chip assays are listed in Table 1. See Figure 8 for

abbreviations.

823

Figure 11. Comparison of epidote LA-ICP-MS and whole-rock geochemical data from the

825 Collahuasi district, showing median, mean, 25<sup>th</sup> and 75<sup>th</sup> percentile ranges. A. Elements that

are concentrated in propylitic-altered rocks relative to epidote. B. Elements that are

827 preferentially partitioned into epidote in propylitic-altered samples.

828

Figure 12. Comparison of whole rock chemistry and epidote chemistry of samples from the Rosario porphyry, and La Grande and Rosario-Poderosa high sulfidation epithermal deposits plotted against calculated radial sample distance from the center of the Rosario porphyry deposit. Red filled circles and red open circles represent individual replacement and vein epidote analyses, respectively. Black open squares represent corresponding whole rock analysis from the same sample. Epidote data are summarized in Table 2. Corresponding rock

chip assays are listed in Table 1.

836

Figure 13. Comparison of whole rock chemistry and epidote chemistry plotted against

calculated radial sample distance from the center of the Ujina porphyry deposit. Symbols

described in Figure 12. Epidote data are summarized in Table 2. Corresponding rock chip

assays are listed in Table 1.

841

Figure 14. Tukey box diagrams for Rosario and La Grande (A) and Ujina (B) epidote 842 analyses (in grey) compared to epidote analyses from greenschist to amphibolite facies 843 regional metamorphic terranes (in black). Vertical axis is locked at 250 ppm to emphasize 844 anomalism in low-level trace elements. Regional metamorphic epidote dataset includes 65 845 analyses from the northern Australian Georgetown Inlier and Harts Range Paleoproterozoic 846 847 terranes (Baker et al., 2017), and 239 analyses from the west Scotland Paleozoic Moine and Dalradian terranes (Wilkinson et al., 2017). Element concentrations below limits of detection 848 are not shown. The Tukey box plot divides the ordered values of the data into four equal parts 849 by finding the median and then the 25<sup>th</sup> and 75<sup>th</sup> percentiles (the 'box'). The median is 850 defined by the horizontal line within the box that spans the interquartile range (IQR) and 851 contains approximately 50 % of the data. The mean is represented by the black circle. The 852 'fence' is defined as the central box (IQR) extended by 1.5 times the length of the box 853 towards the maximum and the minimum. The upper and lower 'whiskers' are then drawn 854 from each end of the box to the fence position. Samples outside of the fence are assumed to 855 be outliers (grey or black circles) and those that are three times the central box length from 856 857 the upper or lower quartile boundaries are highly anomalous and are called far outliers (grey or black triangles). C and D: epidote As versus Sb diagrams for epidote from Rosario and La 858 859 Grande (C) and Ujina (D) plotted against metamorphic epidote from the Georgetown Inlier, Harts Range, Moine and Dalradian terranes. Note that a large proportion of metamorphic 860 analyses were below the limit of detection for As and Sb (typically ~1 ppm for As and 0.1 861 ppm for Sb) and are not shown on these diagrams (Wilkinson et al., this issue). 862 863 **Tables** 864 865 Table 1. Selected whole-rock trace element geochemical analyses from Collahuasi district 866 samples. Distance to nearest porphyry copper deposit (PCD) was calculated as the radial 867 distance from the center of the nearest porphyry deposit, being either Rosario or Ujina. 868 869 Whole rock major and trace element data for all samples are listed in Appendix A. 870 871 Table 2. Selected epidote trace element chemistry from the Rosario and Ujina porphyry Cu-872 Mo deposits, and the La Grande and Rosario-Poderosa Cu-(Ag-Au) high sulfidation 873 epithermal veins. Full list of epidote LA-ICP-MS analyses for all samples is provided in 874 Appendix C. 875

876	
877	Appendix
878	
879	Appendix A – Whole rock geochemical data
880	Appendix B – Electron microprobe data
881	Appendix C – Epidote ICP-MS mineral chemistry data
882	Appendix D – Figure of typical epidote analysis LA-ICP-MS time-resolved spectrum
883	
884	Appendix D. Representative LA-ICP-MS time-resolved spectrum of an analysis of epidote
885	from the Collahuasi district. The inclusion-free spectrum shows analysis of the carrier gas
886	(~30 s) followed by laser ablation analysis of epidote (~60 s). Sample CL09MB140: mafic
887	dike cut by thin epidote veins, ~3 km south of Ujina porphyry deposit.
888	